**Critical Review: Radionuclide Transport,
Sediment Transport, and Water Quality
Mathematical Modeling; and Radionuclide
Adsorption/Desorption Mechanisms**

**Battelle Pacific Northwest Labs.
Richland, WA**

**Prepared for
Nuclear Regulatory Commission
Washington, DC**

Jan 81

**U.S. Department of Commerce
National Technical Information Service
NTIS**

MASTER *sp*

Critical Review: Radionuclide Transport, Sediment Transport, and Water Quality Mathematical Modeling and Radionuclide Adsorption/ Desorption Mechanisms

Prepared by Y. Onishi, R. J. Seme, E. M. Arnold, C. E. Cowan, F. L. Thompson

Pacific Northwest Laboratory
Operated by
Battelle Memorial Institute

Prepared for
U.S. Nuclear Regulatory
Commission

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

Available from

GPO Sales Program
Division of Technical Information and Document Control
U. S. Nuclear Regulatory Commission
Washington, D. C. 20555

Printed copy price: _ _

and

National Technical Information Service
Springfield, Virginia 22161

NRC FORM 335 (7-77)		U.S. NUCLEAR REGULATORY COMMISSION BIBLIOGRAPHIC DATA SHEET		1. REPORT NUMBER (Assigned by DDC) NUREG/CR-1322 PNL-2901	
4. TITLE AND SUBTITLE (Add Volume No., if appropriate) Critical Review: Radionuclide Transport, Sediment Transport and Water Quality Mathematical Modeling; and Radionuclide Adsorption/Desorption Mechanisms				2. (Leave blank)	
7. AUTHOR(S) Y. Onishi, R.J. Serne, E.M. Arnold, C.E. Cowan, F.L. Thompson				5. DATE REPORT COMPLETED MONTH YEAR August 1980	
9. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) Pacific Northwest Laboratory Richland, WA 99352				DATE REPORT ISSUED MONTH YEAR January 1981	
12. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) Division of Safeguards, Fuel Cycle, and Environmental Research Office of Nuclear Regulatory Research U.S. Nuclear Regulatory Commission Washington, DC 20555				10. PROJECT/TASK/WORK UNIT NO. ch	
				11. CONTRACT NO. FIN B2271	
13. TYPE OF REPORT			PERIOD COVERED (Inclusive dates)		
15. SUPPLEMENTARY NOTES				14. (Leave blank)	
16. ABSTRACT (200 words or less) This report describes the results of a detailed literature review of radionuclide transport models applicable to rivers, estuaries, coastal waters, the Great Lakes, and impoundments. Some representative sediment transport & water quality models were also reviewed to evaluate if they can be readily adapted to radionuclide transport modeling. The review showed that most available transport models were developed for dissolved radionuclides in rivers. These models include the mechanisms of advection, dispersion, & radionuclide decay. Since the models do not include sediment and radionuclide interactions, they are best suited for simulating short-term radionuclide migration where: 1) radionuclides have small distribution coefficients, & 2) sediment concentrations in receiving water bodies are very low. Only 5 of the reviewed models include full sediment & radionuclide interactions: CHMSED developed by Fields; FETRA, SERATRA, and TODAM developed by Onishi et al, & a model developed by Shull and Gloyna. The 5 models are applicable to cases where: 1) the distribution coefficient is large; 2) sediment concentrations are high; or 3) long-term migration & accumulation are under consideration. The report also discusses radionuclide adsorption/desorption distribution ratios and addresses adsorption/desorption mechanisms and their controlling processes for 25 elements under surface water conditions. These elements are: Am, Sb, C, Ce, Cm, Co, Cr, Cs, Eu, I, Fe, Mn, Np, P, Pu, Pm, Ra, Ru, Sr, Tc, Th, ³ H, U, Zn and Zr.					
17. KEY WORDS AND DOCUMENT ANALYSIS			17a. DESCRIPTORS		
Radionuclides Computer Models Sediment Models Surface Water			Transport Models Sorption Mechanisms Distribution Coefficients Long-Term Transport		
17b. IDENTIFIERS/OPEN-ENDED TERMS					
18. AVAILABILITY STATEMENT Unlimited			19. SECURITY CLASS (This report) Unclassified		21. NO. OF PAGES
			20. SECURITY CLASS (This page) Unclassified		22. PRICE \$

Critical Review: Radionuclide Transport, Sediment Transport, and Water Quality Mathematical Modeling; and Radionuclide Adsorption/ Desorption Mechanisms

Manuscript Completed: August 1980
Date Published: January 1981

Prepared by
Y. Onishi, R. J. Seme, E. M. Arnold, C. E. Cowan, F. L. Thompson

Pacific Northwest Laboratory
Richland, WA 99352

Prepared for
Division of Safeguards, Fuel Cycle and Environmental Research
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
NRC FIN No. B2271

ABSTRACT

This report describes the results of a detailed literature review of radionuclide transport models applicable to rivers, estuaries, coastal waters, the Great Lakes, and impoundments. Some representative sediment transport and water quality models were also reviewed to evaluate if they can be readily adapted to radionuclide transport modeling.

The review showed that most available transport models were developed for dissolved radionuclides in rivers. These models include the mechanisms of advection, dispersion, and radionuclide decay. Since the models do not include sediment and radionuclide interactions, they are best suited for simulating short-term radionuclide migration where: 1) radionuclides have small distribution coefficients, and 2) sediment concentrations in receiving water bodies are very low. Only five of the reviewed models include full sediment and radionuclide interactions: CHNSED developed by Fields; FETRA, SERATRA, and TODAM developed by Onishi et al., and a model developed by Shull and Gloyna. The five models are applicable to cases where: 1) the distribution coefficient is large; 2) sediment concentrations are high; or 3) long-term migration and accumulation are under consideration.

This report also discusses radionuclide adsorption/desorption distribution ratios and addresses adsorption/desorption mechanisms and their controlling processes for 25 elements under surface water conditions. These elements are: Am, Sb, C, Ce, Cm, Co, Cr, Cs, Eu, I, Fe, Mn, Np, P, Pu, Pm, Ra, Ru, Sr, Tc, Th, ³H, U, Zn and Zr.

SUMMARY

A comprehensive literature survey was conducted to assess radionuclide transport models that are applicable to surface waters. Twenty-eight models were examined for their inclusion of transport and fate mechanisms (and their formulations), applicability, limitations, and past application results for different types of water bodies, i.e., rivers, estuaries, coastal waters, the Great Lakes, and impoundments. Eighteen representative sediment transport and twenty-six conventional water quality models were also reviewed to determine if these types of models can be easily adapted to radionuclide migration phenomena in surface waters.

Most radionuclide transport models are based on the advection/diffusion equation. These models range from simple analytical solutions to sophisticated numerical models. For some simplified cases, analytical solutions provide useful information on radionuclide distributions with very minor efforts. Numerical models, however, can accommodate a wide variation of channel geometry, flow distribution, and sediment and radionuclide distributions.

The study revealed that the important mechanisms of radionuclide transport and fate are: 1) advection and dispersion of radionuclides by current, surface waves, and turbulent mixing; 2) radionuclide decay; 3) radionuclide contributions from outside sources and subsequent mixing; and 4) interaction between radionuclides and sediment and soluble constituents such as complexing ligands.

Most available radionuclide transport models were developed for dissolved radionuclides in rivers and include the first three mechanisms. These models are best suited to short-term radionuclide migration where: 1) radionuclides have small distribution coefficients, K_d , and 2) sediment concentrations in receiving water bodies are very low. Most water quality models can also simulate dissolved radionuclide transport with minimal modifications (if any) to the models. When only dissolved radionuclide transport is concerned, the water quality models developed by Leendertse; Yotsukura and Sayre; and Dailey and Harleman are some of the more sound models with good past application.

Another table (see Table 8.95), based on solution thermodynamics, was constructed to predict what species of each element would predominate in environmental waters. Based upon the nature of the predominant solution species, qualitative predictions on adsorption and mobility of the radionuclides can be made.

The review of radionuclide adsorption/desorption mechanisms indicated that additional research is needed for a better understanding of sediment and radionuclide interactions. In accordance, the following activities are recommended:

1. determination of radionuclide adsorption mechanisms
2. evaluation of factors that influence radionuclide/geologic media interactions
3. experimental consideration of the effects of redox potential on radionuclide migration
4. characterization of organic ligands; evaluation of the influence of organic ligands on radionuclide migration
5. determination of thermodynamic data for several solution species
6. generation of K_d data that can be used in a comparative mode
7. maintenance of a bank of such K_d data
8. determination of radionuclide adsorption and desorption reaction kinetics with sediments.

CONTENTS

ABSTRACT	iii
SUMMARY	v
1. INTRODUCTION	1.1
2. CONCLUSIONS AND RECOMMENDATIONS	2.1
2. GENERAL DESCRIPTION OF MATHEMATICAL MODELS	3.1
RADIONUCLIDE TRANSPORT MODELS	3.1
WATER QUALITY AND SEDIMENT TRANSPORT MODELS	3.6
REFERENCES FOR CHAPTER 3	3.11
4. RADIONUCLIDE TRANSPORT IN NON-TIDAL RIVERS	4.1
PHYSICAL MECHANISMS OF RADIONUCLIDE TRANSPORT IN NON-TIDAL RIVERS	4.1
MATHEMATICAL MODELS FOR RIVERS	4.7
REFERENCES FOR CHAPTER 4	4.55
5. RADIONUCLIDE TRANSPORT IN ESTUARIES	5.1
PHYSICAL MECHANISMS OF RADIONUCLIDE TRANSPORT IN ESTUARIES	5.1
MATHEMATICAL MODELS FOR ESTUARIES	5.2
REFERENCES FOR CHAPTER 5	5.21
6. RADIONUCLIDE TRANSPORT IN OCEANS AND GREAT LAKES	6.1
PHYSICAL MECHANISMS OF RADIONUCLIDE TRANSPORT IN OCEANS AND GREAT LAKES	6.1
MATHEMATICAL MODELS FOR OCEAN AND THE GREAT LAKES	6.8
REFERENCES FOR CHAPTER 6	6.15
7. RADIONUCLIDE TRANSPORT IN LAKES AND RESERVOIRS	7.1
PHYSICAL MECHANISMS OF RADIONUCLIDE TRANSPORT IN LAKES AND RESERVOIRS	7.1

	MATHEMATICAL MODELS FOR LAKES AND RESERVOIRS . . .	7.5
	REFERENCES FOR CHAPTER 7	7.15
8.	RADIONUCLIDE ADSORPTION/DESORPTION	8.1
	MECHANISMS	8.1
	SELECTION CRITERIA AND SOURCES OF RADIONUCLIDES IN THE ENVIRONMENT	8.18
	ELEMENT LITERATURE REVIEW	8.23
	AMERICIUM	8.25
	ANTIMONY	8.43
	CARBON	8.50
	CERIUM	8.52
	CESIUM	8.64
	CHROMIUM	8.83
	CURIUM	8.101
	EUROPIUM	8.107
	IRON	8.124
	NEPTUNIUM	8.131
	PHOSPHORUS	8.137
	PLUTONIUM	8.144
	PROMETHIUM	8.175
	RADIUM	8.179
	RUTHENIUM	8.187
	STRONTIUM	8.201
	TECHNETIUM	8.224
	THORIUM	8.230
	TRITIUM	8.239

URANIUM	8.245
ZINC	8.259
ZIRCONIUM	8.268
CONCLUSIONS AND EVALUATION	8.278
REFERENCES FOR CHAPTER 8	8.289

FIGURES

3.1	Particle Movement	3.10
4.1a	Overall Model Structure	4.13
4.1b	Water Transport Model	4.13
4.2	Longitudinal Distributions of Dissolved, Particulate and Total Cesium-137 Concentrations in the Clinch River, Tennessee	4.26
4.3	Plug Flow River Model	4.30
4.4	Mixed Tank Model	4.31
4.5	Comparison Between Simulated and Measured Transverse Concentration Distributions, Transects 3 and 4 in the Missouri River	4.41
4.6	Dissolved Oxygen Calibration of PIONEER Model	4.44
4.7	Dissolved Oxygen Verification of PIONEER Model	4.44
4.8	Observed and Simulated Transport Rate Versus Measured Flow Velocity for Complete Set of Available Sampling Dates in the Rio Grande River Near Bernalillo, New Mexico	4.49
4.9	Measured and Simulated Values of Volumetric Sediment Discharge Rates in the Hudson River at a Cross Section 10 Miles Upstream from the Battery	4.50
4.10	Theoretical and Observed Longitudinal Distribution of Tracer Particles: North Load River Field Experiment	4.53
5.1	Tidally Averaged Sediment Concentration of Each Sediment Type for the Net Freshwater Input Discharge of 58.3 m ³ /sec in the James River Estuary	5.7
5.2	Tidally Averaged Sediment Concentration of Each Sediment Type for the Net Freshwater Input Discharge of 247 m ³ /sec in the James River Estuary	5.7
5.3	Tidally Averaged Particulate Kepone Concentrations for the Net Freshwater Discharge of 58.3 m ³ /sec in the James River Estuary	5.8
5.4	MRC Estuary Model	5.10

5.5	Comparison of Computed and Measured Values of Velocity and Salinity in the James River Estuary	5.12
5.6	Channel-Junction Definition for Computational Mesh . .	5.16
5.7	Suspended Sediment Concentrations During Spring Tide in the Savannah Estuary	5.18
6.1	Comparison of Computed and Measured Temperature Distributions in the Conowingo Reservoir in the Vicinity of the Peach Bottom Atomic Power Station . .	6.11
7.1	Compartments of the Lake Ecological Model of Vanderploeg, Booth and Clark	7.6
7.2	MRC Mixed Tank Lake Model	7.8
8.1	The Activity of Various Americium Species in Equilibrium with $\text{AmO}_2(\text{s})$ in an Oxidizing Soil Environment . . .	8.26
8.2	Particulate Formation of $\text{Am}(\text{III})$ in Var River Water as a Function of Changes in pH	8.28
8.3	Particulate Formation of $\text{Am}(\text{III})$ in Sea Water as a Function of Changes in pH	8.28
8.4	Equilibrium Time for Particulate Formation and Adsorption on Sediments of $\text{Am}(\text{III})$ in Var River Water and Its Desorption from Sediments in the Sea Water	8.29
8.5	Adsorption of $\text{Am}(\text{III})$ on Sediments in Var River Water at Different pH Values	8.29
8.6	Desorption of $\text{Am}(\text{III})$ from Sediments in the Sea Water Medium at Different pH Levels	8.30
8.7	Distribution Coefficient for ^{241}Am as a Function of Sediment Concentration in Fresh Water	8.31
8.8	Distribution Coefficient for ^{241}Am as a Function of pH in Fresh Water-Sediment System	8.32
8.9	Distribution Coefficients for ^{241}Am as a Function of pH in Marine Water-Sediment System	8.32
8.10	Effect of Varying EDTA Concentration on Kd Values of ^{241}Am	8.38
8.11	The Activity of Various Antimony Species in Equilibrium with $\text{Sb}_2\text{O}_3(\text{s})$ with $\text{pH} = 3.0$ and $\text{pF}^- = 4.5$	8.45

8.12	The Activity of Various Cerium Species in Equilibrium with $\text{CePO}_4(\text{s})$ in an Oxidizing Soil Environment	8.54
8.13	Distribution Coefficient of ^{244}Ce in Sediment	8.59
8.14	Distribution Coefficient of Several Minerals as a Function of Sodium Concentration	8.73
8.15	The Activity of Various Cobalt Ions in Equilibrium with $\text{CoCO}_3(\text{s})$ in an Oxidizing Soil Environment	8.90
8.16	Variation of Adsorption of ^{60}Co at Constant Carrier Concentration and sediment Load with Varying pH	8.92
8.17	Variation of Desorption of Trace Elements at Constant Adsorbed Trace-Element Concentration and Sediment Load with Varying pH	8.93
8.18	The Activity of Various Curium Ion Species in Equilibrium with $\text{Cm}(\text{OH})_3(\text{s})$	8.102
8.19	The Activity of Various Europium Species in Equilibrium with $\text{Eu}(\text{OH})_3(\text{s})$	8.108
8.20	The Influence of pH on the Activity of Europium in Solution	8.111
8.21	Sorption of ^{131}I onto Leitha Sediment as a Function of Grain Size	8.123
8.22	The Activity of Various Neptunium Species in Equilibrium with $\text{NpO}_2(\text{s})$ in an Oxidizing Soil Environment	8.132
8.23	Removal of Phosphate by Roanoke River Solids as a Function of pH	8.140
8.24	The Effect of Prior Contact Time on the Desorption of Phosphorus from Solids	8.141
8.25	The Effect of Variations in Salinity on the Uptake of Phosphorus	8.142
8.26	The Activity of Various Plutonium Species in Soil Solution in Equilibrium with $\text{PuO}_2(\text{s})$ at pH 8	8.146
8.27	The Activity of Various Plutonium Species in Soil Solution in with $\text{PuO}_2(\text{s})$ in a Mildly Oxidizing Soil Environment	8.146

8.28	Particulate Formation of Pu(III, IV, VI) in Var River Water as a Function of Changes in pH	8.150
8.29	Particulate Formation of Pu(III, IV, VI) in Sea Water as a Function of Changes in pH	8.150
8.30	Equilibrium Time for Adsorption on Sediments of Pu(IV) in Var River Water and Its Desorption from Sediments in the Seawater Medium	8.151
8.31	Desorption of Pu(III) and Am(III) from Sediments in the Seawater Medium at Different pH Levels	8.151
8.32	Adsorption of Plutonium by Soil as a Function of pH	8.160
8.33	Effect of pH and Plutonium Oxidation State on the Adsorption of Plutonium by Soil	8.162
8.34	The Activity of Various Ruthenium Species in Equilibrium with RuO ₂ in Oxidizing and Other Conditions	8.190
8.35	The Relative Stability of Various Strontium Solids	8.203
8.36	The Activities of Various Strontium Species in Equilibrium with SrCO ₃ (s) in the Soil	8.204
8.37	Activity of Various Thorium Species in Soil in Equilibrium with ThO ₂ (s)	8.232
8.38	Activity of Various Uranium Species in Equilibrium with Na ₂ UO ₄ in an Oxidizing Soil Environment	8.248
8.39	Adsorption of Zinc at Constant Carrier Concentration and Sediment Load with Varying pH	8.262
8.40	Desorption of Zinc at Constant Adsorbed Trace Element Concentration and Sediment Load with Varying pH	8.262
8.41	Variation of Desorption of Zinc in Sea Water of Different Salinities at Different pH	8.263
8.42	The Activity of Various Zirconium Species in Equilibrium with Zircon and Soil Solution Silica	8.271

TABLES

4.1	Radionuclide Data for Rivers	4.8
4.2	Summary of Radionuclide Transport Model	4.9
4.3	Summary of Sediment Transport Models	4.10
4.4	Summary of Water Quality Models	4.11
5.1	Estuary Data	5.3
6.1	Physical-Chemical States of Radionuclides in Bikini Atoll Lagoon in Percent	6.3
6.2	Ocean and Great Lakes Data	6.6
7.1	Lakes and Reservoirs Data	7.4
8.1	Composition of Burns, Mississippi Montmorillonite	8.4
8.2	Comparison of Experimental and Computed Strontium Kd Values for Montmorillonite	8.4
8.3	Most Potentially Hazardous Elements	8.19
8.4	1975 Summary Liquid Release of Radionuclides from Commercial LWR and PHR Reactors in the United States	8.19
8.5	Annual and Cumulated Releases and Production of Radionuclides from Nuclear Plants and Fuel Reprocessing Plants for the World from 1975 to 2000	8.20
8.6	Nuclide Source Inventory	8.21
8.7	Average Activities of Solution Constituents	8.23
8.8	Sediment Characteristics and Average Kd _{Am} Particle Size Distribution	8.30
8.9	Percent Distribution of Radionuclides After 11 Days of Dialysis Experiment	8.35
8.10	Distribution of ²⁴¹ Am, ¹³⁷ Cs, ¹⁰⁶ Ru, ⁶⁵ Zn, ⁶⁰ Co and ⁵⁹ Fe After 96 hr in a Dialysis Experiment	8.35

8.11	Summary of Adsorption/Desorption Distribution Coefficients with Properties of the Sediment/Water Systems	8.36
8.12	Sediment/Water Kd Values for Lake Washington System as a Function of Different Organic Compounds	8.37
8.13	Americium 50-Day Distribution	8.39
8.14	Antimony Concentrations in Rocks and Sediments	8.43
8.15	Activity and Percentages of Antimony Isotopes	8.46
8.16	¹²⁵ Sb Analysis of Water and Soil Samples from a Seep Near Trench 7	8.48
8.17	Cerium Abundance in Rocks	8.52
8.18	Stable Isotopes of Cerium	8.53
8.19	Cerium Data	8.55
8.20	Kd _{Ce} onto Post-Glacial Clay from Distilled Water	8.56
8.21	Adsorption of ¹⁴⁴ Ce on Suspended Solids	8.62
8.22	Cesium Content of Rocks and Sediments	8.64
8.23	Kd _{Cs} in Various Sediments from Duursma and Eisma	8.68
8.24	Kd _{Cs} on Mitelva River Sediments	8.68
8.25	Distribution of ¹³⁷ Cs Between Sea Water and Sediments	8.70
8.26	Cs Sorption by Clinch River Sediment	8.75
8.27	Properties of Natural Water Samples	8.81
8.28	Adsorption of Radionuclides on Suspended Solids	8.81
8.29	Chromium Concentrations	8.83
8.30	Cobalt Concentrations in Igneous and Sedimentary Rocks and Sediments in ppm	8.88
8.31	Kd _{Co} in Various Sediments from Duursma and Eisma	8.91
8.32	Curium 50-day Distribution Computed from Sheppard et al.	8.104

8.33	Kd Values for ^{242}Cm in Untreated Aiken Clay Loam	8.105
8.34	Europium Content of Sediments and Igneous Rocks in ppm	8.107
8.35	Variation of Trace europium Kd Values on Mol Soils	8.110
8.36	Effect of pH and Europium Concentration on Europium Kd by Burbank Sand	8.112
8.37	Iodine Concentration in Sediments and Rocks	8.115
8.38	Range of Surface Soil Properties Used in the Methyl Iodide and Iodide Sorptions	8.119
8.39	Iron Contents of Sediments	8.124
8.40	$K_{d,e}$ Observed in Marine Sediments	8.125
8.41	Manganese Content of Various Sediments	8.127
8.42	$K_{d,mn}$ Versus Particle Size	8.128
8.43	$K_{d,mn}$ and $t\ 1/2$ for Various Sediments	8.129
8.44	Properties of Soil Samples	8.134
8.45	Neptunium Kd as a Function of Soil and Solution	8.134
8.46	Neptunium 50-day Distribution Values Computed from Sheppard et al.	8.134
8.47	Phosphorus Content of Rocks and Sediments	8.137
8.48	Plutonium Radionuclide Data	8.144
8.49	Sediment Characterization	8.154
8.50	K_{yPu} Results	8.154
8.51	Percent Pu Removed by Extractants	8.157
8.52	Plutonium Adsorption Versus Particle Size	8.158
8.53	Plutonium Kd Values for Quartz of Various Particle Sizes from a 0.001 N HNO_3 -Plutonium Solution	8.159

8.54	Plutonium Kd Values for Different Minerals of Coarse Clay Size from 0.001 N HNO ₃ -Plutonium Solution	8.159
8.55	Rhodes' Plutonium Kd Data as Reported by Evans	8.159
8.56	Removal of Plutonium from pH 7 Water by Several Soil Minerals	8.162
8.57	Plutonium Kd as a Function of Oxidation State	8.164
8.58	Kd Values of ²³⁸ Pu in Untreated Aiken Clay Loam	8.164
8.59	Bikini Atoll Data	8.167
8.60	Kd _{pm} and t 1/2 Values on Selected Sediments	8.177
8.61	Average Radium Content of Various Geologic Media	8.179
8.62	Radium Kd Values from Lime-Neutralized Waste; 1.25 g Exchanger/l of Waste	8.181
8.63	Simulated River Water Composition	8.182
8.64	Radium Distribution Coefficients with the Solution of Table 8.63	8.182
8.65	Abundances of Ruthenium in Igneous Rocks and Rock-Forming Minerals in ppm	8.187
8.66	Ruthenium Contents of Shales	8.188
8.67	Atomic Percentages of Stable Ruthenium Isotopes	8.188
8.68	Ru Sorption Data	8.191
8.69	Ru Sorption in Fresh Water	8.192
8.70	Properties of Natural Water Samples	8.194
8.71	Adsorption of ¹⁰⁶ Ru on Suspended Solids in Natural Waters	8.194
8.72	Ruthenium Distribution Coefficients on a Hanford Soil as a Function of pH	8.197
8.73	Average Strontium Contents of Igneous Rocks	8.201
8.74	Average Strontium Content in Sedimentary Rocks and Sediments in ppm	8.201

8.75	Kd _{sr} and t-1/2 Values	8.206
8.76	Technetium Content of Some Natural Materials	8.224
8.77	Range of Properties of 22 Surface Soils Used in the Pertechnetate Adsorption Studies	8.226
8.78	Properties of Soils Used in Technetium Adsorption Studies	8.227
8.79	Properties of Soil Samples	8.227
8.80	Technetium Kd as a Function of NaHCO ₃ Concentration for a South Carolina Soil Characterized in Table 8.79	8.228
8.81	Thorium Content of Common Rocks and Sediments	8.230
8.82	Abundances of Uranium in Natural Materials	8.245
8.83	Nuclear Properties of Natural Uranium Isotopes	8.246
8.84	Desorption of Uranium from Soils with Distilled Water and Carbonate Solutions	8.249
8.85	Kd Values for Uranium	8.250
8.86	Zinc Concentration in Sediments	8.259
8.87	Zinc Sorption in Marine Environments	8.261
8.88	Distribution of ⁶⁵ Zn in Columbia River Water	8.266
8.89	The Average Zirconium Content of Rocks	8.268
8.90	Natural Isotopes of Zirconium and Their Abundances	8.269
8.91	Zirconium Adsorption on Marine Sediments	8.272
8.92	Zircon-Niobium Kd Values as a Function of pH.	8.273
8.93	Adsorption of ⁹⁵ Zr and ⁹⁵ Nb on Suspended Solids in Natural Waters	8.276
8.94	Factors Report to affect Adsorption of Radioelements over the pH Range of 4 to 9	8.279

8.95	Predominant Solution Species of Elements in a pH 4 to 9, pO_2 0.68 to 80, pCO_2 1.52 to 3.52, pCl^- 0.45 to 3/0, pNO_3^- = pSO_4^{2-} = 3.0, pH^- 4.5 and pH_2PO_4 5.0 Environment Without Organic Ligands	8.281
8.96	Gross Average K_d ml/g for Studied Elements with Emphasis on Oxidizing Conditions	8.288

1. INTRODUCTION

The nuclear energy industry has grown considerably during the past decade, and nuclear power is expected to become one of the major sources to meet the growing need for energy. Although considerable effort is being made to minimize the release of the radioactive wastes into the environment, it is important to assess the potential environmental impact of radionuclide releases. Various pathways exist for exposure of humans and biota to radioactive materials released from nuclear facilities. Hydrologic transport (liquid pathway) is one element in the evaluation of the total radiation dose to man. Exposures can occur from routine or accidental releases of radionuclides in liquid effluents from nuclear facilities. Mathematical models supported by coordinated data collection programs can be useful tools in assessing the hydrologic transport and ultimate fate of radionuclides. In order to assess migration, accumulation and fate of radionuclides in surface waters, mathematical models must include major contaminant transport and fate mechanisms. These mechanisms include:

1. advection and dispersion of radionuclides by flow and surface waves
2. radionuclide decay
3. interaction between sediment and radionuclides such as:
 - radionuclide adsorption by sediment
 - radionuclide desorption from sediment to water
 - transport of particulate radionuclides (those adsorbed by sediment)
 - deposition of particulate radionuclides to ocean and river beds
 - scouring of particulate radionuclides from ocean and river beds
4. contaminant release and contributions from outside point and nonpoint sources and subsequent mixing.

This report gives the results of a comprehensive literature survey conducted to assess radionuclide transport models applicable to surface waters. Models were examined for their inclusion of transport and fate mechanisms, their formulations, applicability, limitations and past application results for each type of water body, i.e., rivers, estuaries, coastal waters, large

• •

lakes (e.g., the Great Lakes), and impoundments. Some representative sediment transport and general (conventional) water quality models were also reviewed to examine if these types of models can be easily adapted for radionuclide transport.

Before fundamental understanding and generalized predictive capability for radionuclide transport in rivers, estuaries, oceans and lakes can be obtained, radionuclide adsorption/desorption and controlling physical and chemical processes must be identified. This report also discusses in depth these mechanisms and processes, and contains a compilation of available knowledge on distribution coefficients obtained under expected ranges in environmental and water conditions. For this study, long half-life or biologically hazardous fission and activation products were evaluated. These elements include Am, Sb, C, Ce, Cm, Co, Cr, Cs, Eu, I, Fe, Mn, Np, P, Pu, Pm, Ra, Ru, Sr, Tc, Th, ³H, U, Zn and Zr.

2. CONCLUSIONS AND RECOMMENDATIONS

The literature review on radionuclide transport, water quality and sediment transport models; and radionuclide adsorption/desorption mechanisms led to the following conclusions and recommendations:

1. Most of the radionuclide transport and water quality models reviewed in this study can simulate dissolved-only radionuclide transport. Models developed by Leendertse; Yotsukura and Sayre; and Dailey and Harleman have sound model formulation and have successful application history. However, the first two models do not include radionuclide decay in the analysis.
2. When: a) distribution coefficients of the radionuclides are large, b) sediment concentrations in a receiving water body are high, or c) long-term radionuclide migration and accumulation are under consideration, dissolved and particulate forms of a radionuclide must be solved simultaneously by including full sediment-radionuclide interactions. Sediment-radionuclide interactions involve radionuclide adsorption/desorption, and transport, deposition and scouring of radionuclides sorbed by sediment. For these cases, the following five models can be used:

One-dimensional model for rivers developed by Shull and Gloyna

One-dimensional model (TODAM) for rivers and well-mixed estuaries developed by Onishi et al.

Two-dimensional model (SERATRA) for rivers and river-run reservoirs developed by Onishi et al.

Two-dimensional model (FETRA) for coastal waters and well-mixed estuaries developed by Onishi et al.

One-dimensional model for rivers developed by Fields.

3. All of the above five models have been applied to actual sites and some of them were partially verified with field data. However, more complete model verification is needed.

4. Radionuclides in solution exist in dynamic equilibrium with bed sediment and suspended sediment. Many factors that are inherent to the sediment and the solution can influence the concentration of the element and its species in solution. These factors include pH, Eh, CEC, type and amount of minerals, solubility of the element, complexing ligands, and competing ions. In order to determine the distribution of the element between solution and solid and its reactions with sediments, the identity and effect on sorption of each factor are needed. To date scientists have not identified the effects of important factors sufficiently.
5. This general lack of systematic evaluation of the effects of important factors is exacerbated by a lack of detailed sediment/water characterization for laboratory and field studies. It is extremely difficult to utilize existing literature to evaluate the effects of geochemical parameters on nuclide sorption because of this lack of system characterization or control. Below is a list of sediment and solution parameters which should be measured during sorption experiments to facilitate quantification of effects and delineation of sorption mechanisms.

Supporting Information Necessary to Complete Kd

There are numerous characterizations that should be performed on geologic media and their pore waters to allow calculations of migration rates or Kds. The characterizations can be broken into two broad categories: physical or hydrologic and geochemical. The relative importance is based on the assumption that insufficient time and funds will be available to perform the complete characterization. If only partial geochemical characterization is possible, in general concentrate on the first seven.

Important Geochemical Characterizations

1. qualitative and quantitative mineralogy including primary and secondary crystalline materials, amorphous coatings, etc.

determined primarily by X-ray diffraction, chemical treatment techniques, and petrographic examination. Calcium carbonate content and hydrous oxide content (amorphous and crystalline) as well as aluminosilicate contents are most important. Scanning electron microscopy and microprobes can be used to determine microstructural mineralogy. These techniques can be very important in assessing the differences between mineralogy and weathering environments of cracks and fractures from the bulk rock material.

2. cation exchange capacity
3. pore water pH, Eh
4. pore water major cation content (Na, Ca, Mg, K)
5. pore water major anion content (Cl, $\text{HCO}_3\text{-CO}_3$, SO_4 , NO_3)
6. pore water SiO_2 content
7. organic content of geologic material.

Less Important Geochemical Characterizations

1. anion exchange capacity
2. distribution of major cations on exchange sites
3. pore water organic content, especially potential ligands (humic, fulvic acids)
4. pore water minor constituents, especially naturally occurring isotopes of important waste nuclides (Sr, Cs, I, U, Ra) and chemically similar elements (Ba, Rb, Br).

Important Physical or Hydrologic Characterizations

1. suspended sediment content (solid/solution ratio)
2. permeability
3. water velocities
4. surface area and particle size distribution
5. in situ temperature
6. time of contact.

6. The probable principal adsorption mechanisms may be deduced from an examination of the factors reported to be important for each element. For example, colloid formation is a good indication of precipitation, as pH also may be. An adsorption sensitivity to cation exchange capacity, competing ions and system pH usually indicates an ion exchange adsorption mechanism. A sensitivity to the redox potential, Eh, usually indicates that the element has changed valence states which typically leads to enhanced sorption via solubility constraints. Chromium, neptunium, phosphorus, plutonium, technetium, and uranium are much more soluble under oxidizing conditions than reducing. Iron and manganese in general exhibit the opposite solubility trends.
7. Based upon the nature of the predominant solution species, qualitative predictions regarding the adsorption and movement of various elements can be made. Bed and suspended sediments mainly show cation exchange capacities (since they carry a large net negative charge) and to a limited extent, anion exchange capacities. Thus, most cations would react with sediments. Relative to each other, the trivalent cations are generally most easily adsorbed, the divalent cations are intermediate and the monovalent cations are adsorbed least. Tritium is unique in that it readily substitutes for hydrogen in water and migrates, therefore, at the same velocity as water. Complicating factors include a higher selectivity of a sediment component for a given cation or a more successful hydrogen ion competition with one cation relative to another. The adsorption of strontium and cesium at low pH is a good example of the latter effect. Strontium is much more easily adsorbed by sediment at low pH than is cesium.
8. The highly charged metal ions tend to polymerize or form colloidal size, charged precipitates. The trivalent metal ions (Am, Cm, Sb, Ru) and quadrivalent or higher charged metal ions (Pu, Th, U, Zr) are known to form polymers. Initially, at lower pH, the polymers are positively charged and at pH 9 become increasingly negatively charged. The result is good adsorption at acidic to neutral pH, and lessened adsorption from pH 9 upward.

9. The behavior of organic complexed species of elements is difficult to predict because of the lack of knowledge regarding the exact nature of the organic ligands, a wide variation in amounts and types of organic ligands, and the size and solubility of these organics. These organic materials can either retain the element or complex it. Many laboratory studies at inflated organic concentrations have shown significant changes in Kds for many elements, but the results for experiments at realistic organic concentrations are less dramatic.
10. At best, the available data suggest trends for the influence of some of the factors that control solution concentrations and interaction with solid matrices. This type of information would not be very useful for quantitatively predicting the general fate of radionuclides in the environment. Additional research and more considered characterization of sediment/water systems are required for general understanding of the behavior of radionuclides.
11. General recommendations to further the pursuit of quantitative understanding of radionuclide adsorption/desorption include:
 - a. more detailed characterization and control of important geochemical parameters
 - b. more concern about proper experimentation, such as studying adsorption only at tracer concentrations below solubility constraints, care in solid/liquid phase separations
 - c. more reliance on thermodynamic principles such as solution speciation and solubility to guide experimental design and data interpretation
 - d. determination of adsorption/desorption kinetics.
12. Experimenters are admonished to attempt to: a) provide data on sorption under controlled Eh, pH and dissolved solids conditions; b) differentiate adsorption from precipitation; c) evaluate inorganic and organic complexation of cationic nuclides; and d) utilize proper scientific design

and state-of-the-art instrumentation and procedures while performing experiments. Critical areas include concentration and techniques of adding radionuclides to waters, solid/liquid phase separation, and length of contact time employed.

3. GENERAL DESCRIPTION OF MATHEMATICAL MODELS

RADIONUCLIDE TRANSPORT MODELS

Transport and fate of radionuclides can be predicted with various degrees of sophistication, ranging from a simple algebraic, mass-balance approach to a multi-dimensional numerical solution to the problems. For example, a simple algebraic approach to the hydrologic transport of radionuclides considers only advection and mixing processes. These processes are represented in a spatially averaged form, using the mixing ratio and average travel time factors. The 1977 Regulatory Guide (US NRC 1977) describes more sophisticated methodologies to solve the radionuclide transport, using the advection-diffusion equation for various categories and classifications of problems, such as initial dilution, nontidal rivers, open coasts, estuaries, and impoundments.

The basic equation of mass conservation of a contaminant expressed in terms of the advection-diffusion equation in Cartesian coordinates is:

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x_i} (U_i C) = \frac{\partial}{\partial x_i} \left(\epsilon_i \frac{\partial C}{\partial x_i} \right) + \sum_{j=1}^N K_j C + \sum_{j=1}^N S_j \quad (3.1)$$

dynamic	advection	diffusion or	decay	sink/source
term	term	dispersion term	term	term

where:

C = concentration of the contaminant

t = time

U_i = velocity term

x_i = Cartesian coordinates

ϵ_i = diffusion/dispersion coefficient

$\sum K_j$ = sum of decay rates for a contaminant

$\sum S_j$ = sum of sink and/or source.

The above equation must be solved simultaneously for all phases of contaminants (e.g., dissolved radionuclides, particulate radionuclides adsorbed

by sediment, biota, etc.). Since it is impossible to solve the coupled equation analytically for a general case, numerical techniques must be used. However, there are some simplified cases when the above equation can be solved analytically. These cases are mostly handling only dissolved radionuclides. Some of the known analytical solutions are discussed below (USNRC 1977).

1. Advection - Diffusion Equation (with only Longitudinal Velocity Components without Decay and Sink/Source Terms)

The governing equation for this case is:

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x} (UC) = \epsilon_x \frac{\partial^2 C}{\partial x^2} + \epsilon_y \frac{\partial^2 C}{\partial y^2} + \epsilon_z \frac{\partial^2 C}{\partial z^2} \quad (3.2)$$

where:

U = longitudinal velocity

x, y, z = longitudinal, lateral and vertical coordinates in Cartesian coordinates.

$\epsilon_x, \epsilon_y, \epsilon_z$ = longitudinal, lateral and vertical dispersion coefficients.

- a. For an instantaneous point source with the constant velocity and diffusion coefficients the solution to this equation becomes:

$$C(x,y,z;t) = M f_x(x;t) f_y(y;t) f_z(z;t) \quad (3.3)$$

where:

$$f_x(x;t) = \frac{1}{2\sqrt{\pi\epsilon_x t}} \exp - \frac{(x-Ut)^2}{4\epsilon_x t}$$

$$f_y(y;t) = \frac{1}{2\sqrt{\pi\epsilon_y t}} \exp - \frac{y^2}{4\epsilon_y t}$$

$$f_z(z;t) = \frac{1}{2\sqrt{\pi\epsilon_z t}} \exp - \frac{z^2}{4\epsilon_z t}$$

M = amount of activity released (say, in curies).

Hence:

$$C(x,y,z;t) = \frac{M}{8(\pi t)^{3/2} \sqrt{\epsilon_x \epsilon_y \epsilon_z}} \exp \left\{ -\frac{1}{4t} \left[\frac{(x-ut)^2}{\epsilon_x} + \frac{y^2}{\epsilon_y} + \frac{z^2}{\epsilon_z} \right] \right\} \quad (3.4)$$

- b. For continuous point source with time dependent-solution, the unsteady solution to Equation (3.2) becomes:

$$C(x,y,z,t) = q_0 C_0 \int_0^t f_x(x;\tau) f_y(y;\tau) f_z(z;\tau) d\tau \quad (3.5)$$

C_0 and q_0 are initial concentration and discharge of effluent. Equation (3.5) must still be solved by some integral technique with a computer.

- c. For a continuous point source with a steady-state solution assuming the vertical concentration to be uniform:

$$f_z(z,t) = \frac{1}{d}$$

where d = the flow depth, the steady-state solution of Equation (3.5) becomes:

$$C(x,y) = \frac{q_0 C_0}{2\pi d \sqrt{\epsilon_x \epsilon_y}} \exp \left\{ \frac{Ux}{2\epsilon_x} \right\} K_0 \left[\frac{U}{2\epsilon_x} \sqrt{x^2 + \frac{\epsilon_x}{y} y^2} \right] \quad (3.6)$$

where $K_0 []$ = the modified Bessel function of the second kind of 0th order.

The solutions described above can only be applied to transport of conservative substances in an infinite domain without boundary conditions. Hence, the applicability of these types is rather limited. Solutions more applicable to radionuclide transport are described later.

2. Advection-Diffusion Equation with a Decay Term

a. Continuous release with the steady-state solution.

A simple diffusion model for steady-state discharge into a water body (e.g., a lake or a coastal area) with a steady flow has the following governing equation:

$$U \frac{\partial C}{\partial x} = \epsilon_y \frac{\partial^2 C}{\partial y^2} + \epsilon_z \frac{\partial^2 C}{\partial z^2} - \lambda C \quad (3.7)$$

where λ is the radionuclide decay rate.

It is assumed that the discharge is located at the point $(0, y_s, z_s)$, i.e., at the origin of the x-axis and a distance y_s from the shoreline and z_s beneath the water surface. It is also assumed that water depth d is constant. The steady-state solution to Equation (3.7) with no lateral boundary conditions is:

$$C(x, y, z) = \frac{M}{2\pi U \sigma_y \sigma_z} f(\sigma_z, z, z_s, d) f(\sigma_y, y, y_s) \exp\left(-\frac{\lambda x}{U}\right) \quad (3.8)$$

where:

$$f(\sigma_z, z, z_s, d) = \sum_{n=-\infty}^{\infty} \left\{ \exp\left[-\frac{(2nd + z_s - z)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(2nd - z_s - z)^2}{2\sigma_z^2}\right] \right\}$$

$$f(\sigma_y, y, y_s) = \exp\left[-\frac{(y_s - y)^2}{2\sigma_y^2}\right] + \exp\left[-\frac{(y_s + y)^2}{2\sigma_y^2}\right]$$

$$\sigma_y = \sqrt{\frac{2\epsilon_y x}{U}}, \quad \sigma_z = \sqrt{\frac{2\epsilon_z x}{U}}$$

For further information on more general uses of this model, the USNRC Regulatory Guide 1.113 may be consulted.

b. Instantaneous release with time dependent solution.

For an instantaneous release of a finite quantity of material from a line source at $x = 0$, $y = y_s$, the governing equation becomes:

$$\frac{\partial c}{\partial t} + U \frac{\partial c}{\partial x} = \epsilon_x \frac{\partial^2 c}{\partial x^2} + \epsilon_y \frac{\partial^2 c}{\partial y^2} - \lambda c \quad (3.9)$$

The solution to this equation is:

$$c = \frac{M}{4\pi\sqrt{\epsilon_x \epsilon_y t}} \exp \left\{ -\frac{(x-Ut)^2}{4\epsilon_x t} - \lambda t \right\} \left\{ \exp \left(\frac{-(y-y_s)^2}{4\epsilon_y t} \right) + \exp \left(\frac{-(y+y_s)^2}{4\epsilon_y t} \right) \right\} \quad (3.10)$$

c. Continuous release with time dependent solution.

The general transient release may be considered as a superposition of instantaneous releases and can therefore be simulated by integrating the instantaneous solution Equation (3.10):

$$c = \int_0^t \frac{Wf(\tau)}{4\pi\sqrt{\epsilon_x \epsilon_y} d(t-\tau)} \exp \left\{ -\frac{(x-U(t-\tau))^2}{4\epsilon_x (t-\tau)} - \lambda(t-\tau) \right\} \left\{ \exp \left(\frac{-(y-y_s)^2}{4\epsilon_y (t-\tau)} \right) + \exp \left(\frac{-(y+y_s)^2}{4\epsilon_y (t-\tau)} \right) \right\} d\tau \quad (3.11)$$

where the release rate $Wf(\tau)$ is say, in curies/sec. In general, this equation must be solved using numerical quadrature.

The above solutions (Equations 3.4, 3.5, 3.6, 3.8, 3.10 and 3.11) can be used to solve radionuclide transport in various water bodies (oceans, estuaries, rivers, lakes and reservoirs) whenever the assumptions imposed during derivation of these equations are satisfied. A more detailed description of radionuclide transport models is presented in Chapters 4 through 7. As shown in these chapters, many radionuclide transport models are available; however, most of them solve only dissolved radionuclides without fully including adsorption/desorption mechanisms. For radionuclides with small distribution coefficients, K_d , (e.g., ^{90}Sr , ^{51}Cr , ^{124}Sb , etc.) which are mostly transported in a dissolved form, these models can adequately simulate transport for both routine and accidental releases especially over the short term, provided there is sufficient information to simulate the flow field during the initial convective period. For radionuclides with large K_d values (e.g., ^{137}Cs , ^{54}Mn , ^{65}Zn , ^{60}Co , ^{46}Sc , $^{238,239,240}\text{Pu}$, etc.) which are easily adsorbed by suspended and bottom sediment and aquatic biota, only a few models are available to solve the migration of these radionuclides (ORNL 1978).

WATER QUALITY AND SEDIMENT TRANSPORT MODELS

Water quality and sediment-only transport models were also reviewed to examine the feasibility of modifying these models for application to radionuclide transport. Water quality models were divided into six groups. Representative models for each group are discussed. The six groups of water quality models are as follows:

Type I. General advection-diffusion equations with (or without) decay and sink/source terms:

$$\frac{\partial C}{\partial t} + u_i \frac{\partial C}{\partial x_i} = \frac{\partial}{\partial x_i} \left(\epsilon_i \frac{\partial C}{\partial x_i} \right) + \sum_{j=1}^m K_j C + \sum_{j=1}^n S_j \quad (3.12)$$

This type of model includes the basic transport mechanisms of advection and diffusion for both conservative and nonconservative substances, and is the most complete form of water quality model. However, the application of this type of model to radionuclide transport with minor modification is valid only for dissolved radionuclides with decay and source (or sink) terms representing radionuclide decay and reduction of dissolved concentration by non-movable sediment or biota. This type of model cannot, however, handle dissolved radionuclide transport, coupled with particulate radionuclide transport, e.g., adsorption and/or desorption of radionuclides by sediment and biota; transport, deposition, and resuspension of contaminated sediment. Necessary modification of these models to convert to transport models for both dissolved and particulate radionuclides, coupled with transport of sorbants (e.g., sediment, biota, etc.) is very extensive.

Type II. Advection equation with (or without) decay and sink/source terms:

$$\frac{\partial C}{\partial t} + u_i \frac{\partial C}{\partial x_i} = \sum_{j=1}^m K_j C + \sum_{j=1}^n S_j \quad (3.13)$$

Type II models do not have a dispersion term. Hence, the application of this type to both water quality and radionuclide transport (with some modification) is more limited than Type I model. This type of model can be applicable to fast-moving rivers.

Type III. Lagrangian routing models with decay and sink/source term:

$$\frac{\partial C}{\partial t} = \sum_{j=1}^m K_j C + \sum_{j=1}^n S_j \quad (3.14)$$

This type of model calculates the concentration of a water quality parameter in a Lagrangian system; i.e., the longitudinal coordinate system is moving with the flow velocity. Although the governing equation does not have any spatial coordinates, the solution is an unsteady, one-dimensional solution

with decay and sink/source occurring during the travel time from one location to the next. One major advantage of this type, as compared to Type II, is that the governing equation is much simpler. The major shortcoming for this type is that the solution must be one dimensional. This type of model is suitable for application to fairly uniform, non-tidal rivers. The application of this model with minor modification to the radionuclide transport is limited to the transport of dissolved radionuclides with decay and adsorption by other substances with constant adsorption rates, or with particulate radionuclide concentrations preassigned.

Type IV. Complete-mix model:

$$\frac{\partial C}{\partial t} = \sum_{j=1}^m K_j C + \sum_{j=1}^n S_j \quad (3.15)$$

Complete-mix models do not have spatial coordinates, and the concentration of a water quality parameter is based on the linear reaction; i.e., change of concentration is proportional to the concentration itself. This type of model can be applied to certain lakes in which concentration changes with time but does not change with location. The applicability of this type of radionuclide transport is very limited. However, application can be made to dissolved radionuclides in well-mixed lakes and particulate radionuclides adsorbed by non-movable bed sediment from known dissolved concentration.

Type V. Diffusion equation with (or without) decay and sink/source terms:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left(\epsilon_i \frac{\partial C}{\partial x_i} \right) + \sum_{j=1}^m K_j C + \sum_{j=1}^n S_j \quad (3.16)$$

These models do not contain the advection term and consequently can be applied only to quiescent water bodies. The application of this type of model for both water quality and radionuclides is accordingly very limited.

Type VI. Monte Carlo Model:

This type of model is not based on a solution to mathematical equation but, rather, describes transport of constituents phenomenologically using a large computer memory bank to store information on movement of constituents at each time step. The procedure can be described as follows (Figure 3.1):

1. A large number of particles with a given weight will be discharged from a source.
2. Each particle discharged into a water body moves downstream from locations A to B with a given flow velocity during one time step.
3. This particle also moves randomly during the same time step from A to C. The distance between A and C is random as is the direction, but the distance has a mean value pre-assigned. This step represents a dispersion phenomenon.
4. By combining the movements that occurred in steps 2 and 3, the particle from the original location A will actually be moved to D at the end of one time step.
5. Weight of the particle will be changed during the one time step due to decay and sink/source.
6. Procedures 2 to 5 will be repeated on all particles discharged into the water body. The distribution of the particle weight in the study area is then used to determine the migration pattern of the constituent.

This method is computationally very stable and has no numerical dispersion problems. This is an attractive alternative to the advection-diffusion equation for the transport phenomenon. This type of model can be applied to either dissolved or particulate radionuclide transport with very minor modification. However, extensive modification is required to couple dissolved and particulate radionuclides with sediment and biota transport phenomena.

FIGURE 3.1. Particle Movement

As discussed above, all water quality models of Types I through VI can be applied to dissolved radionuclide transport with minor modification. However, extensive model modifications would be needed to simulate the transport of dissolved and particulate radionuclides coupled with sediment transport. Among water quality models, Types I and VI are best suited to solve radionuclide transport problems in general.

Sediment transport models as discussed in Chapters 4 through 7 are of two basic types. One is based on a deterministic approach (e.g., the advection-diffusion of suspended sediment), and the other consists of stochastic models (mainly bed load sediment transport) based on the transport of bed materials as a sequence of alternating steps and rest periods with appropriate distribution functions. If sediment-only transport models predict suspended sediment concentration, then they can be used to predict particulate radionuclide transport with fairly minor modification. However, simulating the transport of dissolved and particulate radionuclides coupled with the transport of sediment and/or aquatic biota requires extensive modification to these sediment models.

REFERENCES FOR CHAPTER 3

U.S. Nuclear Regulatory Commission. 1977. Regulatory Guide 1.113 - Estimating Aquatic Dispersion of Effluents from Accidental and Routine Reactor Releases for the Purpose of Implementing Appendix I.

Oak Ridge National Laboratory. 1978. Proceedings of Workshop on the Evaluation of Models Used for the Environmental Assessment of Radionuclide Releases. CONF-770901, September 6-9, 1977, Gatlinburg, TN.

4. RADIONUCLIDE TRANSPORT IN NON-TIDAL RIVERS

The models reviewed in this chapter, as well as in Chapters 5 through 7, fall into three categories:

1. models designed to simulate radionuclide transport in particulate and/or dissolved form
2. water quality models which can be used to simulate the fate of dissolved or particulate radionuclides. These water quality models are discussed in several subcategories as identified in Chapter 3.
3. sediment transport models which can be modified to simulate particulate radionuclide movement. Some of these models also could be used for dissolved radionuclides.

PHYSICAL MECHANISMS OF RADIONUCLIDE TRANSPORT IN NON-TIDAL RIVERS

Radionuclides discharged to rivers are dispersed by currents and turbulent mixing. These radionuclides are also adsorbed from solution onto sediments and biota. This results in a reduction of concentrations of dissolved radionuclides which may be more easily assimilated by aquatic biota than sorbed radionuclides. However, contaminated sediments may be deposited on the river bed, becoming a long-term source of pollution through desorption and resuspension. This process may also create a significant pathway to man. Most of the available methods for evaluating radionuclide transport in surface waters do not account for radionuclide uptake or desorption into water. Furthermore, these methods do not account for transport, deposition and resuspension of contaminated sediments. Models that do not compute sorption effects predict that radionuclides will be flushed from surface waters at the same rate at which water is exchanged (USNRC 1977). In actuality, sorption effects would cause some radionuclides to flush much more slowly, at approximately the rate at which the stream components are exchanged in the water system (USNRC 1978 a,b; USEPA 1978). Hence, in some cases neglecting such detention effects precludes accurate prediction of radionuclide distributions in time and space. This

section presents results of field and laboratory studies which illustrate the importance of the above-mentioned physical and chemical mechanisms affecting radionuclide transport in rivers. Actual adsorption and desorption mechanisms and distribution coefficients for various radionuclides are discussed in length in Chapter 8. The following two examples suffice to indicate the importance of sediment on radionuclide migration:

1. Field measurements taken in the early 1960s indicated that approximately 75% of the dissolved radionuclide, ^{65}Zn , released at the Hanford Site in Washington was adsorbed by river sediment within 200 miles downstream (Haushild et al., 1973).
2. Radionuclide field measurements obtained from the Clinch River near Oak Ridge National Laboratory in Tennessee in the early 1960s indicated that approximately 90% of ^{137}Cs released was adsorbed by the river's suspended sediment within a 10-mile reach downstream of the effluent discharge (Churchill et al. 1965). At the same time, only about 5% of the ^{90}Sr was associated with river sediment.

Moreover, in experimental studies conducted in a 200-ft long hydraulic flume, E. F. Gloyna and his associates (Gloyna et al. 1963-1972) found that interactions with the above-mentioned stream components could have a significant detention effect on the transport of various radionuclides. In instantaneous release experiments in a hydraulic flume, more than 90% of the dye passed through the flume within 1 day under a mean flow with a travel time of 10 hr, whereas only 24%, 18%, 11%, and 28%, respectively, of injected ^{85}Sr , ^{137}Cs , ^{58}Co , and ^{65}Zn were recovered at the downstream end of the flume within 1 day (Shih and Gloyna 1967). Rowe and Gloyna (1964), Yousef and Gloyna (1964), and Shih and Gloyna (1967) have shown that ^{137}Cs and ^{85}Sr can be detected in water, sediments, and plants several months after a single release of these radionuclides. These results reveal the occurrence of adsorption and desorption of these nuclides, which become a longer-term source of pollution limited by radionuclide decay.

Hydrodynamic Transport

Hydrodynamic transport is the principal transport mechanism for radionuclides. The primary hydrodynamic mechanisms are advection and diffusion/dispersion. In the Clinch River system, Parker et al. (1966) found from field studies and mass-balance analyses that most of the radionuclides being discharged from operations at the Oak Ridge National Laboratory passed through in the water phase as dissolved radionuclides, with the exception of ^{137}Cs , which has a large distribution coefficient.

Suspended Sediment

As indicated earlier, sediment plays an important role in radionuclide transport in rivers. One of the earliest investigations to determine the importance of uptake of radionuclides by sediment was conducted by Carritt and Goodgal, who studied the uptake of various radionuclides in solution by suspensions of Roanoke River and Chesapeake Bay sediments, bentonite, fuller's earth, and powdered pyrex glass (Sayre et al. 1963). The percentage of radionuclides sorbed by sediments ranged between 10% and 90%. In addition, one of their tests showed that sorption by the sediment particles resulted in particulate radionuclide concentrations of more than 10,000 times those in the surrounding solution.

Tritremel et al. (1966) conducted tests to examine the uptake of various fission products by typical suspended sediment loads. They found that ^{90}Sr , ^{131}I , ^{140}La and other fission products tested were adsorbed fairly rapidly on the suspensions but were not permanently fixed. Results indicated that 50% of the radionuclides may have redissolved prior to equilibrium conditions. From their data they estimated that sorption by suspended sediment may effect a 25% to 30% reduction of radionuclides in the waste effluents of the reactor discharge into the Leitha-Mühl Canal in Austria.

Existing data indicate that some radionuclides are adsorbed to river sediment rather quickly and then migrate with the sediment movements. Deposition of suspended sediment with adsorbed radionuclides can result in a buildup of radioactivity if the rate of accumulation through deposition exceeds the

rate of natural radioactive decay. Moreover, some of the contaminated sediment could be resuspended, particularly during periods of high flow, and then be redeposited farther downstream. Thus, an understanding of sediment transport mechanisms is essential to the prediction of radionuclide concentrations.

Brisbin et al. (1974) estimated that 7.2% of the ^{137}Cs released to Steel Creek from the Savannah River Laboratory at Aiken, South Carolina, was contained in the bed sediment, thus preventing the movement of a significant amount of ^{137}Cs downstream into the Savannah River. The authors state that the situation under investigation is one of the highest known concentrations of a predominantly single isotope contamination of a natural system.

In field studies conducted on the Clinch and Tennessee Rivers, Pickering et al. (1966) found that bottom sediment in the Clinch River contained 21% of the ^{137}Cs , 9% of the ^{60}Co , 0.4% of the ^{106}Ru and 0.2% of the ^{90}Sr released to the river during nearly 20 years of operation at the Oak Ridge National Laboratory. Moreover, based on vertical distributions of radionuclide concentrations in the bed sediment, they concluded that the ^{137}Cs and ^{60}Co were incorporated in the bottom sediment through adsorption by suspended sediment and subsequent deposition of suspended sediment.

As can be seen, the importance of the adsorption of radionuclides by suspended particles and sediments is well demonstrated from field and laboratory data. However, the mechanisms involved in the sorption processes are not yet clearly understood. Factors which influence sorption include the type of radionuclide, its chemical form and oxidation state, particle size, concentration and mineralogic content of the suspended sediment, and various environmental conditions such as temperature, dissolved oxygen, concentration, pH, oxidation-reduction potential, salinity, presence of competing ions, mixing characteristics, and pollutional stresses. The effects of these various factors have been illuminated to a certain extent by the work of Gloyna et al. (1963-1972).

Particle size is particularly important in sorption processes. It has been determined that sorption capacity of stream sediments is roughly proportional to the available surface area (Sayre et al. 1963). As pointed out by

Sayre et al., the total surface area of 1- μ clay is 1,000 times that for 1-mm sand for a given weight. Nelson et al. (1966) showed that small silt and clay-sized particles contain a much greater concentration of radionuclides than do coarser particles.

Bottom Sediment

Direct sorption by bed sediment appears to have a much smaller effect on radionuclide transport than does sorption by suspended sediment. In hydraulic flume experiments, Bhagat and Gloyna (1965) found that suspended matter subsequently deposited on the bed significantly increased the concentration of ^{103}Ru in the bottom sediment. Only less than 5% of the total ^{103}Ru in the form of $^{103}\text{RuNO}$ was adsorbed directly by bottom sediment. When kaolinite clay suspensions were added, as much as 50% of the $^{103}\text{RuNO}$ in the water was adsorbed by the suspended matter. As a result of deposition, the amount of $^{103}\text{RuNO}$ in the bottom sediment increased from 1% to 15% of the total ^{103}Ru discharged into the flume.

Gloyna and his associates (Reynolds and Gloyna 1963; Rowe and Gloyna 1964; Clanton and Gloyna 1964, Yousef and Gloyna 1964) determined from additional studies that sorption by bed sediment is dependent on contact time, the mineralogical and chemical composition of the sediment, and on physical characteristics. They also found that uptake by bed sediment is only partially or slowly reversible.

Yousef et al. (1970) pointed out that radionuclide migration is rather limited to near the bed surface, while activity in deeper layers results from physical processes such as sediment deposition and erosion. Studies were conducted by Gloyna and his associates (Rowe and Gloyna 1964; Yousef and Gloyna 1964; Bhagat and Gloyna 1974; Shih and Gloyna 1966) to investigate the migration of radionuclides to deeper layers of the bed sediment without deposition or resuspension of sediment. Results showed that the specific activity of the bed sediment decreased exponentially with depth. After 15 to 30 days of contact time, the depth at which the specific activity of the sediment was less than 0.1% of that near the surface was about 2 cm for ^{65}Zn and 14 cm for

^{137}Cs (Gromiec and Gloyna 1973). Radionuclide concentration data from the Columbia River also indicated a penetration of bed sediment by the radionuclides (Gloyna and Ledbetter 1969).

Results of analyses performed by Brisbin et al. (1974) showed that over 68% of the total ^{137}Cs was located in the upper 20 cm (7.9 in.) of bed sediment in Steel Creek near Savannah River Laboratory during 9 years of plant operation (1961 to 1970). Experimental data collected by Mahmoud et al. (1973) using bottom sediment from the Ismailia Canal in Egypt indicated that for both flowing and nonflowing ecosystems the ^{60}Co incorporated in the bottom sediment was detected mainly in the upper layer, while ^{134}Cs and ^{89}Sr migrated to deeper layers.

Biota

Mahmoud et al. (1973) found through laboratory investigations that the maximum uptake of ^{89}Sr , ^{60}Co , and ^{134}Cs by various aquatic plants was reached after 1 to 4 days. A major portion, ranging from 45% to 85% of the sorbed radionuclides, was released after 2 to 4 days.

Gloyna and his associates (Armstrong and Gloyna 1967; Bhagat and Gloyna 1964; Rowe and Gloyna 1964) found that sorption by plant surfaces is rapid and almost completely reversible. They concluded from their experimental results that plants play an insignificant role in radionuclide transport, except perhaps in slow-moving and enriched streams and impoundments. Gloyna notes that radionuclide concentration data from the Clinch River indicate that effects of plant uptake may be neglected in a mass-balance analysis of radionuclides (Gloyna and Ledbetter 1969).

Thus, the data cited above indicate that sediment effects on radionuclide transport are important: 1) if the sediment concentration is high, 2) if radionuclides have high distribution coefficients, and 3) if long-term transport and accumulation of radionuclides are of concern. Under these conditions, if sediment effects are not considered, there is significant potential for erroneous evaluations of radionuclide distributions in surface water.

Sources of dissolved and particulate radionuclide concentration data are listed in Table 4.1. There have been many such studies (Fisher 1970; Nelson et al. 1966; Osterberg et al. 1966; Haushild et al. 1971; etc.). However, only a small sample is given here. The Columbia River in Washington and the Clinch and Tennessee Rivers in Tennessee have been extensively sampled because of the early reactor operations. Good information sources for the Clinch and Tennessee Rivers include Robertson et al. (1973). A summary of Hanford Reservation related work (Columbia River) can be found in U.S. Atomic Energy Commission (1973). In addition, several excellent articles may be found in Pruter and Alverson (1972) and the IAEA Proceedings on "Disposal of Radioactive Wastes into Seas, Oceans, and Surface Waters" (1966). Excellent sources of radionuclide data on the Clinch River are Jenne and Wahlberg (1965) and Cottrell (1959).

MATHEMATICAL MODELS FOR RIVERS

The greatest number of models surveyed were those developed for rivers. These models included radionuclide and sediment transport models, and water quality models. The radionuclide transport models range from those specifically developed to predict the radionuclide concentrations in the river to those developed as a part of a man-dose model. The water quality models include various types as described in Chapter 3. The sediment models are of two principal types: 1) deterministic models based on the advection-diffusion equation or a simpler equation of continuity, and 2) stochastic or probabilistic models.

Summaries of radionuclide transport, water quality, and sediment transport models for all four types of water bodies (non-tidal rivers, estuaries, oceans and the Great Lakes, and impoundments) are shown in Tables 4.2, 4.3, and 4.4, respectively.

Radionuclide Transport Models for Rivers

The radionuclide transport models for rivers cover a wide range of complexity and use. One set of models includes those that are a part of a larger man-dose model. These models generally incorporate dilution of the material

TABLE 4.1. Radionuclide Data for Rivers

Reference	River	Type of Radionuclide Data
Norton, 1962a	Clinch and Tennessee	Particulate forms of ^{106}Ru , ^{137}Cs , ^{90}Sr
Norton, 1962b	Clinch and Tennessee	Dissolved and particulate forms of ^{90}Sr , ^{137}Cs , ^{60}Co , ^{106}Ru
Renn et al., 1964	Rivers near Chesapeake Bay	Particulate ^{65}Zn and ^{55}Fe
Churchill et al., 1965	Clinch and Tennessee	Dissolved and particulate forms of ^{90}Sr , ^{137}Cs , ^{60}Co , ^{106}Ru
Norton, 1965	Clinch and Tennessee	Biota, sediment bound and dissolved ^{90}Sr , ^{137}Cs , $^{103-106}\text{Ru}$, ^{60}Co , ^{144}Ce , $^{95}\text{Zr-Nb}$, ^{90}Y
Berres et al., 1966	Hudson	Dissolved, particulate; biota-adsorbed concentrations of ^{226}Ra , ^{232}Th , ^{40}K , ^{60}Co , ^{54}Mn , $^{95}\text{Zr-Nb}$, ^{137}Cs , ^{144}Ce , ^{106}Ru , ^{228}Ra , ^{65}Zn
Harshbald et al., 1966	Columbia, Lake Wallula	Dissolved and particulate forms of ^{51}Cr , ^{65}Zn , ^{46}Sc , $^{95}\text{Zr-Nb}$, $^{103}\text{Ru-Rh}$, ^{141}Ce
Parker et al., 1966	Clinch and Tennessee	Dissolved and particulate concentrations of ^{90}Sr , ^{137}Cs , ^{60}Co , ^{106}Ru
Perkins et al., 1966	Columbia	Dissolved and particulate radionuclide concentrations
Pickering et al., 1966	Clinch and Tennessee	Particulate concentrations of ^{137}Cs , ^{60}Co , ^{106}Ru , ^{90}Sr
Carrigan et al., 1967	Clinch and Tennessee	Particulate forms of ^{137}Cs , ^{60}Co , ^{90}Sr , ^{106}Ru
Carrigan and Pickering, 1967	Clinch and Tennessee	Particulate forms of ^{137}Cs , ^{106}Ru , ^{90}Sr , ^{144}Ce , $^{95}\text{Zr-Nb}$, ^{131}I , ^{60}Co
Strunkess et al, 1967	Clinch and Tennessee	Dissolved, sediment-bound, biota; ^{90}Sr , ^{137}Cs , ^{60}Co , ^{106}Ru , ^{91}Y , ^{144}Ce , $^{95}\text{Zr-Nb}$, ^{131}I
Sax et al., 1969	Cattaraugus Creek, New York	Dissolved, sediment-bound, and organisms-adsorbed radionuclides of $^{106}\text{Ru-Rh}$, ^{137}Cs , ^{134}Cs , $^{95}\text{Zr-Nb}$, ^{60}Co
Pickering, 1970	Clinch and Tennessee	Dissolved and particulate forms of ^{90}Sr , ^{137}Cs , ^{60}Co , ^{106}Ru
Hubbell and Glenn, 1971	Columbia	Particulate forms of ^{60}Co , ^{65}Zn , ^{54}Mn , ^{46}Sc , ^{51}Cr , ^{106}Ru , ^{40}K , $^{95}\text{Zr-Nb}$
Wrenn et al., 1971	Hudson	Dissolved, sediment-bound, and biota-adsorbed ^{137}Cs
Fukui and Murray, 1973	Data review for several rivers	Dissolved and particulate concentrations of ^{58}Co , ^{60}Co , ^{110}Ag , ^{137}Cs
Robertson et al., 1973	Columbia	Dissolved and particulate concentrations of ^{54}Mn , ^{60}Co , ^{152}Eu , ^{137}Cs , ^{95}Zr , ^{65}Zn , ^{155}Eu , ^{154}Eu , ^{46}Sc , ^{126}Sb , ^{144}Ce , ^{239}Pu
Brislin et al., 1974	Steel Creek near Savannah River	Particulate concentrations of ^{137}Cs
Shore and Gottschalk, 1975	Three Rivers Creek, Savannah River	Dissolved, sediment-bound and organism-adsorbed ^{137}Cs
Ecker and Onishi, 1979	Cattaraugus Creek, Butternilk Creek, Franks Creek	Dissolved and particulate forms of ^{134}Cs , ^{137}Cs , ^{60}Co , ^{141}Ce , ^{144}Ce , ^{155}Eu , ^{228}Ra , ^{226}Ra , ^{106}Ru , $^{95}\text{Zr-Nb}$, ^{238}Pu , $^{239,240}\text{Pu}$, ^{90}Sr , ^{241}Am , ^{244}Cm

TABLE 4.2. Summary of Radionuclide Transport Models

Author and/or Reference	Physical Processes			Chemical Processes			Biological Processes			Environmental Processes			Time Dimension			Solution Technique	Applicable Media	Field Application
	Advection	Dispersion	Retention	Adsorption	Desorption	Decay	Uptake	Release	Transformation	Migration	Retention	Transformation	Scale	Range	Period			
Fletcher and Watson, 1971	X		X													FD	A,L	
Braschi et al., 1973	X			X												A	A,L	X
Soldat et al., 1974	X			X												FD	C,S,A,L	X
Metcalf, 1976	X			X												A	A	X
Martin et al., 1978	X			X												A	A,L	X
Quicker and Chapin, 1978	X		X	X	X											FD	A	X
Shin and Chapin, 1978	X		X	X	X											A	A	
Armstrong and Chapin, 1980	X		X	X	X											FD	A	
Shin and Chapin, 1982	X		X	X	X											FD	A	
Shin and Chapin, 1983*	X		X	X	X											A	A	
Shin et al., 1986, 1977, 1988, 1990, 1992																		
PETRA	X	X	X	X	X	X						X		X	X	FE	C,S,A	X
SCHMIDT	X	X	X	X	X	X						A		X	X	FE	A,L	X
TERRA	X	X	X	X	X	X								X	X	FE,FD	A,S	X
Smith and Watson (Smith et al., 1988a)	X		X	X											X	FD	A,L	X
Palmer, Watson and Arnold (Smith et al., 1988b)	X		X	X											X	A	A	
Fields, 1976 (CHES)	X	X	X	X											X	FD	A	
Charwell, 1978	X	X		X								X			X	FD	C	X
Vanderploeg et al., 1976	X	X		X											X	A	L	X
Quinn, 1976	X	X		X											X	A	L	
Granton et al., 1977				X	X													
ALPHA	X			X	X											I	C,A	
ALPHA	X			X	X											I	C,S,A	
REACT		X	X													I	C,A	
Chapman, 1977		X		X	X											FD	A	
Smith et al., 1977	X	X		X	A											FD	A,L	
Codell (CHES, 1980)																		
ENC River Model	X	X		X												A	A	X
ENC Lake Model	X	X		X												A	L	X
ENC Suburban Model	X	X		X	X											A	C	X
O'Connor and Farley, 1978	X	X		X												FD	C	X

*X = Significant Solution; FD = Finite Difference; FE = Finite Element; I = Integration; P = Probabilistic
 +C = Codell Systems and the Great Lakes; L = Lake and Reservoir Systems; A = River Systems

TABLE 4.3. Summary of Sediment Transport Models

Author and/or Sediment Transport Model	Modeling Techniques		Mechanisms				Hydrodynamics Simulation	No Spatial Dimensions	Dimensionality			Time Dimension Scale	Solution Technique	Applicable Water Body	Field Application
	1D Sediment Transport	2D Sediment Transport	Advection	Diffusion	Dispersion	Sediment Scouring			1D	2D	3D				
Glover, 1964	X	X	X	X	X	X			X			X	A	R	X
Hubbell and Sayre, 1964		X	X	X	X	X			X			X	P	R	X
Sayre and Cheng, 1968	X	X	X	X	X	X			X			X	FD	R	X
Odd and Ouse, 1970	X		X		X	X	X		X			X	FD	E	X
Yang and Sayre, 1971		X	X	X	X	X			X			X	P	R	X
Waldrop and Farnor, 1973	X	X	X								X	X	FD	E	X
Chen, 1973		X	X		X	X	X		X			X	FD	R	X
Thomas, 1974	X	X	X		X	X			X			X	FD	R	X
Leibschuler et al., 1974	X	X	X	X						X		X	FE	E	X
Sethi, 1975	X	X	X	X						X		X	A	E	
Todorovic, 1976		X	X	X	X	X			X			X	P	R	
Brandema and Dively, 1976	X	X	X	X						X		X	FD	R,E	X
Fields, 1976b (LIMSED)		X	X		X	X			X			X	FD	R	X
Spaulding, 1976	X	X	X	X			X				X	X	FD	C,E	X
Mahmood and Ponce, 1976		X	X		X	X	X		X			X	FD	R	
Arikathurai et al., 1977	X		X	X	X	X				X		X	FE	E	X
Erastin et al., 1977 (SEBONE)	X	X	X	X	X	X	X		X			X	I	C,R	X
O'Connor, 1977			X		X	X	X		X	X		X	FD	E	X

X = Analytical solution; FD = Finite Difference; FE = Finite Element; I = Integration; P = Probabilistic
 C = Coastal Systems and Great Lakes; E = Estuarine Systems; L = Lake and Impoundment Systems; R = River Systems

TABLE 4.4. Summary of Water Quality Models

Author and/or Water Quality Models	Modeling Substances		Mechanisms			Hydrodynamics Simulation	Dimensionality				Time Dimension		Solution Technique	Applicable Water Body	Field Application
	Quality	Transfer	Advection	Diffusion/ Dispersion	Production/ Regeneration		0-D Point	1-D Longitudinal	2-D Cross- Sectional	3-D Three- Dimensional	Steady- State	Dynamic			
TYPE I															
Hydroscience, Inc., 1968	X		X	X				X				X	A	C,R	X
Leonardson, 1970	X		X	X		X			X			X	FD	C,E	X
Galley and Marleman, 1972	X		X	X	X	X		X				X	FE	E	X
Leonardson, 1973	X		X	X		X					X	X	FD	C,E	X
Simms, 1973	X		X	X		X					X	X	FD	C	X
Horton et al., 1974	X		X	X	X	X		X				X	FD	R	X
Spragg, 1974	X	X	X	X		X			X			X	FD	C,E	X
Taylor and Davis, 1974	X		X	X		X			X			X	FE	E	
Chen et al., 1976	X		X	X	X	X				X		X	FD	L	X
Baca et al., 1976 (AQUA)	X		X	X	X				X			X	FE	L	X
Yotsukura and Sagro, 1976	X		X	X					X			X	FD	R	X
Zand et al., 1976	X		X	X				X				X	A	R	X
McCoy and Edge, 1977	X		X	X		X			X			X	FE	E	
TYPE II															
Orlob et al., 1967	X		X		X	X		X				X	FD	E	X
Baca et al., 1973 (EXPLORE)	X		X		X	X		X				X	FD	E	X
Bauer and Bennett, 1976	X		X		X			X				X	A	R	X
Gorton and Needham, 1976	X		X		X			X				X	FD	E	X
TYPE III															
Gattello, 1974 (PIONEER)	X		X		X			X			X		FD	R	X
TYPE IV															
Baca et al., 1974 (EUTROPA)	X				X			X				X	I	L	X
Anderson et al., 1976	X				X		X					X	A	L	X
TYPE V															
Hydroscience, Inc., 1968	X		X	X				X				X	A	L	
TYPE VI															
Anlistrom, 1976	X		X	X	X				X			X	P	C	X
PROBABILISTIC															
Stolombeck et al., 1972	X		X	X							X	X	FD	C,E,R	X
Adams et al., 1976	X		X	X			X				X	X	FD	C,E	X
Trant, 1976	X		X	X	X	X	X		X			X	FD	R,C,L	X

*A - Analytical Solution; FD - Finite Difference; FE - Finite Element; I - Integration; P - Probabilistic
 C - Coastal Systems and Great Lakes; E - Estuarine Systems; L - Lake and Impoundment Systems; R - River Systems

by the flow volume of the river and include decay of the radionuclide according to the travel time to a specified downstream point. A few of the models include prediction of sediment concentrations, although the reduction in dissolved radionuclide concentration by adsorption is not accounted for. Most of the other models predict the dissolved radionuclide concentration in the river by solution of the advection-dispersion equation. Source/sink terms in some models are used to simulate uptake by sediment. Very few models solve both dissolved and particulate radionuclide transport by considering dynamic transport of sediment.

The following first five models are man-dose models which contain radionuclide transport in water as submodels.

Fletcher and Dotson (1971); Fletcher, Dotson, Peterson,
and Betson (1973)

The model developed by Fletcher et al. (1973) is one of the earliest models to compute the radionuclide dose to man through liquid and gaseous pathways. Components included in this study are shown in Figure 4.1. As shown in this figure, the liquid pathway model includes dissolved and particulate radionuclide transport and sediment transport. Various options include inputs from numerous point sources, input from air deposition and overland flow, flood deposition and groundwater transport. The liquid pathway model is an unsteady, one-dimensional code and calculates the temporal and spatial (longitudinal) distributions of dissolved radionuclide concentration as well as the concentration of radionuclides attached to suspended and bottom sediments of various sizes. The transport model can also account for the effects of flow stratification and sediment trapping in reservoirs. The dissolved radionuclide concentration at a given location is found by applying the mass conservation equation with radioactive decay as follows:

$$C_{x,t} = \frac{1}{Q_{x,t}} \left\{ Q_{(x-\Delta x, t-\Delta t)} C_{(x-\Delta x, t-\Delta t)} e^{-\lambda \Delta t} + \sum_{i=1}^n Q_i C_i \right\} \quad (4.1a)$$

FIGURE 4.1b. Water Transport Model

FIGURE 4.1a. Overall Model Structure

where

$C_{x,t}$ = dissolved radionuclide concentration at the location x and time t

C_i = dissolved radionuclide concentration of tributary

$Q_{x,t}$ = flow rate at the location x and time t

Q_i = tributary flow rate

λ = radionuclide decay

The sediment transport rate, S , is found analytically from the following equation:

$$S = aQ^b \quad (4.1b)$$

where Q is the flow rate and a and b are constants that must be estimated for each sediment size range. The concentration of radionuclides attached to sediment is calculated from the known dissolved radionuclide concentration and the distribution coefficient value, K_d . Since the amount of radionuclide adsorbed to the sediment is not subtracted from the dissolved concentration, strictly speaking the mass conservation in a stream reach is not satisfied.

This model, as well as man-dose models in the following sections, expresses the very complicated liquid pathway transport with extremely simplified formulations. Consequently, it is very easy to apply this model, but the results may either be overestimated or underestimated. These merits and shortcomings are shared by other man-dose models, as discussed below.

Bramati, Marzullo, Rosa and Zara (1973)

Bramati et al. (1973) developed a simple man-dose model, VADOSA, with two parts; one for gaseous release and the other for liquid discharges. This model incorporates the transfer parameters of 24 radionuclides for liquid releases and 20 radionuclides for gaseous releases in order to calculate annual doses for five critical organs for various critical groups of population. Formulations for the calculation of radionuclide transport are very similar to those of Fletcher et al. (1973) discussed above.

Soldat, Robinson and Baker (1974); Soldat (1976)

These papers discuss a set of models which predict the radionuclide dose to man and other organisms through air, water, soil and food. As a part of the liquid pathway, time-dependent, one-dimensional distributions of concentrations of the radionuclides in the water and those attached to shoreline sediment are calculated. Dissolved radionuclide concentration at a selected location is calculated as in the model of Fletcher et al. (1973) (i.e., by dividing the effluent radionuclide concentration at the point of discharge by a dilution factor and by decaying the radionuclide over the travel time to the selected location; the dilution factor is the ratio of the discharge of the receiving water and the effluent flow). An order of magnitude estimate of the radionuclide concentration adsorbed to shoreline sediment was obtained from the rate of radionuclide transfer from the water to the sediment, the concentration of dissolved radionuclide in the adjacent waters, decay rate and lifetime of the nuclear facility by using the following equation:

$$S_i = K_j C_i \frac{(1 - e^{-\lambda_i t_s})}{\lambda_i} \quad (4.2)$$

where

- S_i = the concentration of nuclide i in the sediment
- C_i = the concentration of nuclide i in the adjacent water
- K_j = mass transfer rate
- λ_i = the decay rate
- t_s = time of exposure or operating time of the facility.

The accumulation of radionuclides in the aquatic biota is calculated from the dissolved concentration, bioaccumulation factor, and decay rate.

Watts (1976)

This is another man-dose model, via aquatic pathways, for chronic radionuclide releases. It was developed by modifying the aqueous phase portion of the Soldat et al. (1974) model discussed above. The unsteady, one-dimensional distribution of dissolved radionuclide concentration is calculated by the following equation:

$$C_i = \frac{R_i}{W} (1-E_i) \exp(-\lambda_i D) \quad (4.3)$$

where

R_i = radionuclide i release rate

W = average stream flow rate

E_i = fraction of material i removed from the stream

λ_i = decay constant of radionuclide i

D = travel time from release point to sample point.

The model was applied to chronic tritium releases to the Savannah River, near Savannah River Laboratory, South Carolina.

Martin, Robbins, Nelson, Cousins and Cullitan (1976)

Martin et al. (1976) developed an unsteady, one-dimensional, man-dose model, RVRDOS, to assess the consequences to man from radioactive liquid effluents through the consumption of drinking water. Rivers and impoundments can be modeled, although the impoundments must be uniformly mixed and the effect of retention time included. The aquatic dispersion model predicts only dissolved radionuclide concentrations by solving for conservation of mass and using the routing technique. The radionuclide concentration at a given location is calculated simply by considering the dilution of the radionuclide effluent by the receiving water and the decrease in radioactivity caused by radionuclide decay. Radionuclide decay is computed using the travel time from the effluent discharge location to the location under consideration. One unique aspect of this model is the fact that parents and daughters of radionuclides can be solved by taking into account the growth rate of daughter radionuclides. In the river simulation, the flow rate downstream cannot be decreased so that diversion of river water cannot be accounted for. The model was developed for and applied to the Mississippi River Basin. However, because of the lack of field data, model verification was not attempted.

The following models are not man-dose models but were developed to predict radionuclide migration in rivers.

Buckner and Hayes (1975); Buckner, Hayes and Watts (1975)

The unsteady, one-dimensional radionuclide transport model developed by Buckner et al. (1975) at Savannah River Laboratory uses the advection-diffusion equation with a source/sink term used to calculate dissolved and sediment-bound radionuclide concentrations. The river is divided into two regions: the main channel and a deadwater zone. The deadwater zone represents backwaters and slow-moving sections of the river, as well as adsorption-desorption with sediment. The source/sink term expressing the diffusion of contaminant between deadwater zone and main channel is represented as:

$$S_i = \frac{MP}{A_s} [W_i - C] \quad (4.4)$$

where

M = the mass transfer coefficient

P = the wetted perimeter between deadwater zone and mainstream

A_s = cross-sectional area of the deadwater zone

W_i = concentration of radionuclide in the deadwater zone

C = concentration of radionuclide in the mainstream.

Adsorption and desorption of radionuclides by sediment and plants are also represented by the source/sink term given as:

$$S_j = T_{sj} [W_j - K_j C] \quad (4.5)$$

where

T_{sj} = mass transfer coefficient between mainstream and compartment j (sediment or plants)

W_j = radionuclide concentration adsorbed by compartment j

K_j = distribution coefficient.

The above formulations of dissolved and particulate radionuclide transport are the same as those developed by Gloyna and his associates (Shih and Gloyna 1967, 1969, 1970; Armstrong and Gloyna 1968; White and Gloyna 1969), as discussed in detail later. Although the concentration of radionuclides attached

to bed sediment and plants is calculated for a particular section of the river, the effects of sediment transportation are not included.

The advection-diffusion equation was solved by a finite difference method. One of the attractive features of the model is that the selection of the best set of parameters for model calibration is made by using a least square approximation and minimizing the error between model prediction and measured data.

The model was applied to the Savannah River for instantaneous releases of dye and tritium which are both in a dissolved form only. Computed and measured results for both cases agreed very well indicating the model can predict dissolved radionuclide migration very well. However, the need to use two different dispersion coefficients (a one order of magnitude difference) for these two cases in the same river suggests either a problem in the accuracy of measured data to be used for model calibration, or the need for the further model improvement. Since the model was applied to dissolved substances only without adsorption/desorption effects, the model must be further tested for its validity for the prediction of dissolved and particulate radionuclide transport with their interactions.

Another paper by Thacketon and Schnelle (1970) discusses the original dead zone model developed by Hayes (1966) in his Ph.D. thesis. The relative merits of the model are discussed, but particular emphasis is placed on the method for determining six parameters used in the model.

Gloyna et al. (1963-1972)

Several unsteady, one-dimensional, mathematical models resulted from a series of studies - "Radioactivity Transport in Water" - undertaken by E. F. Gloyna and his associates at the University of Texas at Austin. Investigations were made of the transport and dispersion of strontium, cesium, ruthenium, cobalt, and chromium with adsorption-desorption mechanisms included. In addition to model development, a series of experiments were conducted in a model river consisting of a dual-channel flume and various other components. Each channel of the metal flume was 200 ft long, 1.25 ft wide, and 2 ft deep with a slope which could be varied between 0 and 0.006.

Three of the resulting models discussed below are based on the unsteady, one-dimensional, advection-diffusion equation with a source/sink term added to include the effect of sorption and desorption by aquatic plants and/or nonmovable bottom sediment. The governing equations for dissolved radionuclides and particulate radionuclides adsorbed by plants and/or bed sediment are as follows:

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = \epsilon_x \frac{\partial^2 C}{\partial x^2} + \sum_j K_j [C_j - K_d C] \quad (4.6)$$

$$\frac{\partial C_j}{\partial t} = K_j [K_d C - C_j] \quad (4.7)$$

where

C = dissolved radionuclide concentration

C_j = concentration of particulate radionuclide attached to j^{th} sorbent such as plants and bed sediment

K_d = distribution coefficient

K_j = mass transfer coefficient for j^{th} sorbent

$\sum_j$ = mass of j^{th} sorbent

U = mean velocity in x direction.

As shown above, the last term in Equation (4.6) expresses the adsorption-desorption mechanisms. The primary differences among the three models discussed below are in the selection of the particulate sorbent (e.g., plants and bed sediment) and the solution technique.

Shih and Gloyna (1967, 1969, 1970). The model developed by Shih and Gloyna (1967) is capable of describing the transport of radionuclides injected instantaneously into a stream. The model takes into account effects of nonmovable bed sediment for adsorption-desorption mechanisms in order to solve dissolved radionuclide concentration in a stream.

Assumptions inherent in the model include a constant average velocity and an initial radionuclide concentration in both water and bed sediment of zero.

Although the solutions are analytical, they contain complicated integrals which must be solved numerically. The authors' method for obtaining an analytical solution from their initial formulation is not clear. Shih and Gloyna also present more general governing equations which incorporate the interaction of dissolved radionuclides with water in the deadwater zone, with plants, and with bed sediment. However, these equations were not solved.

Shih and Gloyna conducted a series of experiments in the river model flume to identify dispersion processes of ^{85}Sr for both continuous and instantaneous releases. The value of the dispersion coefficient was determined through instantaneous releases of dye. A continuous release experiment conducted in the hydraulic flume by using ^{85}Sr was used to determine the value of the mass transfer coefficient. Using these values, Shih and Gloyna compared both their sorption-desorption model and Taylor's dispersed flow model (one-dimensional, advection-diffusion model with no sink/source term) with observed data from model river experiments using instantaneous releases of ^{85}Sr . Values predicted by the dispersed flow model without sorption effects deviated significantly from the observed data, while the sorption-desorption model showed better agreement. These experimental results demonstrate the importance of sorption mechanisms. Shull and Gloyna (1968) note that the solutions developed by Shih and Gloyna work well for low velocity model rivers but produce errors when applied to natural rivers.

Armstrong and Gloyna (1968). Armstrong and Gloyna obtained a more general model by solving the above described equations numerically by an explicit finite difference method. Their model includes the effects of adsorption-desorption by plants. In order to verify the model, they conducted radionuclide dispersion tests in the river model flume for both instantaneous and continuous releases of ^{85}Sr . Agreement of the computer results with the measured data for instantaneous and continuous releases was very good and reasonable, respectively. Since this model is a numerical simulation model, the model applicability is wider than the analytical model developed by Shih and Gloyna. However, their numerical solution requires further improvement because of the instability caused by an initial zero radionuclide concentration on the bed.

Experiments conducted by Armstrong and Gloyna (1967) also revealed the following interesting aspects of adsorption-desorption phenomena: Adsorption of ^{85}Sr by plants is much quicker than desorption from the plants. Rapid sorption of ^{85}Sr by plants is followed by much slower sorption by bed sediment. These findings agree well with those of Whittaker (1951, 1961) who studied ^{32}P sorption phenomena in a lake. Whittaker reported that ^{32}P followed three steps: 1) initial rapid movement to plankton followed by rapid release, 2) a slower movement to attached algae, and 3) an even slower movement to lake sediment. These studies imply that the ecological system of the lake may be one of the important factors in the assessment of radionuclide migration in lakes and reservoirs (Chapter 7). However, Armstrong and Gloyna reported that, within their experimental ranges, aquatic plants played a negligible role in ^{85}Sr transport.

White and Gloyna (1969). The one-dimensional mathematical model developed by White and Gloyna includes the mechanisms of sorption and desorption by both plants and bottom sediment and uses an implicit finite difference solution method. It is capable of treating instantaneous, continuous, or time-varying releases of radionuclide activity. The model showed good agreement when compared with data from experiments in the model river using both continuous and instantaneous releases of ^{85}Sr . The model is the basis for the radionuclide block of the Qual-II model (Norton et al. 1974) discussed later.

All three aforementioned models simulate unsteady, one-dimensional radionuclide transport by accounting for radionuclide adsorption-desorption with bed sediment and aquatic plants. Foundations and formulations of these models are sound. The analytical solution obtained by Shih and Gloyna (1967) is especially useful because it is simple to apply. However, a shortcoming of these models is that these sorbents (sediment and plants) are assumed to be stationary. The models include neither transport, deposition and resuspension of sediment, nor sorption-desorption with suspended sediment. Because direct adsorption by bed sediment has in many cases a much smaller effect on radionuclide transport than does sorption by suspended sediment (Bhagat and Gloyna, 1965), these models are rather limited to rivers and certain lakes where almost no suspended sediment exists.

Shull and Gloyna (1968). A somewhat different type of model from the previously discussed models of Gloyna and his associates was developed by Shull and Gloyna (1968). This model is an unsteady, one-dimensional mathematical model with a 1000-mile computation range capable of simulating both dissolved and particulate radionuclide transport in large rivers with continuous low concentration waste discharges. This routing model, which uses a Lagrangian system, incorporates the effects of advective-mass transport but does not include the dispersion mechanism. An analytical solution technique is used. The model includes stochastic, temporal flow variation; flooding; channel geometry variation with time and distance; generalized boundary sorption; and scour and deposition. A brief description of assumptions inherent in each of these model capabilities follows.

The simulation period for streamflow synthesis was chosen to be 1 month except during a flood period. Channel geometry (i.e., the width and depth of the assumed rectangular cross section) and travel time are functions of the flow rate. Radionuclide sorption includes the combined effects of sorption by bed sediment, uptake by attached plants, and sorption by the fluid dead zone and is expressed by the same formulation as that of the three previous Gloyna models. Sorption occurring in a flood plain is similar to channel sorption except that the initial concentration of radionuclides on the surface is assumed to be zero. For flood plain deposition it was assumed that 1% of the total particulate concentration is dropped in the flood plain. Scour, transport, and deposition of particulate radionuclides in the model are based on the following assumptions:

1. All sorbed radionuclides are near the surface of the benthic system and subject to scour or loosening.
2. All sorbed radionuclides are associated with particles that are small enough to be present in the suspended load, at least half of the time, when they are scoured.
3. A single critical velocity determines the occurrence or nonoccurrence of suspension of this size of particle.

4. During scour, the stream is assumed to be in equilibrium with respect to sediment transport; i.e., it is transporting exactly its capacity at every station so that no net deposition or scour of the benthal system occurs in the river.

Standard output includes monthly transport and storage data for stations at 10, 100, and 1000 miles below the waste source and total storage on the flood plain above the 1000-mile station.

This model was not intended to be used for direct numerical application since the data required for its verification are not empirically available. Rather, it was meant to be used as a guide to understanding system behavior. The authors determined from the model results that some large reservoirs have the potential for accumulating long-lived radionuclides at a rate as high as half the waste release rate. Benthal sorption and desorption, flow variability, and flood plain deposition were determined to be insignificant on a hazard basis for long-lived radionuclides on a long-term basis.

This model is useful, as Shull and Gloyna pointed out, to understanding the system qualitatively. However, there are many assumptions in the model which are arbitrary and which may not be justified (e.g., the flood plain sediment deposition amount) when model results are considered quantitatively.

Onishi et al. (1976, 1980a), Onishi (1977) Onishi and Wise (1979a,b)

Models SERATRA and TODAM

Onishi et al. (1976) developed an unsteady, two-dimensional (longitudinal and vertical) model, SERATRA (Sediment-Radionuclide Transport,) as a means of more realistic prediction of radionuclide migration by coupling it with sediment transport. SERATRA is a finite element model which predicts transport of sediment and radionuclides (and other toxic contaminants). It uses general advection-diffusion equations with decay and sink/source terms and appropriate boundary conditions. The model consists of the following three submodels coupled to describe sediment-contaminant (radionuclide) interaction and migration: 1) a sediment transport submodel, 2) a dissolved contaminant transport submodel, and 3) a particulate contaminant (contaminant adsorbed by sediment) transport submodel.

Since the movements and adsorption capacities of sediment vary significantly with sediment sizes or sediment types, the sediment transport submodel simulates transport, deposition and erosion of three sediment size fractions (or sediment types) of cohesive and noncohesive sediments. The dissolved contaminant transport submodel includes mechanisms of contaminant adsorption and desorption, as well as radionuclide decay and contaminant degradation resulting from hydrolysis, oxidation, photolysis, volatilization and biological activity, where applicable. The particulate contaminant transport submodel simulates transport, deposition and erosion of contaminants associated with each sediment size fraction.

Adsorption-desorption mechanisms were assumed to have occurred between dissolved contaminants and sediments (both suspended and bed sediments). The mechanisms are expressed by a distribution coefficient and a transfer rate which describes how quickly dissolved and particulate contaminant concentrations reach their equilibrium condition, similar to the right hand side of Equation (4.7) (Onishi and Wise 1979b). These formulations assume that adsorption-desorption mechanisms are completely reversible. However, as shown in Chapter 8 in length, these mechanisms are not fully reversible in many instances.

SERATRA also predicts changes of bed conditions for sediment and particulate contaminants, including: 1) riverbed elevation changes due to sediment deposition and scour, 2) longitudinal and vertical distributions of ratio of each bed sediment component, and 3) longitudinal and vertical distributions of particulate contaminants in the river bed. One of the shortcomings of the model is that it has a vertical dispersion coefficient but does not have a longitudinal dispersion term. The model uses a nonuniform vertical distribution of longitudinal velocity to produce sediment and contaminant distributions dispersed from those obtained in cross-sectionally averaged flow cases. However, lack of a longitudinal dispersion term in the model makes it difficult to accommodate an effect of transverse variation of longitudinal velocity, which may become important in large rivers, to spread the sediment and radionuclide cloud longitudinally.

The model was applied to a large river, the Columbia River (approximately 100-km reach), near the Hanford Site, Washington (Onishi 1977) to an intermediate size river, the Clinch River (approximately 37-km reach) near Oak Ridge National Laboratory, Tennessee (Onishi et al., 1979b) and to very small streams, Four Mile and Wolf Creeks (approximately 68-km reach) in central Iowa (Onishi and Wise 1979b), to simulate migration of sediments, radionuclides and pesticides. For the Columbia River, simulation was conducted for the movement of ^{65}Zn with and without the adsorption mechanism to identify effects of ^{65}Zn adsorption by sediment.

For the Clinch River, simulation was also conducted for both continuous and instantaneous releases of ^{137}Cs and ^{90}Sr . These radionuclides were selected not only on the availability of field data but also for their extreme adsorption characteristic (most of the ^{137}Cs is transported with sediment, while the majority of the ^{90}Sr is transported in a dissolved form). Comparison of computed results with measured data for both Columbia and Clinch Rivers indicates good agreement for both sediment and radionuclide distributions, as shown in Figure 4.2 (Onishi et al. 1980a). However, because of very limited data to be compared, the model is not fully tested for its validity. Currently, SERATRA is being applied to the Cattaraugus and Buttermilk Creeks near the West Valley radioactive waste burial site in New York to conduct a comprehensive verification test. Examination of simulation results for the Columbia and Clinch Rivers clearly indicates that suspended sediment has significant effects on radionuclide transport through radionuclide adsorption and desorption, and desorption and resuspension of contaminated sediment.

Additionally, the two-dimensional model, SERATRA, was simplified to a one-dimensional (longitudinal) code Transient One-Dimensional Degradation and Migration Model (TODAM) including the longitudinal dispersion term. This one-dimensional, sediment-contaminant program was then coupled to an unsteady, hydrodynamic model, DWOPER (Freed 1973), to form a new model suitable to many rivers where vertical distributions of sediment and radionuclides are not a major concern. In the special case of the intermittent flow of Mortandad Canyon in Los Alamos, New Mexico, the hydrodynamic model DKNAV (Whelan 1980), rather than DWOPER, was employed to estimate movements of flow, sediment and radionuclides (Onishi et al. 1980).

FIGURE 4.2. Longitudinal Distributions of Dissolved, Particulate and Total Cesium-137 Concentrations in the Clinch River, Tennessee

Onishi et al. (1976, 1979); Onishi and Ecker (1977); Onishi and Wise (1978a,b) Model FETRA

Onishi et al. (1976) also developed another unsteady (as well as steady) sediment-contaminant transport model, FETRA. This model solves longitudinal and lateral distribution of sediment and contaminant transport by including sediment-contaminant interaction and wave-sediment interaction mechanisms. FETRA is applicable to relatively wide and shallow water bodies, such as wide estuaries, coastal waters, the Great Lakes, as well as wide rivers. Detailed descriptions of FETRA are given in Chapter 5.

Fields (1976a)

Fields' model, CHNSED, is capable of simulating the transport of trace contaminants in the dissolved form and the particulate form (adsorbed to sediment) as runoff from the land surface or as flow in a channel. CHNSED is a composite model combining the Wisconsin Hydrologic Transport Model (WHTM) with a sediment transport model for a rectangular stream channel (SEDTRN). Both the WHTM and the SEDTRN models are components of the Unified Transport Model which simulates the transport of a trace contaminant through a watershed ecosystem. In the channel, the dissolved contaminant transport is governed by the hydrologic flow routing of the WHTM, while the adsorbed contaminants are routed according to the sediment transport dynamics of SEDTRN, described below.

Fields uses the distribution coefficient, K_d , to allow for simulation of first-order chemical exchange between the water and the sediment in the channel system. Such exchange is assumed to occur at both input and output of each reach. The K_d value for the pollutant of interest is assumed to be the same for each of the 12 sediment size classes included in SEDTRN and for each river reach. However, in reality K_d values do change significantly with sediment sizes and types due to large variations in exchange capacities and surface areas of sediments with sediment sizes and types (Kennedy 1965; Jenne and Wahlberg 1968). Commonly, the finest sediment clay has a larger K_d value than silt, which in turn has a greater K_d value than sand (Pruter and Alverson, 1972). Although CHNSED does not allow for a variable K_d value, it does include a parameter which must be specified by the user for each sediment size class to indicate whether the size class is to be included in sediment-contaminant interactions. Because CHNSED is not compatible with the other one-dimensional models of the Unified Transport Approach (UTA) program developed by Oak Ridge National Laboratory, another sediment transport model (SEDONE) has been developed (Eraslan et al. 1977; Hetrick et al. 1979). SEDONE will be further discussed in this chapter. Radionuclide transport models applicable to rivers which are also part of the UTA program include RADONE, a one-dimensional, dissolved radionuclide model and HOTSED, a model for the transport of particulate radionuclides (Eraslan et al. 1977), both of which are discussed in Chapter 5.

Chapman (1977)

In the dissolved and particulate contaminant transport model developed by Chapman (1977), the basic equation for dissolved contaminants is a two-dimensional, unsteady, advection-diffusion equation with a sink/source term containing the Freundlich formulation of adsorption-desorption mechanism. In this equation, the longitudinal velocity component was deleted by assuming the flow is uniform and the coordinate system moves with the flow. However, longitudinal velocity varies vertically according to the logarithmic velocity distribution with Von Kármán constant equal to 0.4. The vertical diffusion coefficient was estimated from the vertical velocity distribution and stratification. The longitudinal dispersion coefficient was also calculated from the vertical distributions of the flow. The suspended sediment profile is assumed to be one which is independent of time and longitudinal direction. A particulate contaminant equation is formulated as: the rate of change of particulate concentration is equal to the amount adsorbed by or desorbed from sediment. This type of expression is the same as those obtained by Shih and Gloyna (1967) and Buckner and Hayes (1975). The dissolved and particulate contaminants were then solved numerically by an explicit finite difference scheme.

In general, the model can be applicable to cases with steady flows in uniform channels. However, it has several inherent limitations which preclude its wide application. First, the assumption that flow and sediment concentration are independent of longitudinal distance is not generally valid. Especially, since sediment transport rate is in general proportion to the third to fifth power of velocity, the model assumption of constant sediment concentration with longitudinal distance and time greatly limit its applicability. Secondly, the method to calculate the longitudinal dispersion by using the vertical distribution of flow will underestimate the dispersion in large natural streams. In large natural streams, nonuniformity of transverse distribution of flow dominates the longitudinal dispersion (Fisher 1967) but not by the vertical distribution of flow as Chapman used it to obtain longitudinal distribution coefficient, as shared by SERATRA for its shortcomings. Finally, the model must assume that there is no initial concentration of contaminants in a study region.

Smith et al. (1977)

Smith et al. (1977) reported a compartment model, EXAMS, to predict transport and transformation of potentially harmful chemicals in a freshwater environment. Although the model was developed for toxic chemicals, it is applicable to radionuclides as well. The model, EXAMS, calculates both dissolved and particulate chemicals including the mechanisms of adsorption and desorption and chemical and biological degradation. The model handles each chemical degradation mechanism separately. Chemical degradation results from hydrolysis, oxidation, photolysis, and volatilization. Although the effects of particulate chemical deposition and resuspension are included in the model, the amounts of sediment transport, deposition and scouring must be supplied to the model as input data at each computation point. EXAMS is limited to transport and transformation processes that might occur under steady-state environmental exposure, such as continuous releases of chemicals to steady-state flow and sediment conditions.

Since the model divides the modeling area into a number of completely mixed compartments, it can be applied to streams and lakes as one-, two- or three-dimensional cases. EXAMS uses the predictor-convective method to integrate governing equations. The model was used to study various chemicals including p-cresol, benz(a)anthracene, benzo(a)pyrene, quinoline, benzo(f)-quinoline, 9H-carbazole, 7H-dibenzo(c,g)carbazole, benzo(b)thiophene, dibenzothiophene, methyl parathion, and mirex.

Code11 (NRC Plug-Flow Model) (USNRC 1978)

Code11 at NRC developed a Plug-Flow Model by assuming that the radioactivity from the source was considered to be moving as a plug in a uniform channel downstream to the mouth, as illustrated in Figure 4.3.

In a steady, uniformly flowing, plug-flow channel, concentrations of dissolved and particulate radionuclides, C and C_p , can be described by the following equations:

FIGURE 4.3. Plug Flow River Model

$$U \frac{dC}{dx} = \lambda_1 C_b - \lambda_2 C \quad (4.8)$$

$$C_p = \frac{\lambda_3}{\lambda_4} C \quad (4.9)$$

where

$$\lambda_1 = \frac{K_f}{d_1 K_d}$$

$$\lambda_2 = \lambda + \frac{\epsilon v K_d}{d_1} + \frac{K_f}{d_1}$$

$$\lambda_3 = \lambda + \frac{\epsilon v K_d}{d_2} + \frac{K_f}{d_2}$$

$$\lambda_4 = \lambda + \frac{\epsilon v}{d_2} + \frac{K_f}{d_2 K_d}$$

K_f = the coefficient for direct transfer from the water to bottom sediment

K_d = the equilibrium sorption coefficient

ϵ = the sediment effectiveness factor

- d_1 = the average depth of the water layer
- d_2 = the average depth of the effective sediment layer
- ϵ = the radiological decay coefficient = $\ln 2$ /half life
- U = average velocity in the channel
- v = the sedimentation rate

Equations (4.8) and (4.9) may be solved to give an expression for the water-phase concentration

$$C = \frac{W(t)}{q} \exp \left\{ \left(\frac{\lambda_1 \lambda_3}{\lambda_4} - \lambda_2 \right) x/U \right\} \quad (4.10)$$

where

- x = the distance from the source
- $W(t)$ = the rate of release of radioactive material at the source
- q = the flow-rate past the source

Particulate radionuclide concentrations can then be obtained by Equation (4.9).

Onishi and Whelan (Mixing Tank Model with Sediment Transport)
(Onishi 1980b)

A mixing tank transport model, similar to the one used for the pesticide transport in streams (Onishi et al. 1980b), will be described here (Figure 4.4).

FIGURE 4.4. Mixed Tank Model

The following assumptions are made:

1. River reaches are divided as a series of tanks with which sediment and radionuclide concentrations are completely mixed.
2. Radionuclide and sediment contributions from point and nonpoint sources are treated as lateral influx uniformly distributed along the river reach for each segment.
3. Dissolved and particulate radionuclides are linearly related by a distribution coefficient.
4. Dissolved and particulate radionuclides reach their equilibrium conditions within one time step.
5. There is no particulate radionuclide deposition to the river bed nor resuspension from the bed.

The mass conservation of sediment in the n-th tank leads to the following sediment transport equation;

$$\left. \frac{\partial(SV)}{\partial t} \right|_n = Q_{n-1}S_{n-1} + SL_n - Q_nS_n \quad (4.11)$$

where

- Q_n = flow discharge from n-th tank
- S_n = sediment concentration in the n-th tank
- SL_n = lateral influx of sediment
- V = water volume of the n-th tank
- t = time

Rearranging Equation (4.11), the following sediment transport equation was obtained:

$$\frac{\partial S}{\partial t} = -S_n \left[\frac{1}{V} \left(\frac{\partial V}{\partial t} + Q \right) \right]_n + \frac{Q_{n-1}S_{n-1} + SL_n}{V_n} \quad (4.12)$$

The mass balances of the dissolved and particulate radionuclides in the n-th tank are:

$$\left. \frac{\partial(CV)}{\partial t} \right|_n = Q_{n-1}C_{n-1} + CL_n - Q_n C_n - C_n V_n - S_n V_n K_1 (K_d C_n - C_{Pn}) \quad (4.13)$$

$$\begin{aligned} \left. \frac{\partial(C_P SV)}{\partial t} \right|_n &= S_{n-1} C_{Pn-1} Q_{n-1} + C_{PLn} - S_n C_{Pn} Q_n \\ &\quad - \lambda C_{Pn} S_n V_n + S_n V_n K_1 (K_d C_n - C_{Pn}) \end{aligned} \quad (4.14)$$

where

- C_n = dissolved radionuclide concentration in the n-th tank
- C_{Pn} = particulate radionuclide concentration in the n-th tank
- CL_n = lateral influx of dissolved radionuclide
- C_{PLn} = lateral influx of particulate radionuclide
- K_d = distribution coefficient of radionuclide
- K_1 = transfer rate at which dissolved and particulate radionuclides reach their equilibrium conditions

The total radionuclide mass balance can be obtained by adding Equations (4.13) and (4.14):

$$\begin{aligned} \left. \frac{\partial(CV)}{\partial t} \right|_n + \left. \frac{\partial(C_P SV)}{\partial t} \right|_n &= Q_{n-1}C_{n-1} + CL_n - Q_n C_n - \lambda (C_n + C_{Pn} S_n) V_n \\ &\quad + S_{n-1} C_{Pn-1} Q_{n-1} + C_{PLn} - S_n C_{Pn} Q_n \end{aligned} \quad (4.15)$$

Note that

$$C_{Pn} = K_d C_n \quad (4.16)$$

Substituting Equation (4.16) into Equation (4.15) yields the following equation:

$$\frac{\partial C_n(1 + S_n K_d)}{\partial t} = (1 + S_{n-1} K_d) Q_{n-1} C_{n-1} + (C_{Ln} + C_{Pn}) - (1 + S_n K_d) Q_n C_n - \lambda V_n C_n (1 + S_n K_d)$$

Hence

$$\frac{\partial C_n}{\partial t} = \frac{1}{V_n(1 + S_n K_d)} \left[(1 + S_{n-1} K_d) Q_{n-1} C_{n-1} + (C_{Ln} + C_{Pn}) - (1 + S_n K_d) Q_n C_n - V_n C_n (1 + S_n K_d) - C_n \frac{\partial}{\partial t} \{ V_n(1 + S_n K_d) \} \right] \quad (4.17)$$

Equations (4.13) and (4.16) are then solved to obtain sediment and dissolved radionuclide concentrations, S_n , C_n , in the n -th tank. In general, Equations (4.13) and (4.16) must be solved numerically. However, for the following simplified case, an analytical solution can be obtained:

$$\begin{aligned} C_0 &= 0 \\ C_{Ln} &= 0 && \text{for all } i \geq 2 \\ S_n &= S_{n-1} = \dots = S_i = \text{constant for all } n. \\ Q_n, V_n &\text{ are not functions of time for all } n. \end{aligned}$$

With these conditions, Equation (4.17) may be simplified to

$$\begin{aligned} \frac{\partial C_n}{\partial t} &= \frac{Q_{n-1} C_{n-1}}{V_n} + \frac{C_{Ln} + C_{Pn}}{V_n(1 + S_n K_d)} - \left\{ \frac{Q_n}{V_n} - \lambda \right\} C_n \\ &= \frac{C_n}{V_n} \left\{ Q_{n-1} + \frac{C_{Ln} + C_{Pn}}{(1 + S_n K_d) C_n} \right\} - \left\{ \frac{Q_n}{V_n} + \lambda \right\} C_n \end{aligned} \quad (4.18)$$

For an instantaneous release of $CL_1 + C_p L_1$ (unit of say curies), the concentration of dissolved radionuclide in the n -th river reach (tank) is:

$$C_n = \frac{\frac{CL_1 + C_p L_1}{1 + S_n K_d} \prod_{i=1}^{n-1} Q_i}{\prod_{i=1}^n V_i} \left[\sum_{j=1}^n \frac{(-R_j) \exp(-R_j t)}{\prod_{\substack{k=1 \\ k \neq j}}^{n+1} (R_k - R_j)} \right] \quad (4.19)$$

where

$$R_j = \frac{Q_n}{V_n} + \lambda$$

$$R_{n+1} = 0$$

A particulate radionuclide concentration is then obtained by Equation (4.16). Total radionuclide concentration CT_n is then calculated by:

$$CT_n = C_n + S_n C_{pn} \quad (4.20)$$

Falco, Onishi, and Arnold (Plug Flow Model with Sediment Interaction)
(Onishi 1980)

The following analytical solution was derived here for radionuclide transport in rivers by generalizing an original approach taken by J. W. Falco at EPA Environmental Research Laboratory, Athens, Georgia. The following assumptions are made:

1. The flow is steady and uniform in a uniform channel.
2. Sediment concentration is constant.
3. Radionuclides are released instantaneously along river reaches.
4. Dissolved and particulate radionuclides are linearly related by the distribution coefficient.
5. Dissolved and particulate radionuclides reach their equilibrium conditions within one time step.
6. There is no deposition of particulate radionuclide to the river bed nor resuspension from the bed.

The governing equation and the initial condition of dissolved radionuclide transport are:

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = -\lambda C - SK_1(K_d C - C_p) \quad (4.21)$$

$$C = f(x) \quad \text{at } t = 0 \quad (4.22)$$

where

C = dissolved radionuclide concentration per unit volume of water

C_p = particulate radionuclide concentration per unit weight of sediment

K_1 = radionuclide transfer rate at which dissolved and particulate radionuclides reach their equilibrium conditions

K_d = radionuclide distribution coefficient

S = sediment concentration

U = velocity

t = time

x = longitudinal distance

λ = radionuclide decay rate

For particulate radionuclides, the governing equation and the initial condition are:

$$\frac{\partial C_p}{\partial t} + U \frac{\partial C_p}{\partial x} = -\lambda C_p + K_1(K_d C - C_p) \quad (4.23)$$

$$C_p = g(x) \quad \text{at } t = 0 \quad (4.24)$$

Note that:

$$C_p = K_d C \quad (4.25)$$

Total radionuclide concentration, C_t , is:

$$C_t = C + SC_p = (1 + SK_d)C \quad (4.26)$$

Hence, the total radionuclide transport equation can be obtained by summing Equation (4.21) and a product of sediment concentration and Equation (4.23):

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} + S \frac{\partial C_p}{\partial t} + U \frac{\partial C_p}{\partial x} = -\lambda C - \lambda S C_p \quad (4.27)$$

Substituting Equation (4.25) into Equation (4.27) and rearranging a resulting equation yields:

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = -\lambda C \quad (4.28)$$

The initial condition for total radionuclide transport is:

$$C_T = C + S C_p = f(x) + S g(x)$$

or

$$C = \frac{f(x) + S g(x)}{1 + S K_d} = F(x) \quad (4.29)$$

Equation (4.28) with the initial condition, Equation (4.29) can be solved by the method of characteristics. The solution to Equation (4.28) (i.e., the dissolved radionuclide concentration) then becomes:

$$C = F(x-ut) e^{-\lambda t} \quad (4.30)$$

Concentrations of particulate and total (sum of dissolved and particulate) radionuclides are then computed by Equations (4.25) and (4.26).

If computations for more general radionuclide releases are desired, the following convolution integral method will produce the desired solution:

$$C(t) = \int_0^t C_i(t-\tau)G(\tau)d\tau \quad (4.31)$$

where

$C(t)$ = dissolved concentration at time t

$C_i(t-\tau)$ = analytical solution for concentration at time $t - \tau$ for an instantaneous release which occurred at time $t = 0$

$G(\tau)$ = a function defining a noninstantaneous rate of radionuclide release

Particulate and total radionuclide concentrations for this case are also obtained by Equations (4.25) and (4.26).

Water Quality Models in Rivers

All of the river water quality models except for the model developed by Yotsukura and Sayre (1976) were one-dimensional advection-dispersion models. The models included general source/sink terms which represented a large number of different factors including decay, inflow, various biochemical and chemical transformations as well as hydrodynamic effects.

Water Quality Models of Type I

Norton, Roesner, Evenson, and Monser (1974). Models Qual I and II developed by Norton et al. (1974) are general water quality models including dissolved radionuclide as one of the water quality parameters. The main equation is the unsteady, one-dimensional advection-diffusion equation with decay (Water Quality Model of Type I). The decay term expresses various reactions of water quality parameters. Hence, for radionuclides, the radioactive decay is considered, but full sediment and biotic interactions (e.g., adsorption/desorption; and transport, deposition and erosion of contaminated sediment) was not included in the models. The hydrodynamics can be computed through a subroutine or supplied by a model user. The hydrodynamic subroutine calculates the velocity by assuming steady flow. Solution of the advection-diffusion equation is obtained by an implicit finite difference formulation.

These models are good examples of how the general water quality models can be used to predict the dissolved radionuclide concentration and the limitations of these models for their application to radionuclides with high K_d values.

The model Qual II was utilized by Willis, Anderson, and Dracup (1976) to simulate BOD, DO and total nitrogen in the Truckee River in northern California and Nevada. Agreement between field data and the computer simulation was reasonably good.

Zand, Kennedy, Zellweger and Avanzano (1976). This river water quality model was developed to predict the water quality based on unsteady, one-dimensional advection and diffusion with decay of the substances (Water Quality Model of Type I). The transport equation is solved analytically by assuming the constant velocity. The model was applied to solve migration of chloride, sodium and stable strontium in the Uvas Creek, California.

The field study conducted by Zand et al. indicates that chloride and sodium are not adsorbed by suspended sediment but that a significant amount of stable strontium is attached to the sediment. Interestingly, the agreements between computed and measured results for chloride and sodium are very good, but comparison for the stable strontium indicates poor agreement. This study again demonstrates the importance of radionuclide adsorption-desorption by sediment and the limitation of applicability of water quality models to radionuclide transport.

Yotsukura and Sayre (1976). The model equation is a two-dimensional, advection-diffusion equation without decay and sink-source terms (Water Quality Model of Type I). This water quality model predicts the steady-state, dissolved constituent distribution in a meandering, nonuniform, natural stream. Two features of the equation derived in this paper are that it employs the transverse cumulative discharge (sum of equal-discharged stream tubes) as an independent variable replacing the transverse distance and that it is developed in an orthogonal curvilinear (natural) coordinate system which follows the general direction of the channel flow. With the help of the continuity equation of flow, the transverse advection term, which is one of the very

difficult quantities to measure in a river and which also cannot be neglected in a stream, is eliminated from the advection-diffusion equation by a transformation wherein cumulative discharge replaces transverse distance.

The final equation to be solved is a classic Fickian diffusion equation. This equation can be solved either analytically or by an explicit finite difference method. The model was applied to the Missouri and Potomac Rivers and the Atrisco Feeder Canal in New Mexico. The agreements between field and predicted results are very good to confirm the validity of the model, as shown in Figure 4.5 (Sayre and Yeh 1973).

Water Quality Models of Type II

Hydroscience (1968). This report described a series of water quality models developed for the Hudson River - Lake Champlain Area. These models include those that calculate water quality parameters in either rivers or estuaries. The lake models are discussed in Chapter 7. Models applicable to rivers and estuaries are discussed below.

The river model is a steady, one-dimensional, convection equation with decay and source/sink terms. The diffusion term is not considered (Water Quality Model of Type II, See Chapter 2). To aid in solving the equation, the cross-sectional area of the river is considered constant along the whole length. The equations are then solved analytically by assuming a steady state and mass balance of material entering or leaving the element through advective transport in each geometric element along the river. These analytical solutions have been obtained for transport of conservative and nonconservative substances, including dissolved oxygen.

The estuary model is the same as that developed for rivers except that diffusion is included to predict transport (Water Quality Model of Type I). Geometry of the estuary can be constant or vary as a function of longitudinal distance. Mass balance of material entering or leaving an element through advective transport and diffusive transport is given for each element. Tidally averaged velocity is used for advection. Analytical solutions are given for four options to express channel geometry as a function of distance including the constant channel geometry.

These models have been applied to the Hudson River estuary. The river model has also been applied to the upper Hudson River.

Bauer and Bennett (1976). An unsteady, one-dimensional, water quality model was developed by Bauer and Bennett to simulate the behavior of DO and BOD in streams. The model includes convection, decay and sink/source terms but does not have a diffusion term (Water Quality Model of Type II).

Both nitrogenous and carbonaceous biochemical oxygen demands are calculated by taking into account the settling of material, reaeration and decay. The model equations are solved by a numerical integration technique called the convolution approach. Hence the model can be applied to both steady and unsteady flow fields. In their paper it was stated that the model was verified but the results are not presented in the report.

Overton and Meadows (1976). Overton and Meadows developed a model to predict effects of urban runoff on river water quality. The basic model equation is a one-dimensional, unsteady, advection equation with decay and sink/source terms. However, no diffusion term is included in the model (Water Quality Model of Type II). Combination of decay and sink/source terms can represent effects of general nonpoint source runoff, point source pollution, reaeration, nitrogenous oxygen demand, photosynthesis, respiration and sedimentation on water quality. The equations are solved by an explicit finite difference method. The model was applied to solve the distribution of dissolved oxygen in Third Fork Creek, North Carolina. Some unsteady cases had very good agreement. However, the steady-state solution underpredicted the oxygen deficit at each station.

Water Quality Models of Type III

Waddel et al. (1974), Battelle (1974), Brandstetter and Brown (1977)
Model PIONEER. PIONEER is a steady-state, water quality model solved in Lagrangian coordinates and belonging to Water Quality Models of Type III. As discussed in Chapter 3, a Type III model solves water quality parameters by the first order reaction formula. The resulting set of differential equations is solved by a fourth order Runge-Kutta procedure. The solution is then

assigned to an appropriate longitudinal location by the routine method with a known travel time. Velocity and depth are assumed to be functions of the flow rate, and the travel time through the river reach is calculated from the flow velocity. The following water quality parameters can be calculated by this model:

- total nitrogen
- total dissolved solids
- phosphorus
- coliform bacteria
- ammonia
- nitrite
- nitrate
- biochemical oxygen demand
- chlorophyll a
- dissolved oxygen
- toxic compound.

The model was applied to the South Platte River Basin in Nebraska and Colorado (Maddel et al. 1974), the Chehalis River in Washington (Battelle 1974), and the Chemung River in New York (Brandstetter and Brown 1977). Comparison of computed and measured values for model calibration and verification on dissolved oxygen in the Chemung River shows reasonable agreement (Figures 4.6 and 4.7).

Sediment Transport Models in Rivers

There are two basic methods (deterministic and stochastic approaches) for describing sediment transport in rivers. The deterministic approach is to use the advection-diffusion equation of continuity for sediment, or a routine method similar to that employed for water quality models. This method is represented by the papers by Sayre (1971), Fields (1976a, b), Thomas (1974), Chen (1973) and Mahmood (1976). Glover (1964) discusses practical application of this method to field situations. The remaining models are stochastic models for sediment transport. All of these models are for instantaneous release of sediment except for the very general method of Todorovic (1975) for extension of the general instantaneous solution to a continuous release.

FIGURE 4.6. Dissolved Oxygen Calibration of PIONEER Model (Brown and Brandstetter 1978)

FIGURE 4.7. Dissolved Oxygen Verification of PIONEER Model (Brown and Brandstetter 1978)

Glover (1964)

Glover (1964) describes the application of analytical solutions to unsteady, one and two-dimensional, advection-diffusion equations without decay and source/sink terms to the movement of dissolved materials or small suspended particles. The solutions are for instantaneous line and plane sources, and continuous line sources in streams of uniform cross section. Because of the importance of longitudinal and lateral dispersion in determining the movement of constituents in water, various formulations to estimate these dispersion coefficients are listed, along with longitudinal and lateral dispersion coefficients for many streams and flumes. Computed dispersion coefficients were compared with laboratory and field measurement. Agreement of computed dispersions calculated by the Taylor or the Elder formulas with those obtained from laboratory flumes was very good but differed by several orders of magnitude for streams, mainly due to the nonuniformity of transverse distribution of velocity which occurs in a natural stream. Taylor and Elder derived empirical formulations of both longitudinal and lateral dispersion coefficients based on data obtained from natural streams. Analytical solutions were applied to the South Platte River (Nebraska) by using these longitudinal dispersion coefficients, and to the Columbia River by using the lateral coefficient. Comparison of computed concentrations of salinity to field data indicates reasonable agreement for the South Platte River and very good agreement for the Columbia River.

Sayre and Chang (1968) and Sayre (1971)

Sayre and Chang developed an unsteady, two-dimensional, suspended sediment transport model. The model consists of the advection-diffusion equation and the equation of continuity for sediment. The two equations are:

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} - V_s \frac{\partial C}{\partial y} = \frac{\partial}{\partial y} \left(\epsilon_y \frac{\partial C}{\partial y} \right) + \epsilon_x \frac{\partial^2 C}{\partial x^2} \quad (4.32)$$

and

$$\frac{dM}{dt} = \alpha V_s C(x, 0^+, t) - \gamma w \quad (4.33)$$

where

C = sediment concentration

U = the local velocity

ϵ_y, ϵ_x = the local turbulent diffusion coefficients for longitudinal and vertical direction, x and y , respectively

W = the weight of tracer particles stored per unit area of bed surface

V_s = the settling velocity of the particles

α = a bed absorbency coefficient

γ = an entrainment rate coefficient

$C(X, 0^+, t)$ = the local concentration immediately above the bed

These are in turn coupled with boundary conditions at the river bed and water surface. The bed surface boundary condition states that a mass balance must exist between the flow and the bed, and the water surface boundary condition indicates that no mass transfer occurs across the water surface. Instead of solving these equations analytically for some simplified cases, Sayre (1971) adapted an innovative approach. This alternative method employed by Sayre is to use Aris moment transformation for $c(X, Y, t)$ and $W(X, t)$ to eliminate the variable X , and to obtain a new set of equations which can be solved for the p^{th} moment of the longitudinal distribution (e.g., 1st moment is the mean of the concentration distribution). The elimination of X makes the transformed equations easier to solve; however, some detail is sacrificed because the solutions are for moments of longitudinal distribution of substances rather than the concentrations themselves. The exact numerical method he uses to solve the equation for $p=0, 1, 2$ and 3 is not given but was probably a finite difference method. Using these moments he can calculate the area under the distribution area ($p=0$) and the mean ($p=1$), variance ($p=2$) and skewness ($p=3$) of the distribution function.

No verification or application was given by the authors. Instead, they offered an explanation of difficulties in verifying the model. These difficulties include: 1) difficulties due to differences between spatial representation of experimental results and time variation of computed results, 2) difficulties due to lack of agreement on how to evaluate ϵ_y , and 3) difficulties

due to controversy over whether average settling velocity, V_s , is the same in turbulent flow as in still water. Also due to inadequate knowledge of the dynamics of fluid-particle interaction, particularly close to the bed, some of the parameters cannot be predicted from known flow and sediment properties.

The model is particularly useful because it yields characteristics of the relevant flow. One of the important advantages of using this model is that it is applicable not only to the Taylor (or diffusive) period but also to the convective (or initial) period of mass transport. Most of conventional advection-diffusion equations utilizing Fick's first law of diffusion, strictly speaking, cannot be applied to the convective period.

Sayre and Chang discussed laboratory flume results and compared the results with Fickian diffusion. They also discussed the various diffusion coefficients and how they might be estimated.

Fields (1976a, b)

Fields developed a one-dimensional, sediment transport code, SEDTRN, to calculate sediment load in a single region of a rectangular stream channel. This model uses a sediment transport capacity equation developed by Bagnold (1966) which is based on energy and momentum conservation. Migrating sediment is separated into two components: bed load and suspended load. Bagnold's approach to the calculation of sediment transport rates assumes that the sediment is cohesionless, that sediment aggregation or flocculation does not occur, and that the sediment is uniform and thus can be described by a single density, diameter, volume concentration, and angle of repose (Fields 1976a). However, SEDTRN divides the sediment into 12 different size fractions comprising the full size range of both cohesive and cohesionless sediment: clay (diameter $<4\mu$), silt ($4\mu < \text{diameter} < 62\mu$), and sand ($62\mu < \text{diameter} < 2000\mu$).

SEDTRN predicts the mass transport rate for suspended sediment as a function of volume flow rate, channel properties, and the fall velocity of the suspended sediment. Manning's equation is used to calculate the flow velocity and volume flow rate from channel parameters. SEDTRN provides for computation of both viscous and inertial particle settling through modifications to Stokes' law.

In addition, the model includes a parameter to indicate the tendency for a particulate class to remain in suspension. This tendency parameter is defined as:

the ratio of the time required for particles of size Class I ($I = 1, \dots, 12$) in still water to settle out of suspension to the average time required for particles from all size classes. It is the relative contribution of a sediment size class to the suspended load, assuming equal amounts of each sediment size class on the bed and unlimited availability of resident bed sediment (Fields 1976a).

To compute the bedload transport rate, the model requires a determination of an effective particle diameter for the bed sediment in order to provide a more accurate determination of bedload flux at low flow rates. Fields notes that his effective diameter reflects the degree of coupling of bedload particles to the faster moving water above. It should be noted that Bagnold was unable to test the bedload term in his final transport rate relationship because of a lack of data.

SEDTRN is designed to be combined with a driver code. The composite model resulting from the merging of SEDTRN with the Wisconsin Hydrologic Transport Model was called CHNSED (Channel Sediment Transport Model) (Fields 1976a). A description of its capabilities can be found in an earlier section. To allow for the computation of sediment transport in a multi-reach rectangular stream channel, Fields combined SEDTRN with a driver code which reads input data and contains bookkeeping to account for and route transported sediment between reaches. The resulting model, LINSSED (Fields 1976b), does not require extensive specifications of watershed characteristics as does CHNSED.

LINSSED was applied to the Rio Grande River near Bernalillo, New Mexico, to calculate sediment concentrations in the river for model verification (Fields 1976a,b). Agreement between the field data and computer results was good (Figure 4.8). It should be noted, however, that almost all bed sediment in the Rio Grande River consists of sand; in addition, the suspended sediment is primarily sand (Nordin 1964; Nordin and Beverage 1965).

The "Stream Power" concept (Bagnold 1966; Simons and Sentus 1977), developed by Bagnold, which forms the basis for SEDTRN, has been criticized

FIGURE 4.8. Observed and Simulated Transport Rate (Bedload Plus Suspended Load) Versus Measured Flow Velocity for Complete Set of Available Sampling Dates in the Rio Grande River Near Bernalillo, New Mexico (Fields 1976)

both as a concept and for its applicability to real streams (Graf 1971; Yanoni 1975; Yalin 1972). For example, Bagnold's method is applicable only to cases with high sediment concentrations and cannot be applied to rivers having sediment diameters below 15μ (fine silts and clays) (Graf 1971; Yanoni 1975; Yalin 1972). As stated earlier, most of the particulate radionuclides are associated with finer silt and clay, which have diameters below 15μ .

Upon its development, SEDTRN was one of the components of the Unified Transport Model developed by Oak Ridge National Laboratory (ORNL) to simulate the transport of a trace contaminant through a watershed ecosystem (Fields, 1974). A more recent program at ORNL involves the development of mathematical models for assessment of thermal, chemical, radiological and biological impacts on water bodies from power plants. Because the mathematical formulation and computer code structure of SEDTRN were not compatible with other one-dimensional models of the program, a new one-dimensional, sediment transport model, SEDONE, has been developed by ORNL (Eraslan et al. 1977; Hetrick et al.

1979). The model is a discrete-element formulation based on the sediment mass conservation principles; the formulation includes a layer for suspended sediment, a layer for creeping-bed sediment, and a layer for the stationary resident-bed sediment, with each layer being comprised of particles of different sizes. SEDONE is applicable to both uniformly flowing rivers and tidal-transient estuaries. It has been used to simulate sediment concentration along the Hudson River with reasonable agreement as shown in Figure 4.9 (Eraslan et al. 1977).

FIGURE 4.9. Measured and Simulated Values of Volumetric Sediment Discharge Rates in the Hudson River at a Cross Section 10 Miles Upstream from the Battery (Eraslan et al. 1977)

Thomas (1974)

Thomas has developed one of the most widely used one-dimensional, steady-state, computer codes at the U.S. Corps of Engineers Hydrologic Engineering Center to simulate sediment transport, scour, and deposition in rivers. The flow is assumed to be steady and one-dimensional. In simulating the ability of the stream to transport sediment, the model considers the full range of conditions embodied in Einstein's Bed Load Function plus silt and clay

transport and deposition, armoring, and destruction of the armor layer. The cross section is subdivided into two parts--that part which has a movable bed, and that which does not; and the boundary between these parts remains fixed for the study. The entire movable bed part of the cross section is moved vertically up and down depending on bed scour or deposition. The solution is accomplished by using a finite difference scheme. This model is best suited to predict migration of sand in rivers whose flows do not change with time or change very slowly. Its applicability to the migration of cohesive sediments is improved by replacing an originally used empirical formulation on cohesive sediment erosion and deposition by Partheniades (1962) and Krone (1962) formulations, which are also used by sediment-contaminant models, SERATRA and FETRA.

Chen (1973)

As Ph.D. Thesis work, Chen derived the basic partial differential equations of a gradually varied, unsteady flow in natural alluvial channels and developed an unsteady, one-dimensional model. The model simulates water and sediment routing processes in natural streams, and the degradation and aggradation at the site of hydraulic structures by solving the equations of continuity and motion for sediment-laden flow and the equation of continuity for sediment simultaneously. The equation of continuity of sediment was derived simply from the conservation theory; the sediment inflow minus the sediment outflow is equal to the change of storage of sediment in the control volume. The sediment routing process of the model uses Einstein's Bed Load Function (1950) or Toffaleti's model (1969). He reported that these equations were solved by the linear-implicit finite difference method. Unlike Sayre (1971) and Fields (1976a,b) discussed earlier, his model does not directly provide sediment concentrations but provides river bed elevation changes due to sediment deposition and scouring. The model was applied to lower Mississippi and Missouri Rivers and yields reasonably good agreement with field data. The model applicability is limited to sand-bed rivers.

Mahmood and Ponce (1976)

A one-dimensional, unsteady, mathematical model for simulation of bed elevation changes in sand-bed channel due to transport, erosion and deposition

of sand was developed by Mahmood and Ponce (1976). The governing equations for the model comprise the momentum equation for the water-sediment mixture, and the continuity equations for the water and sediment, a concept similar to that used by Chen (1973) described above. By assuming a steady-state flow and empirical formula on velocity distributions, friction factor, sediment and bed load functions, Mahmood and Ponce reduced these equations to an equation of a local flow depth alone which was then solved by a linearized implicit. The model was applied to hypothetical cases.

Hubbell and Sayre (1964); Sayre and Hubbell (1965)

In alluvial channels with ripple or dune beds, the sediment particles along the bed are transported by surface creep. They move with discrete steps of variable length, between which they are buried for periods of variable duration. Lagrangian probabilistic models (as is the case here) express the transport of bed material particles as a sequence of alternating steps and rest periods. In order to solve this problem, the following steps were taken: It was assumed that step lengths and rest period duration are sets of identically distributed random variables. The length of any particular step and the duration of any particular rest period of a given particle are independent of location and time (homogeneous probability field), which implies that the bed must be flat or nearly flat. The distance traveled by a particle in n steps is gamma distributed and the number of waiting periods, i , in a given time interval is Poisson distributed. However, it is not practical to know the number of steps and rest periods; instead, a function that describes the probability that a particle will have gone a certain distance x in time t regardless of the number of steps is desired.

By using the ideas of joint and conditional probability, a probability density function for longitudinal position of a particle at time t is developed. This one-dimensional, time-dependent function allows calculation of the concentration of trace particles in weight per unit volume of bed material at any point in the river. These same equations were derived independently by Einstein (1937) and Todorovic (1967) not by the stochastic approach but by analytical and experimental approach. Results of the model show good agreement with field and laboratory data (Figure 4.10).

FIGURE 4.10. Theoretical and Observed Longitudinal Distribution of Tracer Particles:
North Loud River Field Experiment (Hubbell and Sayre 1964)

Yang and Sayre (1971)

The unsteady, one-dimensional model developed by Yang and Sayre (1971) is a refinement of the model developed by Hubbell and Sayre (1964). The assumptions and methodology are the same as reported by Hubbell and Sayre except that the distribution of waiting periods is expressed by an exponential distribution function instead of a Poisson function. The results on comparisons with field data had better agreement.

Shen and Cheong (1973, 1977) and Cheong and Shen (1976) discuss extensions of the model presented by Yang and Sayre (1971). They examined the behavior of the model under various conditions, constructed envelopes of concentration distributions, and calculated the mean concentration of sediment in transport at any time. One important conclusion was that the concentration distribution function is initially highly skewed but becomes progressively symmetrical with time. Therefore, after a long period of time the distribution function can be approximated by a Gaussian curve.

Todorovic (1975)

All previously discussed stochastic models were developed for instantaneous release of sediment. Todorovic discusses how any density function for instantaneous release can be used to give a density function of a continuous release with almost all conceivable (nonrandom) release modes. The unsteady, one-dimensional, stochastic model for longitudinal dispersion, developed by Todorovic, is obtained by means of a simple integral transformation from distribution functions of instantaneous release cases. Simple case studies were conducted by applying the model. However, no field application or verification of the model was presented.

- Buckner, M. R., and D. W. Hayes. 1975. "1975 Pollutant Transport in Natural Streams." Presented at the Topical Meeting on Computational Methods in Nuclear Engineering, American Nuclear Society, Charleston, SC.
- Buckner, M. R., D. W. Hayes and J. R. Watts. 1975. Emergency Response Capability for Pollutant Release to Streams and Rivers. DP-MS-75-73, DuPont de Nemours (E.I.) and Co., Savannah River Laboratory, Aiken, SC.
- Carrigan, P. H., Jr., R. J. Pickering, T. Tamura, and R. Forbes. 1967a. Radioactive Materials in Bottom Sediments of Clinch River: Part A, Investigations of Radionuclides in Upper Portion of Sediments. Supplement 2A to Status Report No. 5 on Clinch River Study, ORNL-3721 Suppl. 2A, Oak Ridge National Laboratory, Oak Ridge, TN.
- Carrigan, P. H., Jr. and R. J. Pickering. 1967b. Radioactive Materials in Bottom Sediment of Clinch River: Part B, Inventory and Vertical Distribution of Radionuclides in Undisturbed Core. Supplement 2B to Status Report No. 5 on Clinch River Study. ORNL-3721, Suppl. 2B. Oak Ridge National Laboratory, Oak Ridge, TN.
- Chapman, R. S. 1977. A Model to Investigate the Influence of Suspended Sediment on the Mass Transport of Pollution Open Channel Flow. NASA-TM-X-94601.
- Chen, Y. H. 1973. Mathematical Modeling of Water and Sediment Routing in Natural Channels. Ph.D. Thesis, Department of Civil Engineering, Colorado State University, Fort Collins, CO.
- Cheong, H. F. and H. W. Shen. 1976. "Stochastic Characteristics of Sediment Motion," ASCE 102(HY7):1035-1049.
- Churchill, M. A., J. A. Cragwall, R. W. Andrews and S. L. Jones. 1965. Concentrations Total Sediment Loads and Mass Transport of Radionuclides in the Clinch and Tennessee Rivers. ORNL-3721, Suppl. 1, Oak Ridge National Laboratory, Oak Ridge, TN.
- Clanton, V. S. and E. F. Gloyna. 1964. Radioactivity Transport in Water--Sorption and Release of Radionuclides by Sediments of the Guadalupe River. EHE-10-6404, Technical Report No. 6 to the U.S. Atomic Energy Commission, University of Texas, Austin, TX.
- Cottrell, W. D. 1959. Radioactivity in Silt of the Clinch and Tennessee Rivers. USAEC ORNL-2847, Oak Ridge National Laboratory, Oak Ridge, TN.
- Davies, S., F. Costito and M. Eisenbud. 1966. "Radioactivity in the Hudson River." Proceedings of the First Symposium on Hudson River Ecology. Hudson River Valley Commission of New York.

- Ecker, R. M., and Y. Onishi. 1979. Sediment and Radionuclide Transport in Rivers. Phase 1. Field Sampling Program During Mean Flow Cattaraugus and Buttermilk Creeks, New York. NUREG/CR-1030, PNL-3117, Pacific Northwest Laboratory, Richland, WA.*
- Einstein, H. 1937. Der Geschiebetreibals Wahrscheinlichkeitsproblem. Verlag Raschen and Co., Zurich, Switzerland.
- Eraslan, A. H., E. J. Akin, J. M. Barton, J. L. Bledsoe, K. E. Cross, H. Diamant, D. E. Fields, S. K. Fischer, J. L. Harris, D. M. Hetrick, J. T. Holdeman, K. K. Kim, M. H. Lietzke, J. E. Park, M. R. Patterson, R. D. Sharp, and B. Thomas, Jr. 1977. Development of a Unified Transport Approach for the Assessment of Power-Plant Impact. ORNL/NUREG/TM-89, Oak Ridge National Laboratory, Oak Ridge TN.
- Fields, D. E. 1974. "Modification of the Unified Transport Model to Allow for Sediment Transport and Chemical Exchange," Trace Contaminants in the Environment. LBL-3217. Available from the National Technical Information Service, Springfield, VA, pp. 205-209.
- Fields, D. E. 1976a. CHNSED: Simulation of Sediment and Trace Contaminant Transport with Sediment/Contaminant Interaction. ORNL/NF/EATC-19, Oak Ridge National Laboratory, Oak Ridge, TN.
- Fields, D. E. 1976b. LINSED: A One-Dimensional Multireach Sediment Transport Model. ORNL/CSD-15, Oak Ridge Laboratory, Oak Ridge, TN.
- Fisher, W. L. 1970. Evaluation of Radiological Conditions in the Vicinity of Hanford for 1968. BNWL-1341, Pacific Northwest Laboratory, Richland, WA.
- Fisher, H. B. 1967. "The Mechanics of Dispersion in Natural Streams," Journal of Hydraulic Division. 93(HY,6, ASCE):187-216.
- Fletcher, J. F., W. L. Dotson, D. E. Peterson and R. P. Betson. 1973. "Modeling the Regional Transport of Radionuclide in a Major United States River Basin," Environmental Behavior of Radionuclide Released in the Nuclear Industry. IAEA Vienna.
- Fletcher, J. F. and W. L. Dotson (eds). 1971. Hermes-A Digital Computer Code for Estimating Regional Radiological Effects from the Nuclear Power Industry. USAEC Rep. HEDL-TM-71-1968.
- Freed, D. L. 1973. "Technique for Implicit Dynamic Routing in Rivers with Major Tributaries." Water Resources Research. 9(4):918-926.
- Fukai, R. and C. M. Murray. 1973. "Environmental Behavior of Radiocobalt and Radiosilver Released from Nuclear Power Stations into Aquatic Systems," Environmental Behavior of Radionuclides Released in The Nuclear Industry. Austria. International Atomic Energy Agency, Vienna, pp. 217-241.

Glover, R. E. 1964. Dispersion of Dissolved or Suspended Materials in Flowing Streams - Transport of Radionuclides by Streams. USGS Professional Paper 433-B.

Gloyna, E. F. et al. 1963-1972. "Radioactivity Transport in Water." Technical Reports 1 through 23. U.S. AEC Contract No. AT(11-1)-490, The University of Texas, Austin, TX.

Gloyna, E. F. and J. O. Ledbetter. 1969. Principles of Radiological Health. Marcel Dekker, Inc., New York, NY.

Graf, W. H. 1971. Hydraulics of Sediment Transport. McGraw-Hill Book Company.

Groniec, M. J. and E. F. Gloyna. 1973. Radioactivity Transport in Water -- Final Report. EHE-73-01, Technical Report No. 23 to the U.S. Atomic Energy Commission, Center for Research in Water Resources, University of Texas, Austin, TX.

Haushild, W. L., R. W. Perkins, H. H. Stevens, G. R. Dempster and J. L. Glenn. 1966. Progress Report: Radionuclide Transport in the Pasco to Vancouver, Washington Reach of the Columbia River July 1962 to September 1963 for the Project: The Occurrence, Transport and Disposition of Radionuclides as Solutes and Associated with Fluvial Sediments in the Lower Columbia River. Geological Survey. Open-file Report. U.S. Department of Interior.

Haushild, W. L., H. H. Stevens, Jr., J. L. Nelson and G. R. Dempster, Jr. 1971. Radionuclides in Transport in the Columbia River from Pasco to Vancouver, Washington. Geological Survey. Open-file Report. U.S. Department of Interior, Western Resources Division, Portland, OR.

Haushild, W. L., H. H. Stevens, Jr., J. L. Nelson and G. R. Dempster, Jr. 1973. Radionuclides in Transport in the Columbia River from Pasco to Vancouver, Washington. Geological Survey Professional Paper 433-N, U.S. Geological Survey, U.S. Department of Interior, Portland, OR.

Hayes, J. R. 1963. Mass Transport Mechanisms in Open Channel Flow. Doctoral Thesis. Vanderbilt University. Nashville, TN.

Hetrick, D. M., A. H. Ersoyan, and M. R. Patterson. 1979. SEDONE: A Computer Code for Simulating Tidal-Transient, One-Dimensional Hydrodynamic Conditions and Three-Layer, Variable-Size Sediment Concentrations in Controlled Rivers and Estuaries. NUREG/CR-0430, ORNL/NUREG/TM-256, Oak Ridge National Laboratory, Oak Ridge, TN.

Hubbell, D. W. and W. W. Sayre. 1964. "Sand Transport Studies with Radioactive Tracers." ASCE. 90(HY3):39-68.

- Hubbell, D. W. and J. L. Glenn. 1971. Distribution of Radionuclides in Bottom Sediments of the Columbia River Estuary. Open-File Report. Department of Interior, Portland OR. Water Resources Division, Geological Survey.
- Hydroscience, Inc. 1978. Mathematical Models for Water Quality for the Hudson-Champlain and Metropolitan Coastal Water Pollution Control Project.
- Jenne, E. A. and J. S. Wahlberg. 1965. "Management and Iron Oxide Scavenging of Cobalt 60 in White Oak Creek Sediment, Oak Ridge, Tenn." Am. Geophys. Union Trans. 46(1):70 (Abstract).
- Jenne, E. A. and J. S. Wahlberg. 1968. Role of Certain Stream-Sediment Components in Radioion Sorption. Geological Survey Professional Paper 433-F, U.S. Geological Survey.
- Kennedy, V. C. 1965. Mineralogy and Cation-Exchange Capacity of Sediments from Selected Streams. Geological Survey Professional Paper 433-D, U.S. Department of Interior.
- Krone, R. P. 1962. Flume Studies of the Transport of the Sediment in Estuarine Shoaling Processes. Hydraulic Engineering Laboratory and Sanitary Engineering Research Laboratory, University of California At Berkeley.
- Mahmoud, K. A., Y. A. Yousef, M. M. Ishak, W. E. Y. Abdel-Malik, S. R. Khalil, A. Shafik, R. M. K. El-Shinawy. 1973. "Transfer Mechanism and Concentrating Processes of Certain Radionuclides in the Aquatic Ecology of the Ismailia Canal," Environmental Behavior of Radionuclides Released in the Nuclear Industry. International Atomic Energy Agency, Vienna, Austria. pp. 205-215.
- Mahmood, K., and V. M. Ponce. 1976. Mathematical Modeling of Sedimentation Transients in Sand-Bed Channels. CER75-76KM-VMP28, Engineering Research Center, Colorado State University, Fort Collins, CO.
- Martin, J. A., Jr., C. Robbins, C. B. Nelson, R. D. Cousins, Jr., M. A. Culliton. 1976. A Computer Code (RURDOS) to Calculate Population Doses from Radioactive Liquid Effluents and on Application to Nuclear Power Reactors on the Mississippi River Basin. U.S. EPA, Office of Radiation Programs, Environmental Analysis Division.
- Morton, R. J. (ed). 1962a. Status Report No. 2 on Clinch River Study. Clinch River Study Steering Committee. ORNL-3202, Oak Ridge National Laboratory, Oak Ridge, TN.
- Morton, R. J. (ed). 1962b. Status Report No. 3 on Clinch River Study. Clinch River Study Steering Committee. ORNL-3370, Oak Ridge National Laboratory, Oak Ridge, TN.

- Morton, R. J. (ed). 1965. Status Report No. 5 on Clinch River Study. Clinch River Study Steering Committee. ORNL-3721, Oak Ridge National Laboratory, Oak Ridge, TN.
- Nelson, J. L., R. W. Perkins, J. P. Nielsen, and W. L. Haushild. 1966. "Reactions of Radionuclides from the Hanford Reactors with Columbia River Sediments." Disposal of Radioactive Wastes into Seas, Oceans, and Surface Waters. International Atomic Energy Agency, Vienna, Austria. pp. 139-161.
- Nordin, C. F., Jr. 1964. Aspects of Flow Resistance and Sediment Transport: Rio Grande Near Bernalillo, New Mexico. Water-Supply Paper 1498-H, U.S. Geological Survey, Washington, D.C.
- Nordin, C. F., Jr., and J. P. Beverage. 1965. Sediment Transport in the Rio Grande, New Mexico. USGS Professional Paper 462-F, U.S. Geological Survey, Washington, D.C.
- Norton, W. R., L. A. Roesner, D. E. Evenson, and J. R. Monser. 1974. Computer Program Documentation for the Stream Quality Model, Qual-II. Water Resource Engineers, Inc., Walnut Creek, CA.
- Onishi, Y. 1977. Mathematical Simulation of Sediment and Radionuclide Transport in the Columbia River. BNWL-2228, Pacific Northwest Laboratory, Richland, WA.
- Onishi, Y. 1980. "Section 4. Sediment Effects" of Aquatic Disposal of Radionuclides. Prepared by P. J. Ryan, M. Leonard, G. Segal and Y. Onishi for the Summer School of Health Physics Society.
- Onishi, Y. and R. M. Ecker. 1977. "Mathematical Simulation of Transport of Kepone and Kepone-Laden Sediments in the James River Estuary." Proceedings of Kepone Seminar II.
- Onishi, Y. and S. E. Wise. 1978a. "Mathematical Modeling of Sediment and Contaminant Transport in the James River Estuary." Proceedings of the 26th Annual ASCE Hydraulic Division Speciality Conference on Verification of Mathematical and Physical Models in Hydraulic Engineering. College Park, MD. August 9-11, pp. 303-310.
- Onishi, Y. and S. E. Wise. 1978b. Mathematical Simulation of Transport of Sediment and Kepone in the James River Estuary. PNL-2731, Pacific Northwest Laboratory, Richland, WA.
- Onishi, Y., and S. E. Wise. 1979a. "Finite Element Model for Sediment and Toxic Contaminant Transport in Streams." Proceedings of Hydraulics and Energy Divisions Specialty Conference of ASCE on "Conservation and Utilization of Water and Energy Resources." San Francisco, CA, pp. 144-150.

- Onishi, Y., and S. E. Wise. 1979b. "Mathematical Model, SERATRA, for Sediment-Contaminant Transport in Rivers and Its Application to Pesticide Transport in Four Mile and Wolf Creeks in Iowa." Submitted to U.S. Environmental Protection Agency, Environmental Research Laboratory at Athens, GA by Battelle, Pacific Northwest Laboratories, Richland, WA.
- Onishi, Y., P. A. Johanson, R. G. Baca and E. L. Hilty. 1976. Studies of Columbia River Water Quality--Development of Mathematical Models of Sediment and Radionuclide Transport Analysis. BNWL-B-452, Pacific Northwest Laboratory, Richland, WA.
- Onishi, Y., E. M. Arnold, and D. W. Mayer. 1979. Modified Finite Element Transport Model, FETRA, for Sediment and Radionuclide Migration in Open Coastal Waters. NUREG/CR-1026. PNL-3114, Pacific Northwest Laboratory, Richland, WA.*
- Onishi, Y., D. L. Schreiber, and R. B. Codell. 1980a. "Mathematical Simulation of Sediment and Radionuclide Transport in the Clinch River, Tennessee," Chapter 18 of Processes Involving Contaminants and Sediment. R. A. Baker (ed.), Ann Arbor Science Publisher, Inc. pp. 393-406.
- Onishi, Y., G. Whelan, M. A. Parkhurst, A. R. Olsen, and P. J. Gutknecht. 1980b. Preliminary Assessment of Toxaphene Migration and Risk in the Yazoo River Basin, Mississippi. Submitted to the U.S. Environmental Protection Agency by Battelle, Pacific Northwest Laboratories, Richland, WA.
- Onishi, Y., S. M. Brown, G. Whelan, R. L. Skaggs, K. T. Key, C. T. Kincaid, A. E. Reisenauer, and T. W. Horst. 1980c. Development of a Multimedia Radionuclide Exposure Model for Low-Level Waste Management. PNL-3370, Pacific Northwest Laboratory, Richland, WA.
- Osterberg, C. L., M. Cutshall, V. Johnson, J. Cronin, D. Jennings, L. Frederick. 1966. "Some Nonbiological Aspects of Columbia River Radioactivity." Disposal of Radioactive Wastes into Seas, Oceans and Surface Waters. Symposium, 321, IAEA, Vienna Austria.
- Overton, D. E. and M. E. Meadows. 1976. Mathematical Modeling for Water Quality Management in Streams Under Unsteady Hydraulic Conditions. Research Report No. 55. Water Resources Research Center, University of Tennessee.
- Parker, F. L., M. A. Churchill, R. W. Andrew, B. J. Frederick, P. H. Carrigan, Jr., J. S. Cragwall, Jr., S. A. Jones, E. G. Struxness, and R. J. Morton. 1966. "Dilution, Dispersion and Mass Transport of Radionuclides in the Clinch and Tennessee Rivers." Proceedings of the Symposium on the Disposal of Radioactive Wastes into Seas, Oceans and Surface Waters. International Atomic Energy Agency, Vienna, Austria, pp. 33-54.

Partheniades, E. 1962. A Study of Erosion and Deposition of Cohesive Soils in Salt Water. Ph.D. Thesis, University of California at Berkeley.

Perkins, R. W., J. L. Nelson, W. L. Haushild. 1966. "Behavior and Transport of Radionuclides in the Columbia River Between Hanford and Vancouver, Washington." Limnol. Oceanogr. 11(2):235.

Pickering, R. J. 1970. Composition of Water in Clinch River, Tennessee River, and Whiteoak Creek as Related to Disposal of Low-Level Radioactive Liquid Wastes. Geological Survey Professional Paper 433-J, Department of Interior.

Pickering, R. J., P. H. Carrigan, Jr., T. Tamura, H. H. Abee, J. W. Beverage, and R. W. Andrew, Jr. 1966. "Radioactivity in Bottom Sediment of the Clinch and Tennessee Rivers." Disposal of Radioactive Wastes into Seas, Oceans, and Surface Waters. International Atomic Energy Agency, Vienna, Austria, pp. 57-86.

Pruter, A. T. and D. L. Alverson. 1972. The Columbia River Estuary and Adjacent Ocean Waters--Bioenvironmental Studies. University of Washington Press, Seattle, WA.

Renn, C. E., J. T. O'Connor and I. Wintner. 1964. Adsorption of Radioactive Zinc and Iron on River Silts. NYO-10544.

Reynolds, T. D. and E. F. Gloyna. 1963. Radioactivity Transport in Water--Transport of Strontium and Cesium by Stream and Estuarine Sediments. Technical Report No. 1 to the U.S. Atomic Energy Commission, University of Texas, Austin, TX.

Robertson, D. E., W. B. Silker, J. C. Langford, M. R. Petersen, and R. W. Perkins. 1973. "Transport and Depletion of Radionuclides in the Columbia River." Radioactive Contamination of the Marine Environment. International Atomic Energy Agency, Vienna, Austria. pp. 141-155.

Rowe, D. R. and E. F. Gloyna. 1964. Radioactivity Transport in Water--The Transport of ^{65}Zn in an Aqueous Environment. EHE-09-6403, Technical Report No. 5 to the U.S. Atomic Energy Commission, Center for Research in Water Resources, University of Texas, Austin TX.

Sax, N. I., P. C. Lemon, A. H. Benton and J. J. Gabay. 1969. "Radioecological Surveillance of the Waterways Around a Nuclear Fuel Processing Plant." Radioecological Health Data and Reports. 10(7):289-296.

Sayre, W. W. 1971. "Transport and Dispersion of Fluvial Sediments: Some Mathematical Models and Their Verification by Trace Methods." IAEA Panel on the Uses of Tracers in Sedimentology.

- Sayre, W. W. and T.-P. Yeh. 1973. Transverse Mixing Characteristics of the Missouri River Downstream from the Cooper Nuclear Station. IIHR Report No. 145, Iowa Institute of Hydraulic Research, University of Iowa, Iowa City, IA.
- Sayre, W. W. and F. M. Chang. 1968. A Laboratory Investigation of Open-Channel Dispersion Processes for Dissolved, Suspended and Floating Dispersants. USGS Professional Paper 433-E.
- Sayre, W. W. and D. W. Hubbell. 1965. Transport and Dispersion of Labeled Bed Material. North Locys River, NB, U.S. Geol. Surv. Paper, 433-C.
- Sayre, W. W., H. P. Guy, and A. R. Chamberlain. 1963. Uptake and Transport of Radionuclides by Stream Sediments. Geological Survey Professional Paper 433-A.
- Shen, H. W. and H. F. Cheong. 1973. "Dispersion of Contaminated Sediment Bed Load." J. of the Hydraulics Division. ASCE, 99(HY11):1947-1965.
- Shen, H. W. and H. F. Cheong. 1977. "Statistical Properties of Sediment Bed Profiles." J. of the Hydraulics Division. ASCE, 103(HY11):1303-1321.
- Shih, C. S. and E. F. Gloyna. 1967. Radioactivity Transport in Water--Mathematical Model for the Transport of Radionuclides. EHE-04-6702, Technical Report No. 12 to the U.S. Atomic Energy Commission, University of Texas, Austin, TX.
- Shih, C. S. and E. F. Gloyna. 1969. "Influence of Sediments on Transport of Solutes." J. Hydraulics Div. ASCE 95(HY4):1348-1367.
- Shih, C. S. and E. F. Gloyna. 1970. "Mathematical Model for the Transport of Radionuclides in Stream System." Environmental Surveillance in the Vicinity of Nuclear Facilities. Reinig, W. C. (ed.), Charles C. Thomas Publishing Co., Springfield, IL.
- Shull, R. D. and E. F. Gloyna. 1968. Radioactivity Transport in Water--Simulation of Sustained Releases to Selected River Environments. EHE-04-6801, Technical Report No. 15 to the U.S. Atomic Energy Commission, University of Texas, Austin, TX.
- Shure, D. J. and M. R. Gottschalk. 1975. "Cesium-137 Dynamics within a Reactor Effluent Stream in South Carolina." Radioecology and Energy Resources. C. E. Cushing, Jr. (ed.), pp. 234-241.
- Simons, D. B. and Senturk, F. 1977. Sediment Transport Technology. Water Resources Publications, Fort Collins, CO.

- Smith, J. H., W. R. Mabey, M. Bohonos, B. R. Holt, S. S. Lee, T.-W. Chou, D. C. Bomberger, and T. Mill. 1977. Environmental Pathways of Selected Chemicals in Freshwater Systems. Part I: Background and Experimental Procedures. EPA-600/7-77-113, Submitted to U.S. Environmental Protection Agency by SRI International, Menlo Park, CA.
- Soldat, J. K. 1976. Methodology for Calculation of Radiation Doses in the Environs from Nuclear Fuel Cycle Facilities. BNML-2075, Pacific Northwest Laboratory, Richland, WA.
- Soldat, J. K., N. M. Robinson and D. A. Baker. 1974. Models and Computer Codes for Evaluating Radiation Doses. BNML-1754, Pacific Northwest Laboratory, Richland, WA.
- Struxness, E. G., P. H. Carrigan, Jr., M. A. Churchill, K. E. Cousin, R. J. Morton, D. J. Nelson, F. L. Parker. 1967. Comprehensive Report of the Clinch River Study. ORNL-4035, Clinch River Study Steering Committee, Oak Ridge National Laboratory, Oak Ridge, TN.
- Thackston, E. L. and K. B. Schnell, Jr. 1970. "Predicting Effects of Dead Zone on Stream Mixing." ASCE Sanitary Engineering Division. 96(SA2):319-331.
- Thomas, W. A. 1974. Scour and Deposition in Rivers and Reservoirs. The Hydrologic Engineering Center, U.S. Army Corps of Engineers, Davis, CA.
- Tritrennel, Ch., G. Knollmayer, E. Wanderer, H. G. Heintschel, and P. Stipanits. 1966. "Behavior of Radioisotopes Released to a Stream." Proceedings of the Symposium on the Disposal of Radioactive Wastes into Seas, Oceans, and Surface Waters. International Atomic Energy Agency, Vienna, pp. 89-105.
- Todorovic, P. 1975. "A Stochastic Model Dispersion of Sediment Particles Released from a Continuous Source." Water Resources Research. 11:66:919-925.
- U.S. Atomic Energy Commission. 1973. Radioactive Waste Management, A Bibliography of Publicly Available Literature Pertaining to the USAEC's Hanford, Washington Production Site. TID-3340.
- U.S. Environmental Protection Agency. 1978. Kepone Mitigating Project Report, Standard and Criteria, Office of Water and Hazardous Materials, Washington, D.C.
- U.S. Nuclear Regulatory Commission. 1976. Regulatory Guide 1.113 - Estimating Aquatic Dispersion of Effluents from Accidental and Routine Reactor Releases for the Purpose of Implementing Appendix I.

- U.S. Nuclear Regulatory Commission. 1978a. Liquid Pathway Generic Study. Impacts of Accidental Radioactivity Releases to the Hydrosphere from Floating and Land-Based Nuclear Power Plants. NUREG-0440.**
- U.S. Nuclear Regulatory Commission. 1978b. Revised Draft Environmental Statement Related to the Proposed Manufacture of Floating Nuclear Power Plants. NUREG-0127 (Revision 1)***
- Waddel, W. W., C. R. Cole, and R. G. Baca. 1974. A Water Quality Model for the South Platte River Basin - Documentation Report. Prepared for the Environmental Protection Agency, Battelle, Pacific Northwest Laboratories, Richland, WA.
- Watts, J. R. 1976. "Modeling of Radiation Doses from Chronic Aqueous Releases." Paper presented at the Health Physics Society Annual Meeting. San Francisco, CA.
- Whelan, G. 1980. Distributed Model for Sediment Yield. Master's Thesis, Mechanics and Hydraulics. University of Iowa, Iowa City, Iowa.
- White, A. and E. F. Gloyna. 1969. Radioactivity Transport in Water--Mathematical Simulation. EHE-70-04, Technical Report No. 19 to the U.S. Atomic Energy Commission, University of Texas, Austin, TX.
- Whittacker, R. H. 1951. Removal of Radiophosphorus Contaminant from the Water in an Aquarium Community. Document HW-28636, Atomic Energy Commission.
- Whittacker, R. H. 1961. "Experiments with Radiophosphorus Tracer in Aquarium Microcosms." Ecol. Monogr. 31:157-188.
- Willis, R., D. R. Anderson and J. A. Dracup. 1976. "Transient Water Quality Modeling in Streams." Water Resource Bulletin. 12(1):157-174.
- Wrenn, M. E., J. W. Lentsch, M. Eisenbad, G. L. Lauer, and G. P. Howells. 1971. "Radiocesium Distribution in Water Sediments and Biota of the Hudson River Estuary from 1964 through 1970." Radionuclides in Ecosystems. pp. 334-343, D. J. Nelson (ed.).
- Yalin, M. S. 1972. Mechanics of Sediment Transport. Pergamon Press.
- Yang, C. T. and W. W. Sayre. 1971. "Stochastic Model of Sediment Dispersion." ASCE. 97(HY2):265-288.
- Yaroni, V. A. Sedimentation Engineering. Prepared by the ASCE Task Committee for the Preparation of the Manual on Sedimentation of the Sedimentation Committee of the Hydraulics Division, ASCE.

Yotsukura, N. and W. W. Sayre. 1976. "Transverse Mixing in Natural Channels." Water Resources Research. 12(4):695-704.

Yousef, Y. A. and E. F. Gloyna. 1964. Radioactivity Transport in Water--The Transport of ⁵⁸Co in an Aqueous Environment. EHE-12-6405, Technical Report No. 7 to the U.S. Atomic Energy Commission, 121 pp.

Yousef, Y. A., Akira Kudo, and E. F. Gloyna. 1970. Radioactivity Transport in Water--Summary Report. EHE-70-05, Technical Report No. 20 to the U.S. Atomic Energy Commission, 80 pp.

Zand, S. M., V. C. Kennedy, G. W. Zellweger and R. J. Avanzeno. 1976. "Solute Transport and Modeling of Water Quality in a Small Stream." J. Res. U.S. Geol. Surv. 4(2):233-40.

*Available for purchase from the NRC/GPO Sales Program, U.S. Nuclear Regulatory Commission, Washington, DC 20555, and the National Technical Information Service, Springfield, VA 22161.

**Available for purchase from the National Technical Information Service, Springfield, VA 22161.

***Available free upon written request to the Division of Technical Information and Document Control, U.S. Nuclear Regulatory Commission, Washington, DC 20555.

5. RADIONUCLIDE TRANSPORT IN ESTUARIES

This chapter reviews models that simulate the transport of radionuclides, sediment and other water quality parameters in estuarine environments. A dominant characterizing feature of estuarine systems is that the flow is oscillatory rather than unidirectional as in rivers. Consequently, the models are dynamic (transient) and do not depend on steady-state conditions.

Included in this chapter are well-known analytical models that solve various special cases determined by simplified versions of advection-diffusion equations.

PHYSICAL MECHANISMS OF RADIONUCLIDE TRANSPORT IN ESTUARIES

Mathematical models for estuaries must simulate flow and transport through a body of water that has a tidal connection with the open sea and receives an influx of fresh water from rivers and other land drainage. The estuarine sea water is measurably diluted by this freshwater inflow. These conditions exist in the lower reaches of rivers, and a host of different kinds of sounds, bays, and inlets.

Pritchard (1967) has divided these possibilities into four classes based upon geomorphological criteria. These are 1) drowned river valleys - e.g. Chesapeake Bay, 2) Fjords - e.g. Norway, British Columbia, 3) bar built estuaries - e.g., Albemarle Sound, North Carolina, 4) estuaries provided by tectonic processes - e.g. San Francisco Bay. This classification indicates the variety of estuarine geomorphology, which together with the variability of estuarine flow, mixing conditions, and salinity distributions present a complex situation for mathematical simulation. In applications to a typical selection of estuaries stable salt wedges, stratifications, or well-mixed conditions might prevail. It often happens that there is a longitudinal division of these conditions in a given estuary so that one condition is not adequate to completely characterize the estuary (Officer 1976).

A major cause of differences in estuaries is the contrast in discharge of sediments from the land drainage (Guilcher 1967). Rivers which carry high concentrations of sediments fill their estuaries more effectively with fluvial sediments than those with smaller sediment loads. The Columbia and Mississippi Rivers flush out some of their sediment loads onto the continental shelf because of their high flow rates. Conversely, marine sediments can penetrate the estuary via the wedge of salt water flowing upstream along the bottom as in the Rhine estuary and Chesapeake Bay (Guilcher 1967).

Another complicating feature of sediment movement in estuaries is the effect of salinity variation in the estuary on the processes of sorption and flocculation. The electrolytic coagulation of charged colloidal particles is influenced by the electrolytic potential of the water holding the particles in suspension. The potential depends upon the total ion concentration in the water and thus it varies with salinity throughout the estuary (Postma 1967).

Mathematical models for estuaries must be able to simulate flow and transport under conditions of pronounced transience with reversing tides and density difference between fresh and saline water. In estuaries, suspended sediment concentrations are high because of high velocities at ebb and flood tide and an infinite supply of fresh input sediment from the river inlets. Furthermore, sediments found in estuaries generally consist of finer particles (a notable exception is the sediment in the Columbia River estuary) which adsorb more radionuclides than coarser sediments. This high concentration of fine suspended sediment supplied from the freshwater drainage makes sediment transport an important mechanism of radionuclide movement through the estuary (Schubel 1975). The importance of sediment transport on the migration of a contaminant is clearly demonstrated by the recent Kepone (pesticide) spill in the James River estuary in Virginia (EPA 1978; Dawson et al. 1978). Some of the radionuclide field data are shown in Table 5.1.

MATHEMATICAL MODELS FOR ESTUARIES

Models reviewed in this chapter include those that simulate transport of radionuclide, sediment and water quality constituents.

TABLE 5.1. Estuary Data

<u>Reference</u>	<u>Waterbody</u>	<u>Type of Data</u>
Hubbell and Glenn (1971)	Columbia River Estuary	Concentration of ^{51}Cr , ^{64}Zn , ^{40}K , ^{46}Sc , ^{106}Ru , ^{54}Mn , ^{60}Co , and ^{95}Zr in bottom sediments
Evans, D. W. and N. H. Cutshall (1972)	Columbia River Estuary	Dissolved and particulate forms of ^{65}Zn , ^{54}Mn , ^{51}Cr , ^{124}Sb , ^{46}Sc
Klingman and Kaufman 1965	San Francisco Bay	Particulate and dissolved forms of ^{95}Zn - ^{95}Nb
Nishiwaki, Y. et al. 1972	Osaka Bay, Japan	Particulate forms of ^{144}Ce and ^{91}Y
Water Resources Data for New York (The State of New York)	Hudson River Estuary	Dissolved and particulate forms of gross alpha, gross beta; dissolved ^{226}Ra and U
Lentsch et al. (1970)	Hudson River Estuary	^{144}Ce , ^{58}Co , ^{60}Co , ^{134}Cs , ^{137}Cs , ^{54}Mn , ^{90}Sr in water and bed sediment.
Lentsch et al. (1971)	Hudson River Estuary	^{137}Cs in water and bed sediment, ^{54}Mn in the river bed
Wrenn et al. (1971)	Hudson River Estuary	Dissolved and particulate forms of ^{137}Cs
Wrenn (1972, 1975)	Hudson River Estuary	^{58}Co , ^{60}Co , ^{134}Cs , ^{137}Cs , ^{54}Mn in water, and bed and suspended sediment
Wrenn et al. (1973)	Hudson River Estuary	Dissolved and particulate forms at ^{60}Co , ^{134}Cs , ^{137}Cs , ^{40}K , ^{54}Mn
Moore (1974)	Hudson River Estuary	Dissolved and particulate forms of ^{134}Cs and ^{137}Cs
Jinks and Wrenn (1975)	Hudson River Estuary	Dissolved and particulate forms of ^{144}Ce , ^{58}Co , ^{60}Co , ^{134}Cs , ^{137}Cs , ^{226}Ra , ^{228}Ra , ^{103}Ru , ^{90}Sr , ^{95}Zr - ^{95}Nb

TABLE 5.1 (contd)

<u>Reference</u>	<u>Waterbody</u>	<u>Type of Data</u>
Wrenn and Jinks (1975)	Hudson River Estuary	^{137}Cs in water and bed sediment
Wrenn et al. (1976)	Hudson River Estuary	^{137}Cs in water and bed sediment
Simpson et al. (1976)	Hudson River Estuary	^{60}Co , ^{134}Cs , ^{137}Cs , $^{239,240}\text{Pu}$ in bed core sediment
Hammond et al. (1977)	Hudson River Estuary	Particulate Ra
Simpson and Williams (1978)	Hudson River Estuary	^{60}Co , ^{134}Cs , ^{137}Cs , ^{40}K , ^{238}Pu , $^{139,140}\text{Pu}$ in bed core sediment
Olsen et al. (1978)	Hudson River Estuary	^{60}Co , ^{134}Cs , ^{137}Cs , ^{40}K in bed core sediment
Wren et al. (1979)	Hudson River Estuary	^{60}Co , ^{134}Cs , ^{137}Cs , ^{40}K , ^{54}Mn in water, and bed and suspended sediment
Maine Yankee Atomic Power Co. (1976, 1978, 1979)	Montsweag Bay, Maine	Dissolved and particulate forms of ^7Be , ^{141}Ce , ^{144}Ce , ^{60}Co , ^{134}Cs , ^{137}Cs , ^3H , ^{40}K , ^{54}Mn , ^{103}Ru , ^{106}Ru , ^{228}Th , ^{95}Zr - ^{95}Nb
Churchill (1976)	Montsweag Bay, Maine	^{58}Co , ^{60}Co , ^{134}Cs , ^{137}Cs , ^{58}Mn , in bed sediment
U.S. Environmental Protection Agency (1976)	Montsweag Bay, Maine	^{228}Ac , ^{214}Bi , ^{58}Co , ^{60}Co , ^{134}Cs , ^{137}Cs , ^{74}Mn , ^{40}K , ^{214}Pb and ^{208}Tl in bed sediment Dissolved gross alpha, beta and gamma and ^3H . Dissolved ^{40}K , ^{137}Cs , ^{222}Rn .

Radionuclide Transport Models

Onishi et al. (1976, 1979); Onishi and Ecker (1977); Onishi and Wise (1978a,b)

Model FETRA

The finite element model, FETRA (Finite Element Transport), simulates transport of sediment and radionuclides (and other contaminants, such as heavy metals, pesticides and other toxic substances) in estuaries and coastal waters. Since the model is an unsteady, depth-averaged, two-dimensional (longitudinal and lateral) model, its applicability to estuaries is limited to vertically well-mixed estuaries. The model is based upon general advection-diffusion equations with decay and sink/source terms with appropriate boundary conditions. Similar to the sediment-contaminant transport model, SERATRA, developed by Onishi (1977), FETRA consists of three submodels coupled to include the mechanisms of sediment-contaminant interaction. The submodels are: 1) a sediment transport model, 2) a dissolved contaminant transport model, and 3) a particulate contaminant (contaminants adsorbed by sediment) transport model. Transport of sediment and particulate contaminant is simulated for each sediment size fraction or sediment type. FETRA handles both linear and quadratic approximations to velocity and depth distributions in order to be compatible with various finite element hydrodynamic models [e.g., RMA II (Norton et al. 1974) and CAFE (Pagenkopf 1976)] which supply hydrodynamic input to FETRA.

The sediment submodel includes mechanisms of: 1) advection and dispersion (longitudinal and lateral) of sediments, 2) wave motion to suspend sediments in both surf and offshore zones, 3) sediment cohesion, 4) sediment deposition on the ocean and river beds, 5) sediment resuspension from the ocean and river-bed (bed erosion and armoring), and 6) outside contributions of sediments and subsequent mixing. The dissolved and particulate contaminant submodels include mechanisms of: 1) advection and dispersion of dissolved and particulate contaminants, 2) adsorption/desorption, 3) radionuclide decay and other chemical/biological degradation, 4) deposition and erosion of particulate contaminants, and 5) contaminant contribution from outside sources and subsequent mixing. FETRA also computes changes on bed conditions of sediment and radionuclides.

In the implementation of the finite element method, triangular elements are used with six nodes associated with each element. Quadratic approximations are made within each element. Onishi et al. (1976, 1979) reported good agreement in comparisons of computed results by FETRA with known analytical solutions of simple one- and two-dimensional advection-diffusion equations.

The model was applied to the James River estuary to determine the longitudinal movement of sediment, and migration of the pesticide, Kepone, in both dissolved and particulate forms under unsteady estuary flow conditions (Onishi and Ecker 1977; Onishi and Wise 1978a,b). Sediment transport modeling was conducted for cohesive and noncohesive sediments, and for organic matter. In the James River study, the model parameters and coefficients to be adjusted were dispersion coefficients and parameters used to calculate deposition and erosion rates of cohesive sediments based on Partheniades (1972) and Krone (1962) formulas. Although the parameters of these two formulas are physically measurable, those values are not usually available. Hence, these parameters were rather arbitrarily adjusted to fit measured sediment concentration. The lack of rationale for selection of these parameters is one of the problems FETRA faces. Other parameters (e.g., Kepone distribution coefficients, sediment sizes, fall velocity, etc.) were determined by theoretical and experimental analyses and field conditions prior to the model simulation. Thus, the major calibration effort was exercised to reproduce sediment distribution patterns similar to measured time-varying longitudinal distributions of sediment concentrations. Model calibration for sediment transport was performed under one flow condition (freshwater input discharge of $58.3 \text{ m}^3/\text{sec}$). The calibration results are shown in Figure 5.1. For the verification of the model, the freshwater input discharge of $247 \text{ m}^3/\text{sec}$ case was tested. The comparison between measured sediment concentrations and computed results for the verification run is shown in Figure 5.2, revealing that the model reproduced two-peaked distributions well (Onishi and Wise 1978a). The good comparison of computed particulate and measured Kepone is shown in Figure 5.3. The model also calculated the scour and deposition of sediment and Kepone in the James River.

FIGURE 5.1. Tidally Averaged Sediment Concentration of Each Sediment Type for the Net Freshwater Input Discharge of 58.3 m³/sec in the James River Estuary (Onishi and Wise 1978a)

FIGURE 5.2. Tidally Averaged Sediment Concentration of Each Sediment Type for the Net Freshwater Input Discharge of 247 m³/sec in the James River Estuary (Onishi and Wise 1978a)

FIGURE 5.3. Tidally Averaged Particulate Kepone Concentrations for the Net Fresh-Water Discharge of $58.3 \text{ m}^3/\text{sec}$ in the James River Estuary (Onishi and Wise 1978a)

Several limitations of FETRA are as follows: 1) the model requires extensive input data which may limit its applicability; 2) it requires rather extensive computer time that a long-term continuous simulation may be prohibitive; and 3) the model treats adsorption/desorption mechanisms as complete reversible mechanisms producing a possible error.

Churchill (1976). An adaptation of the scheme of the FMQA Water Quality model (Orlob et al. 1967) is used by Churchill (1976) with radionuclide sorption included at the bed sediment-water interface. (Description of the FMQA model is given under "Water Quality Models" Section in this chapter.) Radionuclide sorption was modeled by the equation:

$$C = C_0 \left[1 - K_d (1 - e^{-\alpha t}) \right] \quad (5.1)$$

where

- C = radionuclide concentration
- C_0 = radionuclide concentration at time $t = 0$
- K_d = equilibrium constant
- α = constant for exponential radionuclide sorption

In this formulation the channels are allowed to run dry, and resultant flows and velocities are calculated at junction points. The required input is:

- channel dimensions
- initial conditions
 - a) velocities
 - b) cross-sectional areas
 - c) junction heads
- channel orientations
- manning roughness coefficient
- discharges and withdrawals from junctions
- boundary tidal conditions.

The dispersion program requires input on:

- initial concentration at each junction
- rates and concentrations of discharges and withdrawals
- boundary concentrations over the entire simulation period.
- diffusion and sorption constants.

The results of the calculations include water and sediment concentration factors of each radionuclide at each junction at specified times. This model has been field tested in Montsweag Bay and Bailey Cover, Maine, at the site of the Maine Yankee Nuclear power plant. The distributions and magnitudes of the sediment bound radionuclide concentrations were compared with measured values.

Codell (NRC Estuary Model) (USNRC 1978)

For the NRC liquid pathway generic study (USNRC 1978), R. B. Codell and NRC staff described an analytic solution to simplified forms of the

advection-diffusion equation for a core-melt accident transport model. The model is one dimensional with the tidally averaged net downstream currents and with radionuclide-sediment interactions.

As illustrated in Figure 5.4, a water layer of thickness d_1 is in contact with a sediment layer of thickness d_2 . The water layer is moving with a net downstream velocity (nontidal) of U_f , and the bed is moving with a net downstream velocity U_b . Diffusive transport from tidal oscillations in the water and sediment layers is assumed to be with constant longitudinal dispersion coefficients D_x and D_{xb} , respectively. Sedimentation and burial occur uniformly at a rate v .

FIGURE 5.4. NRC Estuary Model

It is assumed that the sediment and water are in chemical equilibrium, and their concentrations are related by the equilibrium distribution coefficient K_d :

$$C_p = K_d C \quad (5.2)$$

where C_p is the radionuclide concentration on the sediment, and C is the radionuclide concentration in the water.

The differential equation describing the concentration in the water phase becomes:

$$\frac{\partial C}{\partial t} + U' \frac{\partial C}{\partial x} = E_L' \frac{\partial^2 C}{\partial x^2} - C \quad (5.3)$$

where

$$U' = \frac{fU + (1-f)U_b K_d}{f + (1-f)K_d}$$

$$E_L' = \frac{fD_x + (1-f)D_x K_d}{f + (1-f)K_d}$$

$$f = \frac{d_1}{d_x + d_2}, \quad (1-f) = \frac{d_2}{d_1 + d_2}$$

The solution to Equation (5.3) for an instantaneous source of 1.0 curie at $x = 0$ is:

$$C = \frac{1}{aA \sqrt{4\pi E_L' t}} \exp \left\{ -\left(\frac{x - U' t^2}{4 E_L' t} - \lambda' t \right) \right\} \quad (5.4)$$

where

$$a = f + (1-f)K_d$$

$$\lambda' = \lambda + \left[\frac{Ukd}{d_2} (1-f) \right] / [f + (1-f)k_d]$$

The solution is generalized for arbitrary releases by using Equation (4.31). Particulate radionuclide concentrations can then be obtained by Equation (5.2).

O'Connor and Farley (1978)

In a recent paper, O'Connor and Farley (1978) describe a hydrodynamic, pesticide-transport, ecological model which was also applied to the James River estuary. The model is quasi two-dimensional (longitudinal-vertically layered) and steady state (tidally averaged) with a capability for the simulation of both dissolved and particulate contaminants. The transport equations used are purely advective with no diffusion being simulated. The momentum equation does not include a longitudinal inertia term resulting in some restriction on the applicability of the model. Comparison of predicted and measured values for the James River case indicates good agreement (Figure 5.5). This model requires various coefficients and parameters requiring rather extensive field data needed to assign values of these parameters, including sediment concentrations at each reach as input data.

FIGURE 5.5. Comparison of Computed and Measured Values of Velocity and Salinity in the James River Estuary (O'Connor and Farley 1978)

Eraslan (1977)

A project at Oak Ridge National Laboratory involves the development of transient, one- and two-dimensional, far-field mathematical models for the assessment of the environmental impact of power plant operations in estuaries

and rivers, lakes and cooling ponds, and coastal regions. The project, known as the "Unified Transport Approach (UTA) for the Assessment of Power Plant Impacts," includes models for thermal, chemical, radiological and biological impacts (Eraslan et al. 1977). Formulations of the UTA models will be fundamentally similar in theory, allowing the application of virtually identical numerical solution methods and computational algorithms. All are discrete-element formulations with Runge-Kutta-Gill numerical solutions.

As part of the UTA program (see Chapter 4), three radionuclide transport models have been developed for application to estuaries. According to Eraslan et al. (1977), RADONE is a transient, one-dimensional transport model for dissolved radionuclides applicable to controlled rivers and estuaries; RADTWO was developed directly from the thermal code, FARTMP, and is a transient, two-dimensional, dissolved-radionuclide transport model for lakes, estuaries, and coastal regions. Neither RADONE nor RADTWO has yet been verified (Eraslan et al. 1977). Technical reports describing these two models have yet to be published, thus precluding detailed model evaluations. A third radionuclide model applicable to estuaries, HOTSET, is a one-dimensional model for the transport of radionuclides adsorbed on sediment (Fields 1976). This preliminary model was constructed by merging the hydrodynamic part of the tidal transient, one-dimensional thermal and salinity code, ESTONE, with the sediment and contaminant transport code, CHNSED (Fields 1976), described in Chapter 4. However, since the mathematical formulation and computer code structure of CHNSED were not compatible with the other one-dimensional UTA models, another one-dimensional sediment transport model, SEDONE, was developed, as discussed in Chapter 4.

Water Quality Models

The following models are applicable for the determination of the behavior of estuarine water quality parameters.

Water Quality Models of Type I

Leendertse (1970, 1973). The model of Leendertse (1970), considered the representative of this type, is a two-dimensional, transient and steady-state

hydrodynamic and water quality model which uses a finite difference solution method. The advection-diffusion equation is solved for dissolved constituents, which could include dissolved radionuclides. There are, however, no such source or decay terms presently included in the formulation. Water levels and constituent concentrations are required on the open boundaries of the modeled region for the entire simulation period. This model has been used successfully to calculate fecal coliform concentrations in Jamaica Bay, New York.

Leendertse et al. (1973) also developed a quasi, three-dimensional (vertically layered), hydrodynamic model for estuaries and coastal seas which also simulates salinity conservation and transport. This model could be used with dissolved radionuclide concentration replacing salinity in the model equation. The computational scheme is a finite difference method. There are no source or sink terms in the model as it is presently written. This model was applied with success to the Chesapeake Bay for the calculation of circulation patterns. This application is described in Leendertse, Alexander and Liu (1973).

Spraggs (1974). A generalized version of Leendertse's model by Spraggs (1974) simulates dissolved contaminants and sediment transport by using the velocity field to trace the trajectories of particles treated as Lagrangian variables. This model has been applied to San Francisco Bay with good results. It should be noted that this model does not include adsorption-desorption mechanics or resuspension of sediment.

McCoy and Edge (1977). A water quality model with essentially the same capabilities as that of Leendertse has been constructed by McCoy and Edge (1977). This model is, however, a finite element model which considers stratification in the estuary.

Taylor and Davis (1974). This is a finite element model with capabilities similar to the model of McCoy and Edge. No sediment transport is included in this model. Cubic isoparametric elements are used to represent the estuary. A brief description appears in Taylor and Davis (1974).

Daily and Harleman (1972). Daily and Harleman (1972) have written one-dimensional model capable of simulating dissolved radionuclide transport. This model incorporates a solution of the dynamic, one-dimensional momentum, and advection-diffusion equations. These governing equations are solved along a network of branched and looped one-dimensional channels using the finite element method. Four constituents--salinity, temperature, biochemical oxygen demand (BOD) and dissolved oxygen (DO)--are included in the mathematical model. There are decay terms for BOD, DO, and temperature. The concentration distributions of these constituents are obtained by solving sequentially the appropriate conservation of mass equations which include transport, mixing, and reaction processes. Transport processes due to tidal motion are specified by a combined solution of the continuity and momentum equations including density effects. The reaction processes are characterized by first-order kinetics. It should be noted that no Coriolis or channel curvature effects are accounted for in this model. The model has given good results in applications at Cork Harbor, Ireland, and the James River in Virginia. The present model may be considered an improved version of earlier models of Lee and Harleman (1971) and Thatcher and Harleman (1972).

Water Quality Models of Type II

Orlob et al. (1967) (FWQA Model). The representative model of this type is the FWQA dynamic estuary model developed by Orlob et al. (1967), and modified and applied by Feigner and Harris (1970). The FWQA model can be used for the one-dimensional simulation of dissolved radionuclides in an estuary. This model was developed by Water Resources Engineers, Inc. for the Federal Water Quality Administration, U.S. Department of the Interior. The FWQA dynamic estuary model will calculate transient tidal flows and tidally varying concentrations of constituents of both conservative and nonconservative substances. The model is applied to a network system of channels and junctions laid out in a pattern which characterizes the geometry of the water body. Thus, the dynamics of water bodies with two-dimensional geometry are simulated with a one-dimensional model. An example of the layout is shown in Figure 5.6. Each channel is treated as a prismatic conduit with a specified length and width.

Junctions are given the properties associated with mass storage, volume, and depth. The one-dimensional motion equations are solved along the channels and the constituent equations are solved at the junctions. The governing equations describe the transfer of mass between junctions and balance of mass at the junctions. The solution technique is a finite difference scheme which will handle up to five dissolved constituents. The model has been applied and verified at San Francisco Bay and San Diego Bay.

FIGURE 5.6. Channel-Junction Definition for Computational Mesh (Chan and Crlob 1972)

Baca et al. (1973) (EXPLORE-I). The river basin water quality model EXPLORE-I of Baca et al. (1973) is a slightly more general version of the FMQA model and is applicable to estuaries and tidally influenced rivers. The numerical features of this model are basically the same as those of the FMQA model except for the added generality of being able to treat up to 16 water quality parameters including DO, BOD, plankton populations, phosphorus cycle dynamics, and nitrogen cycle dynamics.

Sediment Transport Models

Odd and Owen (1972)

A hydrodynamic and sediment transport model for 60 miles of the Thames River estuary is reported in Odd and Owen (1972). In determining the water

movement, the method was to calculate, as a first approximation, the bulk flow, i.e., the flow over the complete depth; and then, as a second approximation, to apportion it between the upper and lower layers. The calculation of the total flow is based on the one-dimensional equations of momentum and continuity, ignoring second order terms which were considered to be insignificant. In the silt movement portion of the model, empirical relations are used to simulate the processes of erosion (Partheniades 1962), transport in suspension, deposition (Krone 1962), bed consolidation, and re-erosion. This model could only be used to simulate the advective transport of radionuclides attached to suspended sediment particles. There are no source and sink terms or diffusion in the governing equation. Comparisons with measured data from the Thames River estuary show good agreement.

Ariathurai, MacArthur and Krone (1977)

The sediment-only transport model of Ariathurai, MacArthur and Krone (1977) could be used for particulate radionuclide transport in estuaries. However, only cohesive sediments are considered by the authors. This is a finite element, transient, cohesive sediment transport model which simulates desposition and erosion in estuarine environments. Either depth-averaged or width-averaged equations may be solved. The bed is considered as layered composite with the physical properties of each sediment layer varying with overburden pressure. Suspended sediment concentrations and the bed profile are calculated at each time step. The solution scheme is to treat the time dependent term $\partial c / \partial t$ as an instantaneous constant and solve the resulting elliptic (advection-diffusion equation) equation for each discrete time. The transient problem is then handled by a finite difference method. The model was applied to the Savannah River estuary to calculate suspended sediment transport. Comparison of computed results with field data indicates reasonable agreement (Figure 5.7).

FIGURE 5.7. Suspended Sediment Concentrations During Spring Tide in the Savannah Estuary (Ariathurai, MacArthur and Krone 1977)

Brandsma and Divoky (Dredged Material Research Program Models) (1976)

Two sediment-only models were designed at Tetra Tech for the U.S. Army Corps of Engineers Dredged Material Research Program (Brandsma and Divoky 1976). The first model is designed for a single instantaneous dump of dredged material. The processes of convective descent, dynamic collapse in the water column and long-term passive diffusion are modeled. The initial cloud of material is assumed to be a hemisphere. The second model is for jet discharge from a fixed or moving vessel with the same descent, collapse and diffusion mechanisms modeled as for the instantaneous dump model. In this case, however, the phenomenon being simulated is essentially that of a sinking jet rather than a shining cloud. In both models the ambient current is assumed to be horizontal and variable in all three dimensions and time. When the models are used in cases of complex ambient currents their performance will be very dependent on good velocity data. In the diffusion simulation, the two-dimensional advection-diffusion equation for a uniform flow field with no lateral boundaries is solved, and the solution is modified to account for nonuniform currents, lateral boundaries and unsteady flow. The modifications are intuitively reasonable but it would be interesting to see mathematical justification that the procedure always converges to a true solution. The approaches represented in these two models are based upon the work of Koh and

Chang (1973) and Fischer (1970, 1972). The numerical solution methods employed are of the finite difference type. These models could be used for radionuclides associated with particulate material only.

Smith (1977)

A longitudinal-vertical sediment transport model was developed by Smith (1977) for coastal seas. This model is dynamic and includes specific (often empirical) sediment transport mechanisms. There are no hydrodynamics in the model formulation. Thus, velocity profiles for the transport model are required from external sources. The concentration field of suspended sediment is derived from the advection-diffusion equation by asymptotic analytical techniques. There are no source or sink terms in the formulation. There is no verification documented in Smith's paper.

O'Connor (1971)

O'Connor (1971) describes one- and two-dimensional, unsteady, suspended sediment models which were applied to the Potomac and Mersey Estuaries. The one-dimensional model is in the vertical direction only, including the sediment fall velocity but no flow velocity. The boundary condition at the bed-water interface is specified in such a manner as to allow a net sediment flux across the interface. Thus, erosion and deposition may be simulated. The two-dimensional model has constituent concentrations varying in the longitudinal and vertical directions but no vertical velocities are included. Both models use finite difference solution schemes.

Waldrop and Farmer (1973)

Waldrop and Farmer (1973) have developed a three-dimensional hydrodynamic and transport model intended for use in sediment transport modeling in a river delta. The effects of buoyancy caused by the difference in density of fresh and saline water are included. In addition, turbulence effects are considered via an eddy viscosity model. The advection-diffusion equations are not solved in this model. Computed flow fields are used to track a distribution of nominal particles representing the suspended load of the river as determined from

field data. The solution scheme employed is an asymptotic time-dependent finite difference technique. The model has been applied to South Pass on the Mississippi River with satisfactory results.

Spaulding (1976), Pavish and Spaulding (1977)

Spaulding (1976) used a hybrid Eulerian-Lagrangian particle-in-cell technique to develop a three-dimensional model capable of handling the long-term, transient or steady-state transport of discrete sediment particles in an estuary or coastal zone. The work of Pavish and Spaulding (1977) is a continuation of this model. The solution algorithm employs a finite difference grid network which horizontally translates with the mean particle motion and expands with the dispersive growth of a marker particle cloud. The vertical cartesian coordinate is nondimensionalized by a transformation, which casts the governing equations in x - y - η space where η is dimensionless. Through the use of the vertical transformation the code can treat complicated bottom topography and the time varying free surfaces as uniform boundaries.

A velocity processor was developed for the interpolation of velocities from a vertically averaged two-dimensional velocity field of a tidally driven, finite difference, hydrodynamic numerical model. The particle-in-cell algorithm is then coupled to the hydrodynamic velocity field by the velocity processor, and utilized to predict the long-term diffusion and advection of dilute neutrally and negatively buoyant suspended sediment clouds resulting from an instantaneous release of barged dredge spoil. The model has been applied to Brown's Ledge in Rhode Island Sound. This model could be used for particulate radionuclide transport in estuaries. However, there are no source, sink or decay terms in the governing equations, and deposition and resuspension mechanisms are not considered.

REFERENCES FOR CHAPTER 5

- Ariathurai, R., R. C. MacArthur, and R. B. Krone. 1977. Mathematical Model of Estuarial Sediment Transport. U.S. Army Corps of Engineers, Waterways Experiment Station, Technical Report D-77-12, Vicksburg, MS.
- Baca, R. G., W. W. Middel, C. R. Cole, A. Brandstetter and D. B. Cearlock. 1973. Explore-I: A River Basin Water Quality Model. Battelle, Pacific Northwest Laboratories, Richland, WA.
- Brandsma, M. G. and D. J. Divoky. 1976. Development of Models for Prediction of Short Term Fate of Dredged Material Discharged into the Estuarine Environment. U.S. Corps of Engineer Contract Report D-76-5 by Tetra Tech Inc., Pasadena, CA.
- Chan, C. W. and G. T. Orlob. 1972. Ecologic Simulation for Aquatic Environments. Prepared for the Office of Water Resources Research, U.S. Department of Interior by Water Resources Engineers, Inc.
- Churchill, J. H. 1976. Measurement and Computer Modeling of the Distribution of Nuclear Reactor Discharged Radionuclides in the Estuarine Sediment Near the Maine Yankee Atomic Power Plant in Wiscasset, Maine. M.S. Thesis, University of Maine, Orono, ME.
- Committee on Tidal Hydraulics of the Hydraulics Division. 1970. "Research Needs on Thermal and Sedimentary Pollution in Tidal Water." J. Hydraulic Division, ASCE. pp. 1539-1548.
- Daily, J. E. and D. R. F. Harleman. 1972. Numerical Model for the Prediction of Transient Water Quality in Estuary Networks. Ralph M. Parsons Laboratory, M.I.T. Report No. 158.
- Dawson, G. W., (Project Manager). 1978. The Feasibility of Mitigating Kepone Contamination in the James River Basin. Submitted to the U.S. Environmental Protection Agency. Battelle, Pacific Northwest Laboratories, Richland, WA.
- Eraslan, A. H. et al. 1977. Development of a United Transport Approach for the Assessment of Power Plant Impact. ORNL/NUREG/TM-89, Oak Ridge National Laboratory, Oak Ridge, TN.
- Evans, D. W. and M. H. Cutshall. 1972. "Effects of Ocean Water on the Soluble-Suspended Distribution of Columbia River Radionuclides." Radioactive Contamination of the Marine Environment. IAEA, Vienna, Austria, pp. 125-140.
- Feigner, K. D. and H. S. Harris. 1970. Documentation Report-FWQA Dynamic Estuary Model. U.S. Department of Interior, Federal Water Quality Administration.

- Fields, D. E. 1976. CHISED: Simulation of Sediment and Trace Contaminant Transport with Sediment/Contaminant Interaction. ORNL/NSF/EAC-19. Oak Ridge National Laboratory, Oak Ridge, TN.
- Fields, D. E. 1977. HOTSED: A One-Dimensional, Tidal-Transient, Discrete Element Model for Simulating Hydrodynamic Conditions and Absorbed and Dissolved Radioisotope Concentration in Controlled Rivers and Estuaries. ORNL/CSD-16. Oak Ridge National Laboratory, Oak Ridge, TN.
- Fischer, H. B. 1970. A Method for Predicting Pollutant Transport in Tidal Water. Water Resources Center Contribution No. 132, College of Engineering, University of California, Berkeley, CA.
- Fischer, H. B. 1972. "A Numerical Model of Estuarine Pollutant Transport." Proceedings of the 13th Coastal Engineering Conference. American Society of Civil Engineers, New York, NY. pp. 2265-2274.
- Guilcher, A. 1967. "Origin of Sediments in Estuaries." American Association for the Advancement of Science. Washington, D.C.
- Hammond, D. E., H. J. Simpson, G. Mathiew. 1977. "Radon 222 Distribution and Transport Across the Sediment-Water Interface in the Hudson River Estuary." Journal of Geophysical Research. 82(27):3913-3920.
- Hubbell, D. W. and J. L. Glenn. 1971. Distribution of Radionuclides in Bottom Sediments of the Columbia River Estuary. U.S. Dept. of Interior Geological Survey Open File Report.
- Huggett, R., D. Haven and M. Nichols. 1978. Kepone-Sediment Relationships in the James River, Virginia Institute of Marine Science, Virginia, Submitted to the EPA Gulf Breeze Environmental Research Laboratory, Gulf Breeze, FL.
- Jinks, S. M., and M. E. Wrenn. 1975. "Radiocesium Transport in the Hudson River Estuary," Chapter 11 of Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms. H. W. Miller and J. W. Stannard (eds.), Ann Arbor Science Publishers, Inc., Ann Arbor, MI.
- Klingman, P. C. and Kaufman, W. J. Transport of Radionuclides with Suspended Sediment in Estuarine Systems. Sanitary Eng. Lab. College of Engineering, University of California, Berkeley, CA. SERL Report No. 65-15.
- Koh, B. C. Y. and Y. C. Chang. 1973. Mathematical Model for Barged Ocean Disposal of Water. Environmental Protection Technology.
- Krone, R. B. 1962. Flume Studies of the Transport of Sediment in Estuarial Shoaling Processes. University of California, Hydraulic Engineering Laboratory and Sanitary Engineering Research Laboratory.
- Lee, C. H. and D. R. F. Harleman. 1971. One-Dimensional, Real-Time Model for Estuarine Water Quality Prediction. Report 16070 DGM, Water Quality Office, Environmental Protection Agency, Washington, D.C.

- Leendertse, J. J. 1970. "A Water Quality Simulation Model for Well Mixed Estuaries and Coastal Seas." Vol. 1, Principles of Computation. RM-6230-RC.
- Leendertse, J. J., R. C. Alexander and S. L. Liu. 1973. "A Three-Dimensional Model for Estuaries and Coastal Seas." Volume 1, Principles of Computation, R-1417-OMPR.
- Lentsch, J. W., M. E. Wrenn, T. J. Kneip, and M. Eisenbud. 1970. "Manmade Radionuclides in the Hudson River Estuary." Proceedings of the Fifth Annual Health Physics Society, Midyear Topical Symposium on "Health Physics Aspects of Nuclear Facility Siting." Idaho Falls, ID. Vol. II, pp. 499-528.
- Lentsch, J. W., T. J. Kneip, M. E. Wrenn, G. P. Howells, and M. Eisenbud. 1971. "Stable Manganese and Manganese-54 Distributions in the Physical and Biological Components of the Hudson River Estuary." Proceedings of the Third National Symposium on Radioecology. U.S. AEC, CONF-710501-P2, pp. 753-768.
- Maine Yankee Atomic Power Co. 1976. Maine Yankee Atomic Power Co. Annual Report.
- Maine Yankee Atomic Power Co. 1978. Maine Yankee Atomic Power Co. Annual Radiological Environmental Surveillance Report 1 January 1977 - 31 December 1977. Engineering Office, Environmental Engineering Department.
- Maine Yankee Atomic Power Co. 1979. Maine Yankee Atomic Power Co. Annual Radiological Environmental Surveillance Report 1 January 1978 - 31 December 1978. Engineering Office, Environmental Engineering Department.
- McCoy, J. E. and B. L. Edge. 1977. Methodology for Applying the Finite Element Method to Partially Stratified Estuaries. Report No. 66, Water Resources Research Institute, Clemson University, Clemson, SC.
- Moore, H. L. 1974. "An Investigation of Factors Influencing Radiocesium Cycling in Estuarine Sediments of the Hudson River." Ph.D. Thesis, School of Engineering and Science, New York University.
- Nichols, M. M. 1972. "Sediments of the James River Estuary, Virginia," Geo. Soc. Amer. Mem. 133:169-212.
- Nishiwaki, Y., Y. Honda, Y. Kimura, H. Morishima, T. Koga, Y. Miyaguchi and H. Kawai. 1972. "Behavior and Distribution of Radioactive Substances in Coastal and Estuarine Waters." Radioactive Contamination of the Marine Environment. IAEA, Vienna, Austria, pp. 177-193.
- Norton, W. R., L. A. Roesner, D. E. Evason, and J. R. Monser. 1974. Computer Program Documentation for the Stream Quality Model, QUAL-II, Water Resources Engineers, Inc., Walnut Creek, CA.

- O'Connor, B. A. 1971. "Mathematical Model for Sediment Distribution." Proceedings, Fourteenth Congress of the International Association for Hydraulic Research. pp. 195-202.
- O'Connor, D. J. and K. J. Farley. 1978. "Preliminary Analysis of Kepone Distribution in the James River." Kepone in the Marine Environment. U.S. EPA Research Laboratory, Sabine Island, Gulf Breeze, FL.
- Odd, M. V. M. and M. W. Owen. 1972. "A Two Layer Model of Mud Transport in the Thames Estuary." Proc. Inst. Av. Eng. Supplement 9, 175.
- Officer, Charles B. 1976. Physical Oceanography of Estuaries. John Wiley and Sons, New York, NY. 454 pp.
- Olsen, C. R., H. J. Simpson, R. F. Bopp, S. C. Williams, T. H. Peng and B. L. Deck. 1978. "A Geochemical Analysis of the Sediments and Sedimentation in the Hudson River Estuary." Journal of Sedimentary Petrology. 48(2):401-418.
- Onishi, Y. and R. M. Ecker. 1977. "Mathematical Simulation of Transport of Kepone and Kepone-Laden Sediments in the James River Estuary." Proceedings of the Conference, "Kepone Seminar II." September 21-22, 1977, Easton, MD.
- Onishi, Y., P. A. Johanson, R. G. Baca, and E. L. Hilty. 1976. Studies of Columbia River Water Quality--Development of Mathematical Models for Sediment and Radionuclide Transport Analysis. BNL-B-452, Prepared by Pacific Northwest Laboratory, Richland, WA, for U.S. Energy Research and Development Administration.
- Onishi, Y. and S. E. Wise. 1978a. "Mathematical Modeling of Sediment and Pesticide Transport in the James River Estuary." Proceedings of 26th Annual Hydraulic Division Specialty Conference on Verification of Mathematical and Physical Models in Hydraulic Engineering. College Park, MD, August 9-11, pp. 303-310.
- Onishi, Y. and S. E. Wise. 1978b. Mathematical Simulation of Transport of Sediment and Kepone in the James River Estuary. PNL-2731. Pacific Northwest Laboratory, Richland, WA.
- Onishi, Y., E. M. Arnold, and D. W. Mayer. 1979. Modified Finite Element Transport Model, FETRA, for Sediment and Radionuclide Migration in Open Coastal Waters, NUREG/CR-1026, PNL-3114, Pacific Northwest Laboratory, Richland, WA.*
- Orlob, G. T., R. P. Shubinski and K. D. Feigner. 1967. "Mathematical Modeling of Water Quality in Estuarial Systems." Proceedings of the National Symposium of Estuarine Pollution. Stanford University.
- Pagenkopf, J. R., G. C. Christodoulou, B. R. Pearce and J. J. Connor. 1976. A User's Manual for Case I, A Two-Dimensional Finite Element Circulation Model. Report No. 217, Massachusetts Institute of Technology.

- Partheniades, E. 1962. A Study of Erosion and Deposition of Cohesive Soils in Salt Water. Ph.D. Thesis, University of California.
- Pavish, D. L. and M. L. Spaulding. 1977. Development and Application of a Three-Dimensional Numerical Model for Predicting Pollutant and Sediment Transport Using an Eulerian-Lagrangian Marker Particle Technique. Rhode Island Ocean Engineering Dept. Kinston, RI.
- Pritchard, D. V. 1967. What is an Estuary: Physical Viewpoint. Estuaries, Edited by G. H. Lauff. American Association for the Advancement of Science, Washington, D.C.
- Postma, A. 1967. "Sediment Transport and Sedimentation in the Marine Environment." American Society of the Advancement of Science. Washington, D.C.
- Schubel, J. R. 1975. Distribution and Transportation of Suspended Sediment. Effects of Energy Related Activities on the Atlantic Continent Shelf. B. Manowitz (ed.). Brookhaven National Laboratory, Upton, NY.
- Simpson, H. J., C. R. Olsen, R. M. Trier, and S. C. Williams. 1976. "Man-Made Radionuclides and Sedimentation in the Hudson River Estuary." Science. 194:178-183.
- Simpson, A. J. and S. C. Williams. 1978. "Plutonium and Cesium Radionuclides in the Hudson River Estuary." Annual Technical Progress Report, December 1, 1974 - November 30, 1975, Columbia University, Palisades, New York, Lamont-Doherty Geological Observatory.
- Smith, J. D. 1977. "Modeling of Sediment Transport on Continental Shelves." The Sea. 6. E. D. Goldberg et al. (ed.), John Wiley and Sons, New York, NY.
- Spaulding, M. 1976. Numerical Modeling of Pollutant Transport Using a Lagrangian Marker Particle Technique. NASA Langley Research Center, Hampton, VA. NASA/TRX-73938.
- Spraggs, L. D. 1974. Numerical Simulation of Dredged Material Dispersion - San Pablo Bay, San Francisco. Vol. I, Model Development. Report EGU-2774 San Francisco District, U.S. Corps of Engineers.
- Taylor, C and J. M. Davis. 1974. "Numerical Model of Dispersion in Estuaries." Finite Element Methods in Flow Problems. J. T. Oden et al. (ed.), UAH Press.
- Thames Estuary Flood Prevention Investigation. 1970. Mathematical Silt Model Studies. Report No. Ex. 479, Hydraulics Research Station, Wallingford, Berkshire, England.

Thatcher, M. L. and D. R. F. Harleman. 1972. A Mathematical Model for the Prediction of Unsteady Salinity Intrusion in Estuaries. Tech. Rep. No. 144, Ralph M. Parsons Laboratory, Department of Civil Engineering, Massachusetts Institute of Technology.

The State of New York, "Periodic Report of the Water Quality Surveillance Network 1965 Through 1967, Water Years."

The State of New York. 1976. "Water Resources Data for New York, Water Year 1975."

The State of New York. 1977. "Water Resources Data for New York, Water Year 1976."

The State of New York. 1978. "Water Resources Data for New York, Water Year 1977."

U.S. Environmental Protection Agency. 1976. Radioactive Isotopic Characterization of the Environment Near Wiscasset, Maine Using Pre- and Post-Operational Surveys in the Vicinity of the Maine Yankee Nuclear Reactor. Environmental Analysis Division, Office of Radiation Programs, Washington, D.C.

U.S. Environmental Protection Agency. 1978. Kepone Mitigating Project Report. Standard and Criteria Office of Water and Hazardous Materials, Washington, D.C.

U.S. Nuclear Regulatory Commission. 1978. Liquid Pathway Generic Study. Impacts of Accidental Radioactivity Releases to the Hydrosphere from Floating and Land-Based Nuclear Power Plants. NUREG-0440.**

Waldrop, W. R. and R. C. Farmer. 1973. Three-Dimensional Flow and Sediment Transport at River Mouths. Tech. Rept. No. 150. Coastal Studies Institute, Louisiana State University, Baton Rouge, LA.

Wrenn, M. E. and S. M. Jinks. 1975. "The Dosimetric Implications of Releases to the Aquatic Environment from the Nuclear Power Industry." Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms. H. W. Miller and J. W. Stannard (eds.), Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Wrenn, M. E., J. W. Lentsch, M. Eisenbud, G. J. Lauer, and G. P. Howells. 1971. "Radiocesium Distribution in Water, Sediment and Biota in the Hudson River Estuary from 1965 through 1970." Third National Symposium on Radioecology, Oak Ridge, Tennessee.

Wrenn, M. E. et al. 1972. Radioecological Studies of the Hudson River. Progress Report to Con. Edison Company of New York.

Wrenn, M. E., S. M. Jinks, M. Cohen, and L. M. Hairr. 1973. "¹³⁷Cs and ¹³⁴Cs Distribution in Sediment, Water and Biota of the Lower Hudson River and Their Dosimetric Implications for Man." Proceedings of the Third International Congress of the International Radiation Protection Association Meeting. Washington, D.C.

Wrenn, M. E. 1975. Radioecological Studies of the Hudson River. New York University Medical Center, Progress Report prepared for the Consolidated Edison Company of New York.

Wrenn, M. E., et al. 1976. "A Mathematical Model Describing Radiocesium Transport in the Hudson River Estuary." Proceedings of the Fourth Symposium on Hudson River Ecology. Bear Mountain, NY, Paper No. 10.

Wrenn, M. E., M. P. Singh, M. Cohen, M. Eisenbud, P. Linsalata, S. Schaffer, C. T. Cook and D. Wohlgemuth. 1979. Radioecological Studies of the Hudson River: The Distribution of Beta-Gamma-Emitting Radionuclides--Progress Report 1976 and 1977. Institute of Environmental Medicine, New York University Medical Center, prepared for the Consolidated Edison Company of New York.

*Available for purchase from the NRC/GPO Sales Program, U.S. Nuclear Regulatory Commission, Washington, DC 20555, and the National Technical Information Service, Springfield, VA 22161.

**Available for purchase from the National Technical Information Service, Springfield, VA 22161.

6. RADIONUCLIDE TRANSPORT IN OCEANS AND THE GREAT LAKES

This chapter discusses models for oceans and the Great Lakes that simulate migration of contaminants through a numerical solution of the advection-diffusion equations. Radionuclide concentration data were obtained and evaluated as to their suitability for model input and verification.

PHYSICAL MECHANISMS OF RADIONUCLIDE TRANSPORT IN OCEANS AND THE GREAT LAKES

Oceans

Radionuclides discharged to coastal waters are dispersed by coastal currents, surface waves and turbulent mixing and are also adsorbed from solution onto marine sediment. The major driving forces to migrate radionuclide in coastal waters are advection and dispersion. As discussed in earlier chapters, the sediment-radionuclide interactions become important if: 1) radionuclides have large distribution coefficients; 2) receiving water bodies have large sediment concentrations of especially fine sediment; and/or 3) long-term migration, accumulation and fate of radionuclides are concerned. In general, radionuclides tend to have smaller distribution coefficients and there are less sediment concentrations (except nearshore zone) in coastal waters than other surface waters (USNRC 1978a; Schubel 1975). Hence, effects of sediment on radionuclide migration in coastal waters tend to be less important than those appearing in other surface waters. However, long-term migration, accumulation and fate of radionuclides with large half lives are still subject to sediment-radionuclide interactions. Considerable data exist to suggest that adsorption to and subsequent transport of marine sediment is an important radionuclide transport process. Some examples are:

1. studies of radionuclide concentration in the vicinity of the Windscale Nuclear Reprocessing Plant on the English Coast of the Irish Sea (Hetherington 1976; Livingston and Bowen 1976)
2. studies of fallout radionuclide concentrations at Bikini and Eniwetok atolls in the Central Pacific Ocean (Nevissi and Schell 1974, 1975a,b; Schell 1973, 1974, 1976)

3. radionuclide concentration measurements in the coastal waters of Washington State (Schell 1977)
4. open ocean sediment core samples from the North and South Atlantic Oceans and the Mediterranean Sea (Noshkin and Bowen 1973).

Data from the Irish Sea near the Windscale Fuel Reprocessing Plant show that 95% of the plutonium and 20% of the cesium discharged to the Irish Sea from the plant have been adsorbed onto marine sediment and have remained in the Irish Sea. The remaining percentages of plutonium and cesium are in the dissolved form (Hetherington 1976) which is subject to be flushed from the sea. Hetherington concludes that, on the basis of ^{239}Pu and ^{137}Cs in core samples from the Windscale vicinity, sedimentation of material which has been contaminated while in suspension is the primary mechanism by which both of these radionuclides are deposited in marine sediment.

Numerous reports were reviewed which contained data on the physical-chemical states of radionuclides and their concentrations obtained from field studies conducted at Bikini and Eniwetok atolls. As an example of this information, Table 6.1 shows percentages of particulate, colloidal and soluble forms of various radionuclides. This table was taken from Schell (1974).

As indicated in the table, bismuth was found to be 90% colloidal, while europium and americium exhibited great variability in their forms with high percentages in particulate form for some measurements. Plutonium exhibited the greatest range of variability and was found to exist in particulate, colloidal, and soluble forms. Schell (1977) states that in the near coastal waters of Washington State more than 75% of the ^{210}Pb present is associated with particulate material (0.3 mm). Furthermore, Schell mentions that ^{210}Po is generally found in the particulate form in Washington State waters.

The distribution of radionuclides in the bottom sediment of the Columbia River estuary is discussed by Hubbell and Glenn (1971). Livingston and Bowen (1976) have studied fallout radionuclide concentrations at Buzzards Bay, Massachusetts, and have found that ^{241}Pu and ^{240}Pu are largely bound to marine sediment. The data reviewed have shown that a relatively large number

TABLE 6.1. Physical-Chemical States of Radionuclides in Bikini Atoll Lagoon in Percent (Schell 1974)

Element	Particulate Percent		Colloidal Percent	Soluble Percent
	Range	Mean		
⁶⁰ Co	15- 50	30	variable	variable
⁵⁵ Fe	30- 52	52	45	10
²⁰⁷ Bi	3- 22	10	90	none
¹⁵⁵ Eu	18-100	variable	variable	none
²⁴¹ Am	30-100	variable	variable	none
^{239,240} Pu	4- 75	variable	variable	variable
^{235,238} U	none	not determined		100

of radionuclides can exist in particulate and colloidal forms. Those radionuclides in this group with high K_d values can be transported by marine sediment and should be considered via marine sediment movement in an oceanic radionuclide transport model. Thus, even though the suspended sediment load over much of the middle and outer continental shelf can be as much as several orders of magnitude less than the corresponding load in lakes and rivers, ocean transport of marine radionuclides with higher K_d values via suspended sediment cannot be neglected.

For radionuclides with smaller K_d values (say, less than 10^4), the suspended sediment concentration in most of the continental shelf is too small to adsorb significant amounts of dissolved radionuclides especially for short-term transport (Schubel 1975). However, as reported by Schubel (1975) in the long term (over a period of years) suspended sediment may still play an important role in the ultimate removal of radionuclides. Furthermore, he reported that the periodic resuspension of fine-grained bottom sediment in estuaries, other coastal basins, and tidal reaches of rivers constitutes a very effective scavenging mechanism for radionuclides because of an essentially infinite supply of new sediment.

Additional factors can be considered for examining the sediment-radionuclide interaction. For example, severe storms and floods typically increase the suspended sediment load on the continental shelf by as much as one order of magnitude. This higher sediment concentration increases the interaction between radionuclides and sediment during the storm and flood period, and thereafter patterns of radionuclide transport will be changed with a higher percentage of radionuclides being bound by marine sediment. Secondly, much of the bottom deposits of the outer shelf are comprised of fine sediment and organic matter subject to resuspension by surface wave stresses. In many cases this sediment shows a residual landward flow in the inner third of the shelf. Release of radioactive material and scavenging by this sediment would tend to transport radionuclides shoreward. In the nearshore zone, particularly in areas influenced by the discharge of rivers, the suspended sediment load is very high and the transport of radionuclides by this sediment would be important.

In the event that discharges of low-level radioactive effluents to coastal waters continue (as well as some accidental spills), the need for a quantitative understanding of coastal radionuclide transport will be more compelling. Consequently, it is important to obtain a general capability of radionuclide transport modeling by including mechanisms of advection, dispersion, surface waves, sediment-radionuclide interactions and radionuclide decay.

The Great Lakes

The radionuclide transport in the Great Lakes is in general much more complex than those in the coastal waters. This complexity is a product of the complex behavior of currents, waves, wind, sediment transport and thermocline (USNRC 1978a,b).

Field studies in the Great Lakes have revealed that coastal currents are predominantly parallel to shore and have typical speeds of 10 cm/sec to 20 cm/sec (0.33 to 0.66 ft/sec). Currents generally persist for several days; then, in direct response to wind shifts, they quickly reverse and persist in the opposite direction for several days (Csanady 1970, 1972). Each reversal

of the current is usually accompanied by large-scale mass exchange with off-shore waters that effectively removes contaminants from the nearshore zone (Csanady 1970). Contaminants flushed from the nearshore zone are dispersed in the large-scale turbulence offshore, unimpeded until effects of the other shorelines are felt.

Many of the contaminants are adsorbed by lake sediment mainly due to fairly high suspended sediment concentration and a more pronounced tendency for contaminants (radionuclides) to be adsorbed onto particulate materials in fresh water (Walgren and Nelson 1973). It has been observed that areas of heavy sedimentation in the Great Lakes are also areas of high radionuclide concentration.

Resuspension of radionuclides from the sediment to the water column is well documented in the Great Lakes. Walgren and Nelson (1973) have conducted studies in Lake Michigan which show that due to sorption and desorption by sediments, ^{239}Pu and ^{137}Cs (to a lesser extent) are depleted from the surface waters during summer and are returned during the winter mixing period to nearly the concentration of the previous spring.

Mixing of dissolved radionuclides can be limited by a thermocline. Eventually, however, dissolved radionuclides are nearly uniformly mixed in the lakes due to several seasonal overturns in the lakes mixing the dissolved radionuclides with deep waters. The characteristic mixing time for an instantaneous release is estimated to be from several weeks to several months, depending upon lake size and prevailing hydrologic conditions (Csanady 1970; Murthy et al. 1974). Some radionuclides are eventually flushed out of the lakes by the flow-through of fresh water. Others remain largely attached to sediments. The flushing time for the Great Lakes is on the order of years to tens of years, depending upon the particular lake volume and flow-through rate. Some of the existing radionuclide data sources for oceans and the Great Lakes are listed in Table 6.2.

TABLE 6.2. Ocean and Great Lakes Data

References	Water Body	Type of Radionucleide Data
Heft et al. (1973)	Humboldt Bay, California	60K, 137Cs and 65Zn in water and bed sediment
Noshkin et al. (1976)	Humboldt Bay, California	60Co, 134Cs, 137Cs and 54Mn in water and bed sediment
Harrison et al. (1976)	Humboldt Bay, California	60Co, 137Cs, 54Mn and 65Zn in water and bed sediment for a discharge canal of the Humboldt Bay power plant
Blanchard et al. (1976)	New Jersey coast of Atlantic near the Oyster Creek Power Plant	Dissolved 137Cs and 90Sr, 60Co, 134Cs, 137Cs, 40K, 54Mn, 226Ra, 125Sb, 252Th in bed sediment
Dunster (1958)	Irish Sea	Dissolved 106Ru
Manchline (1963)	Irish Sea	Dissolved 144Ce, 137Cs, 106Ru, 89Sr, 90Sr, 95Zr-95Nb
Longley and Templeton (1965)	Irish Sea	144Ce, 137Cs and 106Ru in the shore silt
Templeton and Preston (1966)	Irish Sea	106Ru in water and bed sediment 90Sr in unfiltered sea water
Perkins and Williams (1966)	Irish Sea	144Ce, 137Cs, 40K, 106Ru, 95Zr-95Nb in the bed core sediment
Jefferies (1968, 1970)	Irish Sea	144Cs, 137Cs, 106Ru, 95Zr-95 in the bed sediment.
Mitchell (1969, 1971a,b, 1973, 1975)	Irish Sea	144Ce, 137Cs, 40K, 106Ru, 241Am, 95Zr-95Nb in sea water and bed sediment
Preston et al. (1971)	Irish Sea	144Ce, 137Cs, 106Ru, 95Zr-95Nb in sea water and bed sediment
Jefferies et al. (1973)	Irish Sea	Dissolved 137Cs
Hetherington and Jefferies (1974)	Irish Sea	144Cs, 106Ru, 95Zr-95Nb in bed sediment
Hetherington et al. (1975)	Irish Sea	Dissolved and particulate forms of 137Cs and 239Pu
Hetherington (1976a,b)	Irish Sea	Dissolved 137Cs, 239Pu, 241Am and 238Pu. 239-240Pu in sea water and bed sediment
Mitchell (1977a,b)	Irish Sea	144Ce, 134Cs, 137Cs, 106Ru, 95Zr-95Nb in bed sediment

TABLE 6.2. (contd)

References	Water Body	Type of Radionuclide Data
Hunt (1979)	Irish Sea	^{144}Ce , ^{60}Co , ^{134}Cs , ^{137}Cs , ^{239}Pu , $^{239-240}\text{Pu}$, ^{106}Ru , ^{95}Zr - ^{95}Nb in bed sediment
Pentreath et al. (1980)	Irish Sea	^{137}Cs , ^{99}Tc , $^{239-240}\text{Pu}$ in bed sediment. Distribution coefficients of ^{241}Am , ^{242}Cm , ^{244}Cm , $^{239-240}\text{Pu}$
Schell (1973)	Bikini and Eniwetok atolls	Dissolved and particulate forms of ^{241}Am
Nevisi and Schell (1974)	Bikini and Eniwetok atolls	Dissolved and particulate forms of ^{240}Po , ^{239}Pu , ^{240}Pu
Schell (1974)	Bikini and Eniwetok atolls	Dissolved and particulate forms of ^{60}Co , ^{55}Fe , ^{207}Bi , ^{155}Eu , ^{241}Am , ^{239}Pu , ^{240}Pu , ^{235}U , ^{238}U
Nevisi and Schell (1975)	Bikini and Eniwetok atolls	Dissolved and particulate forms of ^{155}Eu , ^{207}Bi , ^{241}Am , ^{239}Pu , ^{240}Pu , ^{210}Pb
Schell (1976)	Bikini and Eniwetok atolls	Dissolved and particulate forms of ^{239}Pu , ^{240}Pu , ^{241}Am , ^{207}Bi , ^{155}Eu , ^{60}Co , ^{55}Fe , ^{210}Po
Dauersma and Bosch (1970)	Atlantic	Adsorption-desorption generic study
Dauersma (1972)	Atlantic and Mediterranean	Dissolved and particulate forms of ^{54}Mn , ^{55}Fe , ^{60}Co , ^{65}Zn , ^{90}Sr , ^{95}Zr , ^{106}Ru , ^{137}Cs , ^{144}Ce , ^{147}Pu
Noshkin (1972)	Atlantic	^{241}Am , ^{239}Pu , ^{137}Cs , ^{90}Sr in marine sediment and biota
Silker (1972)	North Pacific	Dissolved and particulate forms of ^7Be , ^{106}Ru , ^{95}Zr - ^{95}Nb , ^{144}Ce
Noshkin and Bowen (1973)	Atlantic and Mediterranean	Dissolved and particulate forms of ^{241}Am , ^{239}Pu , ^{240}Pu
Livingston and Bowen (1976)	Atlantic	Dissolved and particulate forms of ^{241}Am , ^{239}Pu , ^{240}Pu
Lerman and Taniguchi (1972)	Great Lakes	Particulate ^{90}Sr
Robbins and Edgington (1975)	Great Lakes	Particulate ^{137}Cs , ^{210}Pb , ^{239}Pu , ^{240}Pu

MATHEMATICAL MODELS FOR OCEAN AND THE GREAT LAKES

As in previous chapters, these models include those that simulate radionuclide transport, water quality, and sediment transport. Thermal plume models are included in addition.

Radionuclide Transport Models

The models described in this section are analytical and numerical models designed to simulate radionuclide transport. The following analytical radionuclide transport models are described in the NRC report (USNRC 1976).

A simple diffusion model for steady-state discharge into a lake or coastal area with a known steady shoreline current has governing equations expressed in Equation (3.7). As discussed in Chapter 3, it is assumed that the discharge is located at the point $(0, y_s, z_s)$, i.e., at the origin of the x-axis and a distance y_s from the shoreline and z_s beneath the water surface. For a large lake of constant depth, d , and straight shoreline, the solution is given in Equation (3.8). For further information on more general uses of this model, the USNRC Regulatory Guide 1.113 (USNRC 1976) may be consulted.

For instantaneous and general transient releases of a finite quantity of material from a line source of $x=0, y=y_s$, solutions are given by Equations (3.10) and (3.11), respectively.

Of the numerical models, there are two models which can be applied to oceans and the Great Lakes.

Onishi et al. (1976, 1979), Onishi and Ecker (1977), Onishi and Wise (1978a,b)

Onishi et al. (1976) developed an unsteady, two-dimensional (lateral and longitudinal), sediment-contaminant transport model which utilizes the finite element computation method with the Galerkin weighted residual technique. This model, FETRA (Finite Element Transport Model), has general advection-diffusion equations with decay and sink/source terms and consists of a sediment transport submodel, a dissolved contaminant transport submodel, and a particulate contaminant transport submodel coupled together as discussed in Chapter 5.

In most environments in coastal areas and large lakes (e.g., the Great Lakes), marine and lake sediments are mostly suspended by waves which themselves can transport only small amounts of suspended sediment. The sediment suspended by wave action is then transported mostly by a current which, in most cases, is too small to suspend sediment by itself. Hence, the original FETRA code was modified to include sediment-wave interactions in both offshore and surf zones to extend its applicability to coastal waters and to a lesser extent large lakes (e.g., the Great Lakes) where wave action is one of the mechanisms of sediment and radionuclide transport.

FETRA uses the following concept to compute the erosion and deposition rates of sand: if the amount of sand being transported is less than what the flow and wave can carry, the current and waves will scour sediment from the ocean bed until an actual sediment load is equal to the carrying capacity or until the available bed sediments are all scoured, whichever occurs first. Conversely, sand will be deposited if the actual sediment load is above the flow and wave capacity to carry sediments. For an offshore zone, sediment capacity was computed by formulations developed by Liang and Wang (1973). For surf zone, Komar's formula (1977) is used to calculate the sediment transport capacity. For cohesive sediments, Partheniades' (1962) and Krone's (1962) formulas for erosion and deposition rates are used. The applicability of the last two formulas in wave-dominated coastal waters is somewhat questionable. However, there are no alternative formulations currently available.

In order to compute offshore and littoral transport of sediment, thus particulate radionuclide, by these formulas, wave characteristics are needed. This was accomplished with: 1) inclusion of wind-induced wave mechanisms built in FETRA, and 2) a wave refraction program (Bodson 1967; Ecker and Degraça 1974) which is used in conjunction with FETRA.

FETRA is a depth-averaged, two-dimensional model and cannot include effects of thermocline and seasonal overturns appearing in the Great Lakes. Hence, the applicability of FETRA to the Great Lakes is very limited. The migration of radionuclides in the Great Lakes can be simulated by: 1) a three-dimensional model which can run very fast to be able to cover both

short- and long-term migration, 2) a combination of a three-dimensional model for a short term and a mixing tank model for a long term, or 3) a set of nearshore, offshore and mixing tank models (USNRC 1978a,b) to cover both short- and long-term radionuclide migration and accumulation.

Eraslan et al. (1977)

As discussed in Chapter 5, one- and two-dimensional dissolved radionuclide transport models, RADONE and RADTWO, respectively, were developed for estuaries and oceans (Eraslan et al., 1977). RADTWO was developed from the thermal code FARTMP, a tidal-transient, two-dimensional model applicable to lakes, estuaries, and coastal regions. Technical reports have not been published for either RADTWO or FARTMP, thus precluding detailed model evaluations for the purposes of this study. However, an unsteady, two-dimensional model reported by Eraslan (1975) appears to have a formulation similar to these models mentioned above. According to Eraslan et al. (1977), FARTMP includes a hydrodynamic simulation, for which the user must specify the two velocity components of the flow field in order to obtain the flow depth at a given location and time. Results from a simulation of the Peach Bottom Atomic Power Station on the Conowingo Reservoir in the Hudson River showed excellent agreement with field-measured data for the temperature distributions as shown in Figure 6.1.

Water Quality Models

The following are water quality mathematical models suitable for ocean and Great Lakes application. These models could be used only to simulate the movement of dissolved radionuclides. The models described in the following section are divided into types of models based upon their governing equations (see Chapter 3).

Water Quality Models of Type I

Leendertse (1970, 1973). The model of Leendertse (1970), described in Chapter 5, is also applicable to oceans and the Great Lakes. This model, the representative of Type I models, is based on a rigorous treatment of the governing differential equations. The model would be suitable only for dissolved radionuclides.

FIGURE 6.1. Comparison of Computed and Measured Temperature Distributions in the Conowingo Reservoir in the Vicinity of the Peach Bottom Atomic Power Station (Eraslan et al. 1977)

Other water quality models of this class which can be used for oceans and the Great Lakes include that of Spraggs (1974) which was discussed in detail in Chapter 5.

Simons (1973). Simons (1973) has designed a hydrodynamic and thermal structure for the Great Lakes. Both a homogeneous and a multilayered model are described. The transport equation is shown below:

$$\frac{\partial(\theta)}{\partial t} + \frac{\partial(U\theta)}{\partial x} + \frac{\partial(V\theta)}{\partial y} + \frac{\partial(W\theta)}{\partial z} + \frac{\partial \epsilon_{\theta}}{\partial x} \frac{\partial \theta}{\partial x} + \frac{\partial}{\partial y} \left(\frac{\epsilon_{\theta} \partial \theta}{\partial y} \right) + \frac{\partial}{\partial z} \left(\frac{\epsilon_z \partial \theta}{\partial z} \right) = 0 \quad (6.2)$$

where

$\theta = T - T_0$ = the temperature anomaly

(U, V, W) = local velocity vector

ϵ_0 = horizontal eddy diffusivity

ϵ_z = vertical eddy diffusivity

For both models, the equations are solved in a vertically integrated form.

The nonlinear vertical acceleration is included and approximated with special assumptions about the vertical profiles of horizontal motions and the relation of bottom stresses to volume transport. There are no source, sink, or decay terms included in the model formulation. Both of these models could be made suitable for simulating dissolved radionuclide transport if a dissolved radionuclide is assumed to be a conservative substance. The governing equations are solved with a finite difference numerical scheme. Some one- and two-dimensional test calculations have been performed and are reported in Simons (1973). Preliminary computations with a homogeneous model and a four-layered stratified model are reported in Simons (1971) and Simons (1972).

Chen et al. (1975) (The Lake Ontario Model). This is a water quality ecological model which solves a form of the advection-diffusion equation with source or sink terms. Thus, dissolved radionuclide transport can be simulated with this model. The model was developed at Tetra Tech, Inc. by Chen, Lorenzen and Smith (1975). Phosphorus and nitrogen cycle dynamics and plankton and fish population dynamics are also included in the model. The flow is calculated in the x-z (longitudinal-vertical) plane by a finite difference method. The calculations are performed for the transient and/or steady-state cases. The model has been applied to Lake Ontario and the verification status is reported in Chen, Lorenzen and Smith (1975).

Monte Carlo Models (Type VI)

Battelle Oil Slick Model (Ahlstrom et al., 1975). The oil slick model is a two-dimensional, steady-state and/or transient transport model intended to simulate the movement of oil slicks in marine waters. The oil slick model can be used for dissolved radionuclide transport modeling in marine or Great Lakes

regions. The hydrodynamic equations are not included in the model formulation so the velocity field must be supplied by external means. Adsorption mechanics are considered in the oil slick model. The solution scheme is known in the literature as the discrete parcel random walk method (see Chapter 3, Model Type VI). This method is similar in some ways to Monte Carlo transport analysis and is based on the movement of a hypothetical entity referred to as a discrete parcel. A Lagrangian approach is used for simulating the parcel advection and a homogeneous Markov random walk process is used to model the dispersive component. If thousands of such parcels are released in a passive flow field and their discrete paths are followed and recorded as a function of time, then the density of the ensemble may be interpreted as the concentration of a particular constituent, in this case crude oil or some chemical fraction of the oil.

Sediment Transport Model

W. Leimkuhler (1974)

This model solves a two-dimensional, vertically integrated form of the advection-diffusion equation. It is capable of handling both the transient and steady-state cases. The solution technique employed is a finite element (Galerkin) method which uses a linear weighting function. The velocity field used in the code must be externally supplied. Source and sink terms as well as decay terms are included in the formulation. A continuous source of sediment load with no deposition or resuspension is assumed. Preliminary verification against simple analytical solutions of one- and two-dimensional cases has been completed. In addition, the model was applied to predict suspended sediment dispersion in Massachusetts Bay. Certain stability criteria to be used in computer implementation of the model should be noted.

Thermal Plume Model

Adams, Stolzenbach and Harleman (1975)

Adams et al. (1975) have developed two models intended for use in simulating buoyant thermal plumes. One is an integral jet thermal plume model for predicting the near-field temperatures due to buoyant surface discharges. The

other is a far-field model in which the three-dimensional excess temperatures are calculated by superimposing the temperature distributions resulting from discrete, vertically-distributed line sources which are treated by the method of moments. Ambient currents, which can vary in the vertical direction and in time, surface heat loss, and turbulent diffusion in all directions are considered.

The models could be modified, with some effort, for use in modeling dissolved radionuclide transport. Comparison of model predictions with field data can be found in Adams et al. (1975). These comparisons show satisfactory agreement considering all of the assumptions which must be made to run integral models.

REFERENCES FOR CHAPTER 6

- Adams, E. E., K. D. Stolzenbach and D. R. F. Harleman. 1975. Near and Far Field Analysis of Buoyant Surface Discharges into Large Bodies of Water. Report No. 205. Ralph M. Parson Laboratory, Department of Civil Engineering, MI.
- Ahlstrom, S. W. 1975. A Mathematical Model for Predicting the Transport of Oil Slicks in Marine Waters. Battelle, Pacific Northwest Laboratories, Richland, WA.
- Blanchard, R. L., W. L. Brinck, H. E. Kolde, H. L. Frieger, D. M. Montgomery, S. Gold, A. Martin, and B. Kahn. 1976. Radiological Surveillance Studies at the Oyster Creek BWR Nuclear Generating Station. EPA-520/5-76-003, U.S. Environmental Protection Agency, Office of Radiation Programs, Eastern Environmental Radiation Facility, Cincinnati, OH.
- Csanady, G. T. 1970. "Dispersal of Effluents in the Great Lakes." Water Research. 4:78-114.
- Csanady, G. T. 1972. "Response of Large Stratified Lakes to Wind." Journal of Physical Oceanography. 2(1):3-13.
- Chen, C. W., M. Lorenzen, and D. J. Smith. 1975. A Comprehensive Water Quality Ecological Model for Lake Ontario. TETRA TECH Inc., Lafayette, CA.
- Dunster, H. J. 1958. "The Disposal of Radioactive Liquid Wastes into Coastal Waters." Proceedings of the 2nd United Nations International Conference on the Peaceful Uses of Atomic Energy. 18:390-399. United Nations, New York.
- Duursma, E. K., and M. G. Gross. 1971. "Marine Sediments and Radioactivity." Radioactivity in the Marine Environment. pp. 147-161. National Academy of Sciences.
- Duursma, E. K., and C. J. Bosch. 1970. "Theoretical, Experimental, and Field Studies Concerning Diffusion of Radioisotopes in Sediments and Suspended Particles of the Sea - Part B Methods and Experiments." Netherland J. of Sea Research. 4:395-469.
- Duursma, E. K. 1972. "Specific Activity of Radionuclides Sorbed by Marine Sediments in Relation to the Stable Element Composition." AEA Proceedings.
- Edgington, D. N. and J. A. Robbins. 1970. "Patterns of Deposition of Radionuclides in Sediments." Nonbiological Transport and Transportation of Pollutants and Land and Water: Processes and Critical Data Required for Predictive Desorption. National Bureau of Standards. Gaithersburg, MD.

- Eraslan, A. H. 1975. A Transient, Two-Dimensional, Discrete - Element, Far-Field Model for Thermal Impact Analysis of Power Plant Discharges in Coastal and Offshore Regions. Part 1: General Description of the Mathematical Model and the Results of an Application. ORNL-4940, Oak Ridge National Laboratory, Oak Ridge, TN.
- Eraslan, A. H. 1977. Development of a Unified Transport Approach for the Assessment of Power-Plant Impact. ORNL/NUREG/TM-89, Oak Ridge National Laboratory, Oak Ridge, TN.
- Harrison, F. L., K. M. Wong and R. E. Heft. 1976. Interactions of Radionuclides in Water, Particulates, and Oysters in the Discharge Canal of a Nuclear Power Plant. UCRL-51974. Lawrence Livermore Laboratory, University of California, Livermore, CA.
- Heft, R. E., W. A. Phillips, H. R. Ralston, and W. A. Steele. 1973. "Radionuclide Transport Studies in the Humboldt Bay Marine Environment." Symposium on the Interaction of Radioactive Contaminants with the Constituents of the Marine Environment. IAEA, Vienna, pp. 595-614.
- Heft, R. E., W. A. Phillips, H. R. Ralston, and W. A. Steele. 1972. Radionuclide Transport Studies in the Humboldt Bay Marine Environment. UCRL-73745, Lawrence Livermore Laboratory, Livermore, CA.
- Hetherington, J. A. 1976a. Behavior of Plutonium Nuclides in the Irish Sea, Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms. Morton and Miller, Eds, Ann Arbor Science, 1976.
- Hetherington, J. A. 1976b. Radioactivity in Surface and Coastal Waters of the British Isles, 1974. Ministry of Agriculture, Fisheries and Food. Directorate of Fisheries Research. Fisheries Radiobiological Laboratory, Technical Report FRL 11, Lowestoft.
- Hetherington, J. A. and D. F. Jefferies. 1974. "The Distribution of Some Fission Product Radionuclides in Sea and Estuarine Sediments." Netherlands Journal of Sea Research. 8(4):319-338.
- Hetherington, J. A., D. F. Jefferies, and M. B. Lovett. 1975. "Some Investigations into the Behavior of Plutonium in the Marine Environment." Impact of Nuclear Releases into the Aquatic Environment. International Atomic Energy Agency, Vienna, pp. 193-210.
- Hubbell, D. W. and J. L. Glenn. 1971. Distribution of Radionuclides in Bottom Sediments of the Columbia River Estuary. U.S. Dept. of the Interior. Geological Survey. Open File Report.
- Hunt, G. J. 1979. Radioactivity in Surface and Coastal Waters of the British Isles, 1977. Aquatic Environment Monitoring Report No. 3. Ministry of Agriculture, Fisheries and Food. Directorate of Fisheries Research, Lowestoft. ISSN 0142-2499.

- Jefferies, D. F. 1968. "Fission-Product Radionuclides in Sediments from the Northeast Irish Sea." Helgolander Wiss. Meeresunters. 17:280-290.
- Jefferies, D. F. 1970. "Exposure to Radiation from Gamma-Emitting Fission-Product Radionuclides in Estuarine Sediments from the Northeast Irish Sea." W. C. Reinig (Ed.). Environmental Surveillance in the Vicinity of Nuclear Facilities, Charles C. Thomas, Springfield, IL, pp. 205-216.
- Jeffries, D. F., et al. 1973. "Distribution of Cesium-137 in British Coastal Water." Marine Pollution Bull. pp. 118-122.
- Koh, B. C. Y. and Y. C. Chang. 1973. Mathematical Model for Barged Ocean Disposal of Water. Environmental Protection Technology Series EPA 660/2-73-029. U.S. EPA, Washington, DC.
- Leendertse, J. J. 1970. "A Water Quality Simulation Model for Well Mixed Estuaries and Coastal Seas." Principles of Computation. Vol. I. RM-6230-RC.
- Leendertse, J. J., R. C. Alexander, and S. L. Liu. 1973. "A Three-Dimensional Model for Estuaries and Coastal Seas." The Rand Corp. Principles of Computation. Vol. I, The Rand Corporation, R-147-OMPR.
- Leinkuhler, W., J. Connor, J. Wang, G. Christodoulou and S. Sundgren. 1974. "Two-Dimensional Finite Element Dispersion Model." Symposium on Modeling Techniques. ASCE San Francisco, California.
- Lerman, A. and H. Taniguchi. 1972. "Strontium-90 - Diffusion Transport in Sediments of the Great Lakes." J. of Geophysical Research 27:474-481.
- Livingston, H. D. and V. T. Bowen. 1976. Contrasts Between Marine and Freshwater Biological Interactions of Plutonium and Americium. U.S. Energy Research and Development Administration, Health and Safety Laboratory Environmental Quarterly, HASL-315.
- Livingston, H. D. and V. T. Bowen. 1976. "Americium in the Marine Environment Relationships to Plutonium." Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms. Morton and Miller Eds., Ann Arbor Science.
- Longley, H. and W. L. Templeton. 1965. "Marine Environmental Monitoring in The Vicinity of Windscale." In B.C. Godbold and J. K. Jones (eds). Radiological Monitoring of the Environment, Pergamon Press, Oxford, pp. 219-247.
- Mauchline, J. 1963. The Biographical and Geographical Distribution in the Irish Sea of Radioactive Effluent from Windscale Works, 1959 to 1960. UKAEA Report AHSB (RP) R 27.

- Mitchell, N. T. 1969. Radioactivity in Surface and Coastal Waters of the British Isles, 1968. Ministry of Agriculture, Fisheries and Food, Fisheries Radiobiological Laboratory, Technical Report FRL5, Lowestoft, Suffolk.
- Mitchell, N. T. 1971a. Radioactivity in Surface and Coastal Waters of the British Isles, 1969. Ministry of Agriculture, Fisheries and Food, Fisheries Radiobiological Laboratory, Technical Report FRL7, Lowestoft, Suffolk.
- Mitchell, N. T. 1971b. Radioactivity in Surface and Coastal Waters of the British Isles, 1969. Ministry of Agriculture, Fisheries and Food, Fisheries Radiobiological Laboratory, Technical Report FRL8, Lowestoft, Suffolk.
- Mitchell, N. T. 1973. Radioactivity in Surface and Coastal Waters of the British Isles, 1971. Ministry of Agriculture, Fisheries and Food, Fisheries Radiobiological Laboratory, Technical Report FRL9, Lowestoft, Suffolk.
- Mitchell, N. T. 1975. Radioactivity in Surface and Coastal Waters of the British Isles, 1972-1973. Ministry of Agriculture, Fisheries and Food, Fisheries Radiobiological Laboratory, Technical Report FRL10, Lowestoft, Suffolk.
- Mitchell, N. T. 1977a. Radioactivity in Surface and Coastal Waters of the British Isles, 1975. Ministry of Agriculture, Fisheries and Food, Fisheries Radiobiological Laboratory, Technical Report FRL12, Lowestoft, Suffolk.
- Mitchell, N. T. 1977b. Radioactivity in Surface and Coastal Waters of the British Isles, 1976. Part I: The Irish Sea and its Environs. Ministry of Agriculture, Fisheries and Food, Fisheries Radiobiological Laboratory, Technical Report FRL11, Lowestoft, Suffolk.
- Murthy, C. R., G. Kullenberg, H. Westerberg, and K. C. Miner. 1974. "Large-Scale Diffusion Studies." IFYGL Project 89 mm, Paper No. 14, Canada Centre for Inland Waters.
- Nevissi, A. and W. R. Schell. 1974. Polonium-210 and Plutonium-239, 240 in Biological Samples of Bikini and Eniwetok Atoll Waters. Laboratory of Radiation Ecology, University of Washington, Seattle, WA.
- Nevissi, A. and W. R. Schell. 1975. "Efficiency of a Large Volume Water Sampler for Some Radionuclides in Salt and Fresh Water." Proc. 4th Nat. Symp. on Radiation Ecology. Oregon State University, Corvallis, OR.
- Nevissi, A. and W. R. Schell. 1975a. "Distribution of Plutonium and Americium in Bikini Atoll Lagoon." Health Physics. 28:539-547.
- Noshkin, V. E. 1972. Ecological Aspects of Plutonium Dissemination in Aquatic Environments. Health Physics. 22:537-549.

- Noshkin, V. E. and V. T. Bowen. 1973. "Concentrations and Distributions of Long-Lived Fallout Radionuclides in Open Ocean Sediments." Radioactive Contamination of the Marine Environment. IAEA, Vienna, Austria, pp. 671-686.
- Noshkin, V. E., W. L. Robison and F. L. Harrison. 1976. Radiological Dose to Man Through the Marine Pathway from Reactor Operations at Humboldt Bay, California. UCRL-52160. Lawrence Livermore Laboratory, University of California, Livermore, CA.
- Onishi, Y. and R. M. Ecker. 1977. "Mathematical Simulation of Transport of Kepone and Kepone-Laden Sediments in the James River Estuary." Proceedings of the Conference, Kepone Seminar II. September 21-22, 1977. Easton, MD.
- Onishi, Y., P. A. Johanson, R. G. Baca, and E. L. Hilty. 1976. Studies of Columbia River Water Quality -- Development of Mathematical Models for Sediment and Radionuclide Transport Analysis. BNL-B-452. Pacific Northwest Laboratory, Richland, WA. Prepared for U.S. Energy Research and Development Administration.
- Onishi, Y. and S. E. Wise. 1978a. "Mathematical Modeling of Sediment and Pesticide Transport in the James River Estuary." Proceedings of 26th Annual Hydraulic Division Specialty Conference on Verification of Mathematical and Physical Models in Hydraulic Engineering. College Park, MD. August 9-11, 1978. pp. 308-310.
- Onishi, Y. and S. E. Wise. 1978b. Mathematical Simulation of Transport of Sediment and Kepone in the James River Estuary. PNL-2731. Pacific Northwest Laboratory, Richland, WA.
- Pentreath, R. J., D. F. Jefferies, M. B. Lovett, and D. M. Nelson. 1980. "The Behavior of Transuranic and Other Long-Lived Radionuclides in the Irish Sea and its Relevance to the Deep Sea Disposal of Radioactive Wastes." NEA OECD (Nuclear Energy Agency of the Organization of Economic Coordination and Development) Seminar on Radioecology, (Held in Tokyo, Japan, Oct. 1-5, 1979), NEA, Paris.
- Perkins, E. J. and B. R. H. Williams. 1966. The Biology of the Solway Firth in Relation to the Movement and Accumulation of Radioactive Materials. II. The Distribution of Sediments and Benthos. P. G. Report 587 (CC), United Kingdom Atomic Energy Authority Production Group.
- Preston, A., D. F. Jefferies, and M. T. Mitchell. 1971. "Experience Gained from the Controlled Introduction of Liquid Radioactive Waste to Coastal Waters." Nuclear Techniques in Environmental Pollution. International Atomic Energy Agency, Vienna, pp. 629-643.
- Robins, J. A. and D. N. Edgington. 1975. "Determination of Recent Sedimentation Rates in Lake Michigan Using Pb-210 or Cs-137." Geochim Cosmochim Acta. 39:285-304.

- Schell, W. R. 1973. Studies of Concentrations of Unreported Long-Lived Radionuclides in Biota and Ocean Sediments at Bikini and Eniwetok Atolls - Annual Progress Report 1972-1973. Laboratory of Radiation Ecology, University of Washington, Seattle, WA.
- Schell, W. R. 1974. Concentrations and Physical-Chemical States of Radionuclides in Bikini Atoll Lagoon Water. Laboratory of Radiation Ecology, University of Washington, Seattle, WA.
- Schell, W. R. 1976. "Biogeochemistry of Transuranics," Bikini-Annual Progress Report (25) Feb. 1970, (26) Feb. 1976. Laboratory of Radiation Ecology, University of Washington, Seattle, WA.
- Schell, W. R. 1977. "Concentration, Physico-Chemical States and Mean Residence times of ^{210}Pb and ^{210}Po in Marine and Estuarine Waters." Geochimica et Geophysica Acta. 41:1019-1031.
- Schubel, J. R. 1975. "Distribution and Transportation of Suspended Sediment," Effects of Energy Related Activities on the Atlantic Continental Shelf. Bernard Manowitz (ed.). Brookhaven National Laboratory, Upton, NY.
- Silker, W. B. 1972. Horizontal and Vertical Distributions of Radionuclides in the North Pacific Ocean. Battelle, Pacific Northwest Laboratories, Richland, WA.
- Simons, T. J. 1973. Development of Three-Dimensional Numerical Models of the Great Lakes. Scientific Series No. 12. Inland Water Directorate, Canada Centre for Inland Waters, Burlington, Ontario.
- Simons, T. J. 1971. "Development of Numerical Models of Lake Ontario." Proc. 14th Conf. Great Lakes Res., pp. 654-669.
- Simons, T. J. 1972. "Development of Numerical Models of Lake Ontario, Part 2." Proc. 15th Conf. Great Lakes Res., pp. 655-672.
- Spraggs, L. D. 1974. Numerical Simulation of Dredged Material Dispersion - San Pablo Bay, San Francisco, Vol. I, Model Development. Report EGU-2774. U.S. Corps of Engineers, San Francisco, CA.
- Templeton, W. L. and A. Preston. 1966. "Transport and Distribution of Radioactive Effluents in Coastal and Estuarine Waters of the United Kingdom." Disposal of Radioactive Wastes into Seas, Oceans, and Surface Waters. International Atomic Energy Agency, Vienna, pp. 267-289.
- U.S. Nuclear Regulatory Commission. 1976. Regulatory Guide 1.113. Estimating Aquatic Dispersion of Effluents from Accidental and Routine Reactor Releases for the Purpose of Implementing Appendix I.

U.S. Nuclear Regulatory Commission. 1978a. Liquid Pathway Generic Study. Impacts of Accidental Radioactivity Releases to the Hydrosphere from Floating and Land-Based Nuclear Power Plants. NUREG-0440.*

U.S. Nuclear Regulatory Commission. 1978b. Revised Draft Environmental Statement Related to the Proposed Manufacture of Floating Nuclear Power Plants. NUREG-0127 (Revision 1).**

Walgren, M. A. and D. M. Nelson. 1976. Residence Times for ^{239}Pu and ^{137}Cs in Lake Michigan Water. Argonne National Laboratory Radiological and Environmental Research Division Annual Report, Part III, Ecology, January-December 1973, ANL-8060, pp. 85-92.

*Available for purchase from the National Technical Information Service, Springfield, VA 22161.

**Available free upon written request to the Division of Technical Information and Document Control, U.S. Nuclear Regulatory Commission, Washington, DC 20555.

7. RADIONUCLIDE TRANSPORT IN LAKES AND RESERVOIRS

This chapter discusses models for lakes and reservoirs that can be used to simulate the migration of contaminants. The mechanisms which result in transport of a contaminant are much different from the mechanisms in rivers or estuaries. In lakes and reservoir systems, biotic interactions become more important and physical movement of the water tends to be less important than for other types of water bodies. The various types of models discussed in this chapter include models for radionuclide transport, water quality, and thermal plume dispersion.

PHYSICAL MECHANISMS OF RADIONUCLIDE TRANSPORT IN LAKES AND RESERVOIRS

Because of the slower flow in relatively deep confined areas, unique processes to lakes and reservoirs are responsible for the distribution and movement of the radionuclides in these impoundments. These major processes can be broken down into three categories: 1) flow conditions, 2) sediment interaction, and 3) biotic interaction. The relative importance of these three mechanisms depends on the nature of lakes and reservoirs, inflow characteristics, and the chemical characteristics of the radionuclide.

In lakes with large inflows and outflows, the flow will be dominated by these currents. This is commonly seen in lakes which are expansions of river systems. In most lakes, however, the principal physical processes causing movement of the water and associated substances are: 1) wind-induced currents, 2) turbulence and stratification and 3) seiches. Wind-induced currents result from the piling up of water on the leeward side of the lake. Equalization of head results in return flow currents. Since the magnitude and direction of the current is dependent on wind, they are time dependent. Seiches or periodic currents may result from continuous or persistent wind conditions (Hutchinson 1957). Both of these currents may result in movement of bottom material from shore areas to other shore areas or deeper sections.

Turbulence and stratification are major mechanisms for preventing or causing transport of radionuclides, nutrients, and other chemicals in lake ecosystems (Hutchinson 1957). Thermocline can effectively trap dissolved

radionuclides in certain parts of the lake. For example, Hasler and Likens (1963) reported that after introduction of radionuclides to a stratified lake, horizontal transport of the radionuclides occurred but little or no vertical transport was observed. Other research also reported by Hasler and Likens (1963) indicated that there is very little vertical movement of radionuclides, especially through the thermocline. If the lake is stratified the radionuclide will remain in the layer it enters. In most lakes, however, some mixing occurs each fall and spring due to seasonal overturns in lakes resulting in more vertically uniform distributions of dissolved radionuclides.

For many radionuclides which become readily adsorbed to sediment, sedimentation from river inflows and sediment-water interaction become important processes in determining the radionuclide distribution in a lake or reservoir. Once the radionuclide becomes attached to the sediment its fate will be essentially the same as that of the sediment (Lomenick and Gardner, 1965; Lomenick and Tamara, 1965; Lerman and Taniguchi, 1971). Because of the decrease in velocity of the river inflow when entering lakes and reservoirs, extensive sedimentation occurs. Thus, the radionuclide can be trapped in the bottom sediment. Because of radionuclide desorption from the bed sediment, it is possible to have a higher radionuclide concentration in the hypolimnion (bottom layer). This is mixed through the water column at spring and fall turnover. Hence contaminated bed sediment is an important and continuous source of radionuclides to the water and organisms. Lerman and Lietzke (1975) and Hakonson and Whicker (1975) have discussed the importance of this mechanism in lakes. Hakonson and Whicker (1975) estimated that 82% of the ^{133}Cs added to Twin Lakes in Colorado was attached to the sediment. The importance of sediment as a sink for nutrients and as a continuous release source for these same nutrients is demonstrated in Westerdahl (1973).

The most complex component of the radionuclide distribution in lakes and reservoirs is that due to biotic interaction. As with the sediment-radionuclide interaction, the importance of this mechanism is related to the chemical characteristics of the radionuclide, especially its biochemical affinity. Most studies on biological uptake of radionuclides have looked only

at the concentration of radionuclides in organisms and bioaccumulation factors but have not assessed the relative importance of radionuclide uptake by aquatic biota to the overall migration of radionuclides in impoundments. Some measured concentrations and bioaccumulation factors suggest that the biotic compartments can store large quantities of some radionuclides (Emery and Klopfer 1974, 1976; Emery and Garland 1974; Emery and McShane 1978; Patzer 1976). This is especially true of photoplankton taking up certain radionuclides such as ^{137}Cs and ^{90}Sr which tend to act biochemically like potassium and calcium, respectively (Kahn et al. 1971 and Pendleton and Hanson, 1958).

Hakonson and Wicker (1975) measured the distribution of ^{133}Cs among the various lake system components. Cesium-133 is readily adsorbed to sediment and is biologically active. Sediment accounted for 82% of the radionuclide, water for 3%, and 15% was accounted for in the biotic components. The seston accounted for most of the biotic uptake. Similar results were observed by Emery and Klopfer (1974, 1976), Emery and Garland (1974), and Emery and McShane (1978) for transuranics in a pond ecosystem.

The biota can also act as vectors to transport radionuclides horizontally or vertically through the stratified lakes. Although ^{131}I has very little biological affinity, Hasler and Likens (1963) reported significant lateral movement of ^{131}I in the bodies of aquatic insect larva. This movement would be even more significant for biologically active radionuclides. Hutchinson and Bowen (1947) also observed the downward movement of radionuclides in sinking plankton through the thermocline into the hypolimnion. Vertical migration of zooplankton was also suggested as a possible means to distribute radionuclides vertically through the thermocline (McCarter et al. 1952). Although these data imply the possible importance of biotic uptake, presently there are not enough data to quantify its impact on the radionuclide migration in the impoundments.

Data sources for distribution of radionuclides in lakes and reservoirs are given in Table 7.1.

TABLE 7.1. Lakes and Reservoirs Data

References	Lake	Type of Radionuclide Data
Lomenick and Gardiner (1965)	White Oak Lake	Sediment-bound ^{106}Ru , ^{137}Cs , ^{60}Co , ^{90}Y , ^{90}Sr
Lomenick and Tamura (1965)	White Oak Lake	Sediment-bound ^{137}Cs , ^{106}Ru , ^{60}Co
Lerman and Lietzke (1975)	Lake Erie Lake Ontario	Dissolved and sediment bound ^{137}Cs , ^{90}Sr
Lerman and Taniguchi (1971)	Lake Superior	Dissolved and sediment-bound radionuclides
	Lake Michigan	Dissolved radionuclides
	Lake Huron	Dissolved radionuclides
	Lake Ontario	Dissolved and sediment-bound radionuclides
Kahn et al. (1971)	Sherman Reservoir	Dissolved, sediment-bound and organism-bound forms ^{90}Sr , ^{137}Cs
Hakanson and Whicker (1975)	Twin Lake in Colorado Rockies	Dissolved and sediment-bound ^{137}Cs
Hasler and Likens (1963)	Stewart's Dark Lake, Tub Lake Wisconsin	Dissolved and organism-bound ^{131}I
Pendleton and Hanson (1958)	Pond on Hanford Reservation	Dissolved, sediment-bound, and organism-bound ^{137}Cs
Hutchinson and Bowen (1974)	Linsley Pond	Dissolved and organism-bound ^{32}P
McCarter et al. (1952)	Small Lake Nova Scotia	Dissolved and sediment-bound ^{32}P
Volchok	Great Miami River, North Pond, South Pond, Miami-Erie Canal	Dissolved and sediment-bound ^{238}Pu
Volchok (1975)	Great Miami River, North Pond, South Pond, Miami-Erie Canal	Dissolved and sediment-bound ^{241}Am , ^3H
Robertson et al. (1973)	Lake Mallula in the Columbia River	Dissolved and sediment-bound forms of ^{144}Ce , ^{137}Cs , ^{60}Co , ^{152}Eu , ^{155}Eu , ^{55}Fe , ^{54}Mn , ^{40}Sc , ^{126}Sb , ^{65}Zn , ^{239}Pu
Haushild et al. (1966)	Lake Mallula in the Columbia	Dissolved and sediment-bound forms of ^{144}Ce , ^{54}Cr , $^{103}\text{Ru-Rh}$, ^{46}Sc , ^{65}Zn , $^{95}\text{Zr-Mb}$
Emery and McShane (1978)	200 U-pond Z-19 Ditch, Hanford Reservation	Dissolved, sediment-bound and organism-bound forms of ^{241}Am , ^{239}Pu , ^{238}Pu , ^{240}Pu , ^{60}Co , ^{59}Fe , ^{51}Cr , ^{54}Mn , etc., ^{65}Zn , ^{90}Sr , $^{95}\text{Zr-Mb}$, ^{106}Ru , ^{134}Cs , ^{137}Cs , ^{140}Bg

MATHEMATICAL MODELS FOR LAKES AND RESERVOIRS

The categories of lake models discussed here are radionuclide models, water quality models and thermal plume models. The water quality models were classified according to their governing equations, as described in Chapter 3. There are no sediment transport computer models specifically developed for impoundments.

Radionuclide Models for Lakes and Reservoirs

The first two models discussed below are very simple, compartmentalized models which do not include any physical transport mechanisms that can influence the radionuclide distribution. These models would be most applicable in systems where currents and stratification do not exist. The other three models are more applicable to reservoirs or lakes that are part of a river system.

Vanderploeg, Booth and Clark (1976)

This model is a lake ecological model designed to simulate radionuclide transfer from the dissolved radionuclide concentration in a stagnant, non-stratified, shallow, eutrophic lake to fish through the food chains. Interactions among various constituents are shown in Figure 7.1. The interactions of the dissolved radionuclides with the bottom sediments and interstitial water are also included. A linear system-analysis model was developed to simulate time-dependent dynamics of specific activity and radionuclide concentration. However, the model does not solve spatial variations. Similar to the model developed by Booth (1975), all governing equations are expressed by the first order reaction form; i.e., the rate of change of the constituent concentration is directly proportional to the concentration of the constituent. The model equations are solved by an analytical method using matrix manipulations (Clark et al. 1974).

The model was applied to White Oak Lake near Oak Ridge National Laboratory, Oak Ridge, Tennessee. The time history of ^{137}Cs concentration in the water was used as an input condition to solve other constituent concentrations, and reasonably good agreement was attained. The authors concluded from this

FIGURE 7.1. Compartments of the Lake Ecological Model of Vanderploeg, Booth and Clark (1976)

study that the bottom sediment was found not to be a major source of ^{137}Cs to be taken up by the biota because reasonable agreement between the computed results and field data was obtained without taking into account the interactions of bottom sediment and biota. However, the good agreement does not necessarily imply that all model assumptions and model structure are correct. Full verification of this statement can only be made if the model results with all organism-sediment reactions included are found to be nearly identical to

results without their interactions. Since this model is a compartment ecosystem model and no dynamic movements of water and sediment are considered, the model applicability is limited to lakes with no measurable inflows and outflows.

Booth (1975)

This model is also a compartment model which was developed to calculate the concentration of radionuclides in water, bottom sediment and interstitial fluid. Interactions among the sorbents are also accounted for. Bottom sediments were divided into two parts, one which interacts with overlying water and interstitial water, and the other which is an ultimate sink adsorbing radionuclides from interstitial water. The governing equations of these four compartments are the first order reaction forms without spatial variations. The concentration of radionuclides attached to the sediment is then calculated from a known K_d value and the concentration of known dissolved radionuclides. Radionuclide decay is also contained implicitly in the equation. The model does not include velocity components and suspended sediment in the water. However, the rate of bed elevation change can be prescribed in the model to account for sedimentation rate in a lake. Hence, the best application of this model would be for large lakes and reservoirs where retention time is large. No verification or application of the model was presented although the results of a sensitivity analysis were given.

Onishi et al. (1976) Onishi (1977a, b)

The unsteady, two-dimensional (longitudinal and vertical), sediment-contaminant transport model, SERATRA, discussed in Chapter 4 is also applicable to impoundments. As discussed in Chapter 4, this model was applied to two rivers, the Columbia and Clinch Rivers, for river reaches including fast moving free-flow regions and slow moving regions (reservoirs) behind dams.

Eraslan et al. (1977)

As stated in Chapter 5, RADTWO is an unsteady, two-dimensional model for dissolved radionuclide transport in lakes, estuaries, and coastal regions. The model is one component of the UTA program being developed at Oak Ridge National Laboratory (Eraslan et al. 1977).

Code11 (NRC Mixed Tank Lake Model) (USNRC 1978)

Code11 at NRC developed a mixed tank model with sedimentation effects included for lakes and reservoirs (USNRC 1978). As shown in Figure 7.2, this unsteady model divides a lake into water and bed sediment compartments through which radionuclides are exchanged by direct adsorption/desorption mechanisms and sediment deposition. The following model assumptions were made:

- Water inflow and outflow are constant but can be different.
- Sedimentation rate is constant.
- Sediments are not introduced to the lake nor removed from the lake.
- The sediment layer thickness remains constant by assuming that if the sedimentation occurs, the portion of the original bed layer becomes inactive and is eliminated from the analysis.
- Dissolved and particulate radionuclides are in equilibrium conditions.
- Both dissolved and particulate radionuclides decay.

FIGURE 7.2. NRC Mixed Tank Lake Model

Based on these assumptions, Codell derived analytical solutions of dissolved radionuclide concentration in the water compartment and of particulate radionuclide concentration in the bed sediment compartment for an instantaneous radionuclide release. His instantaneous solutions may be generalized using the convolution integral as shown in Figure 4.30. Detailed model derivation is described in USNRC (1978).

Water Quality Models in Lakes

The water quality models for lakes are of three basic types. The first type is based on the convection-diffusion equation with decay and source/sink terms (Water Quality Models of Type I). This is the most general type of a model and would be most applicable when inflow and/or outflow conditions dominated the hydrodynamics as in many reservoirs. The second type includes the effects of transfer of constituents between layers in stratified lakes as the result of diffusion or sinking of organisms but does not include the advection term (Water Quality Models of Type V). This type of model can be used for lakes where water movement is minimal. The third type of model contains no hydrodynamic components (Water Quality Models of Type IV) and can be used mostly for long-term approximations to the amount of constituent in the lake system.

Water Quality Models of Type I

Baca (1977a,b). The AQUA model belongs in the Water Quality Model Type I category and is an unsteady, two-dimensional, convection-diffusion equation with decay and sink/source terms. It is a detailed limnological model based on the dynamics of heat and mass transport and chemical and biological transformations.

The detailed limnetic model is actually composed of two parts: 1) a hydrothermal model, and 2) a water quality model. The hydrothermal model uses five major processes to describe the thermal cycle and its effect on lake stratification and mixing to solve velocity and temperature distributions. These processes are: 1) internal heat transport, 2) advection and wind-induced mixing, 3) atmospheric heat exchange, 4) formation and melting of ice

cover, and 5) stratified fluid flow. The outputs from this model are used to describe the flow and temperature fields for the water quality model. This water quality model takes into account the chemical and biochemical transformations as well as the trophic interactions of phytoplankton and zooplankton to predict the values of: phytoplankton biomass, zooplankton biomass, nitrogen, phosphorus, dissolved oxygen, biochemical oxygen demand, temperature, suspended sediment and total dissolved solids. Model formulations are very similar to those of the Lake Ontario model (Simons 1971-1973) described in Chapter 6. The system of equations is solved by a finite element technique with the Galerkin weighted residual method. This model was also calibrated and verified with data from Mt. Bold Reservoir (Gasperino et al. 1977; Baca et al. 1977a,b; Brandstetter 1977), and Long Lake Reservoir (Gasperino and Soltero 1977).

Hydroscience - Near-Field Steady Advection-Diffusion Equation (1968).

The first of the four Hydroscience models described here is a steady, two-dimensional, advection-diffusion equation with a decay term. This model also simulates water quality in the vicinity of streams or outfalls entering a lake. In this case, a proper evaluation is made of the phenomena of advection, decay and dispersion to define profiles of substances influencing water quality. The governing equation consists of a longitudinal advection term, a vertical diffusion term and a decay term, and is solved analytically with constant velocity, diffusion coefficient and decay rate. This model is applicable to lakes where flow moves in the longitudinal direction with a uniform velocity.

Water Quality Models of Type V

Hydroscience - Stratified Lake Model (1968). An unsteady, one-dimensional, water quality model was developed by Hydroscience (1968) to solve the vertical distribution of conservative substances (primarily heat) in stratified lakes.

As a short-term model, a lake can be viewed as thermally stratified. It is assumed that advection and source terms are not important and the governing equation contains only two terms, unsteady and diffusion terms. By assuming that initial concentration (or water temperature) is zero and that the concentration (or water temperature) is expressed by a cosine curve with time at the

water surface, the governing equation was analytically solved to obtain the diffusion of the substance (or transfer of heat) in the vertical water column. The model has not yet been applied to an actual field case.

Hydroscience - Near-Field Steady Diffusion Model (1968). The near-field diffusion of nonconservative substances is solved by this steady, two-dimensional, diffusion model with a decay term. This model was developed to consider water quality in the vicinity of streams or sewage outfalls entering a lake. It assumes that the concentration of bacteria at any point beyond the initial mixing area is a function of turbulent diffusion and natural die-off of the bacteria. The governing equation was solved analytically in a polar coordinate system, assuming that two diffusion coefficients and the decay rate are constant. However, because of the lack of a convection term, the model applicability is rather limited.

Water Quality Models of Type IV

Baca et al. (1974). The model developed by Baca et al. (1974) is a complete mixed tank model. The model solves a long-term lake eutrophication process based on a phosphorus balance by simulating inorganic, particulate and total phosphorus, chlorophyll a, and Secchi disk depth. In order to describe effects of a stratified and a well-mixed period on the phosphorus cycle, the model solves the lake eutrophication process for two separate upper and lower layers.

The most important constituents of the model are the source/sink terms relating the various biochemical effects on phosphorus cycling. The analysis and formulation of the model is thus based on four basic limnetic processes:

1. nutrient loading and effective flushing
2. nutrient uptake and regeneration
3. sediment-water interactions
4. formation and migration of the thermocline.

For convenience and expedience, these physical, chemical and biological processes are "lumped" into simple mathematical characterizations expressed by decay and sink/source terms. The mathematical formulation of the eutrophication model consists of two sets of linear ordinary differential equations

which were solved by the fourth-order Runge-Kutta technique. The model was calibrated by using one year of field data and verified with the following year's data from Mt. Bold Reservoir near Adelaide, Australia (Gasperino et al. 1977; Baca et al. 1977a,b,; Brandstetter et al. 1977) and Lake Washington, Washington (Baca and Arnett, 1976).

Anderson, Dracup, Fogarty, and Willis (1976). This unsteady, water quality model can only be applied to deep lakes where convection and dispersion may not be important in determining water quality. The model equations are the first order reaction forms consisting of only decay and source/sink terms without any spatial dimensions considered. The source/sink terms include production of the nonconservative water quality parameters. The model simulates many water quality parameters including dissolved oxygen, biochemical oxygen demand, PO_4 , NH_4 , organic nitrogen, dissolved solids, NO_2 , NO_3 , coliform bacteria and chlorophyll a. Layers representing the epilimnion, thermocline and hypolimnion are modeled separately, except: 1) during spring turnover the three layers are mixed and the constituents are redistributed, and 2) during the summer, organic nitrogen and some phosphorus are transferred from one layer to another through settling of organisms. No information is given on how the model equations are solved although most likely these equations were solved by some computer integration method. The model was applied to Deer Creek Reservoir in Utah to simulate distribution of DO, BOD, organic nitrogen and NO_3 during an 8-month period. However, the field data were not sufficient to allow verification of the model.

Hydroscience - Long-Term Lake Model (1968). The last hydroscience model is a long-term, complete mixed tank, water quality model; thus it is an unsteady model which consists of three terms: unsteady, decay, and sink/source terms.

The long-term lake model predicts the changes of lake water quality over a geological time scale. The water body is considered completely mixed due to the year-to-year spring turnover. The governing equations express the mass balance of nonconservative substances; the change in mass of a constituent over a time period is equal to the sum of: 1) the amount entering minus the

amount leaving and 2) decay and sink/source (chemical decay, settling of materials, reintroduction of material from lake bottom to water, etc.). In its formulation, the difference between the amount entering and leaving is expressed as a sink/source term. Lakes can be treated as one water body, or two stratified layers through which constituents may interact. The concentrations of these substances were obtained by solving the governing equations analytically.

Thermal Plume Models in Lakes

One important class of water quality models is the thermal plume models that predict the movement of heated water entering lakes. These models are different from those described above because they include the heated water's buoyancy effects which influence the movement of flow. It is possible to adapt these models to radionuclide transport, but the physical mechanisms in these two types of transport are quite different. Care must be used when making application of a thermal plume model to radionuclide modeling. Dissolved radionuclide transport may be simulated by thermal plume models by assuming the radionuclide plume to be a nonbuoyant plume. Particulate radionuclides may be treated as a negative buoyant plume. However, it is not feasible to use a thermal plume model to solve the migration of both dissolved and particulate radionuclides with their interaction. The two models discussed below are representative of the two basic types of thermal plume models: 1) "integration" model and 2) full hydrothermal model.

Stolzenbach and Harleman (1971, 1973); Stolzenbach et al. (1972); Stolzenbach (1972, 1975). The derivation of this integration model starts with the three-dimensional, steady hydrodynamic, and advection-diffusion equations to solve the temperature distributions of heated water discharged into the surface of a lake. The basic methodology was to reduce these equations to a first order, one-dimensional, ordinary differential equation which can then be solved numerically by the fourth order Runge-Kutta method. The heated water is discharged from a rectangular open channel at the surface of an infinite water body which may or may not have currents of its own. The following assumptions were made to allow the equations to be reduced to first

order ordinary differential equations: 1) steady-state flow, 2) hydrostatic pressure, 3) the Boussinesq approximation of the water density gradient, 4) the boundary layer flow assumptions, 5) the heated water to be treated as a jet, and 6) the velocity and temperature distributions around the centerline of the plume to be expressed by similarity functions. Thus, the first order, one-dimensional, ordinary differential equation derived from the three-dimensional equations with these assumptions expresses the change in temperature along the centerline of the plume only. The temperature along the centerline is then used to estimate temperatures along two other coordinates by using a pre-assigned similarity function (e.g., normal distribution) to obtain three-dimensional distributions of water temperature.

Independent verifications of this model and other thermal plume models were conducted by Dunn et al. (1975) at Argonne National Laboratory. They reported that this model did not predict the temperature distribution very well except in the very near-field region. Particularly the computed plume width reveals poor agreement with field data. In this verification study, the computed results were compared with field data of dispersion of heated plume discharged from power plants into the Great Lakes. Dunn et al. (1975) also reported that the model cannot predict the temperature distribution accurately if ambient water velocities are greater than one-tenth of the initial heated jet velocity.

Trent (1975). In contrast to the abovementioned model of Stolzenbach et al. (1972), the second modeling approach adopted by Trent (1975) uses few assumptions. The governing equations of the model, VECTRA, are the coupled steady/unsteady, two-dimensional equations for momentum, continuity, state, and advection-diffusion with a source term. These equations were solved by converting the Navier-Stokes equations and equations of continuity into stream function and vorticity equations which no longer contain a pressure term. These equations, together with the state and advection-diffusion equations, were then solved by an implicit finite difference scheme.

The model was applied to San Diego Bay to solve steady, two-dimensional velocity field, sediment concentration, and water temperature distributions

(Onishi 1976). It was also applied to the cooling tower plume dispersion process. Computer results and measured data obtained by laboratory physical modeling provide good agreement (Onishi and Trent 1976). This model is applicable to oceans, rivers, lakes, and reservoirs but not applicable to estuaries because it does not have a tidal motion mechanism of hydrodynamics.

REFERENCES FOR CHAPTER 7

- Anderson, D. R., J. A. Dracup, T. J. Fogarty and R. Willis. 1976. "Water Quality Modeling of Deep Reservoirs." J. Water Poll. Control Ed. 48:134-146.
- Baca, R. G. and R. C. Arnett. 1976. A Limnological Model for Eutrophic Lakes and Impoundments. Prepared for Office of Research and Development, U.S. EPA, Washington, DC, by Battelle, Pacific Northwest Laboratories, Richland, WA.
- Baca, R. G., M. W. Lorenzen, R. D. Mudd, and L. V. Kimmel. 1974. A Generalized Water Quality Model for Eutrophic Lakes and Reservoirs. Prepared for Office of Research and Monitoring, U.S. EPA, Washington, DC, by Battelle, Pacific Northwest Laboratories, Richland, WA.
- Baca, R. G., A. F. Gasperino, A. Brandstetter and A. S. Myhres. 1977a. Model Formulation, Calibration and Verification Part 2 of Water Quality Models for Municipal Water Supply Reservoirs. Prepared for the Engineering and Water Supply Dept. Adelaide, South Australia by Battelle, Pacific Northwest Laboratories, Richland, WA.
- Baca, R. G., A. S. Myhres, A. Brandstetter and A. F. Gasperino. 1977b. Users Manual Part 3 of Water Quality Models for Municipal Water Supply Reservoirs. Prepared for the Engineering and Water Supply Dept. Adelaide, South Australia by Battelle, Pacific Northwest Laboratories, Richland, WA.
- Booth, R. S. 1975. A System Analysis Model for Calculating Radionuclide Transport Between Receiving Waters and Bottom Sediment. ORNL-TM-4751, Stoudsberg, PA.
- Brandstetter, A., R. G. Baca, A. F. Gasperino and A. S. Myhres. 1977. Summary Part 1 of Water Quality Models for Municipal Water Supply Reservoirs. Prepared for the Engineering and Water Supply Dept. Adelaide, South Australia by Battelle, Pacific Northwest Laboratories, Richland, WA.
- Clark, F. H., R. S. Booth and H. A. Vanderploeg. 1974. User's Manual for MODSOV, a Terminal Operated Program Solving the Linear Matrix Equation $x = Ax + k$. ORNL-TM-4404, Oak Ridge National Laboratory, Oak Ridge, TN.

- Dunn, W. E., A. J. Policastro, and R. A. Paddock. 1975. Surface Thermal Plumes Evaluations. Argonne National Laboratory, Argonne, IL.
- Emery, R. M. and D. C. Klopfer. 1974. The Ecological Behavior of Plutonium and Americium in a Freshwater Ecosystem: Phase I Limnological Characterization and Isotope Distribution. BNML-1867. Pacific Northwest Laboratory, Richland, WA.
- Emery, R. M. and D. C. Klopfer. 1976. "The Distribution of Transuranic Elements in A freshwater Pond Ecosystem." Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms. M. W. Hiltner and J. N. Stannard (eds). Ann Arbor Science, Publishers Inc., Ann Arbor, MI.
- Emery, R. M. and T. R. Garland. 1974. The Ecological Behavior of Plutonium and Americium in a Freshwater Ecosystem: Phase II Implications of Differences in Transuranic Isotopic Ratios. BNML-1879, Pacific Northwest Laboratory, Richland, WA.
- Emery, R. M. and M. C. McShane. 1978. Radioecology of Nuclear Waste Ponds and Streams on the Hanford Site. PNL-2499, Pacific Northwest Laboratory, Richland, WA.
- Eraslan, A. H. et al. 1977. Development of a Unified Transport Approach for the Assessment of Power-Plant Impact. ORNL-MUREG-TM-89. Oak Ridge National Laboratory, Oak Ridge, TN.
- Gasperino, A. F., A. Brandstetter, A. S. Myhres and R. G. Baca. 1977. Mt. Bold Reservoir Data Acquisition and Evaluation Part 4 of Water Quality Models for Municipal Water Supply Reservoirs. Prepared for the Engineering and Water Supply Dept. Adelaide, South Australia, by Battelle, Pacific Northwest Laboratories, Richland, WA.
- Gasperino, A. F. and R. A. Soltero. 1977. Phosphorus Reduction and its Effect on the Recovery of Long Lake Reservoir. Prepared for Washington State Dept. of Ecology. Battelle, Pacific Northwest Laboratories, Richland, WA.
- Hakanson, T. E. and F. W. Whicker. 1975. "Cesium Kinetics in a Montane Lake Ecosystem." Health Physics. 28:699-706.
- Hasler, A. D. and G. E. Likens. 1963. "Biological and Physical Transport of Radionuclides in Stratified Lakes." Radioecology. pp. 463-470. U. Schultz and A. W. Klement (ed.).
- Hutchinson, G. E. 1957. A Treatise on Limnology. Vol. 1. of Geology, Physics and Chemistry. John Wiley and Sons, New York. 1016 pp.
- Hutchinson, G. E. and V. T. Bowen. 1947. "A Direct Demonstration of the Phosphorus Cycle in a Small Lake". Proc. National Academy of Science (U.S.). 33(5):148-153.

Hydrosciences, Inc. 1968. Mathematical Models for Water Quality for the Hudson-Champlain and Metropolitan Coastal Water Pollution Coastal Project. PB-216-922.

Kahn, B. et al. 1971. Radiological Surveillance Studies at a Pressurized Water Nuclear Power Reactor. EPA Report No. RD-71-1.

Lerman, A. and T. A. Lietzke. 1975. "Uptake and Migration of Tracers in Lake Sediments." Limnol and Oceanography. 20(4):497-510.

Lerman, A. and H. Taniguichi. 1971. "Strontium-90 and Cesium-137 in Water and Deep Sediments of the Great Lakes." Radionuclides in Ecosystems. pp. 406-464. D. J. Nelson (ed.).

Lomenick, T. F. and D. A. Gardiner. 1965. "The Occurrence and Retention of Radionuclides in the Sediments of White Oak Lake." Health Physics. 11:567-577.

Lomenick, T. F. and T. Tamura. 1965. "Naturally Occurring Fixation of Cesium-137 on Sediments of Locustrine Origin." Soil Science of America Proceedings. 29(4):383-387.

McCarter, J. A., F. R. Hayes, L. H. Jodray and M. L. Cameron. 1952. "Movement of Materials in the Hypolimnion of a Lake as Studied by the Addition of Radioactive Phosphorus." Can. J. Zool. 30:128-133.

Onishi, Y. 1976. Assessment of the Impact of the Proposed Wildlife Reserve Island in South San Diego Bay on the South Bay Power Plant. Prepared for San Diego Gas and Electric Company, San Diego, CA by Battelle, Pacific Northwest Laboratories, Richland, WA.

Onishi, Y., P. A. Johanson, R. G. Baca and E. L. Hilty. 1976. Studies of Columbia River Water Quality -- Development of Mathematical Models for Sediment and Radionuclide Transport Analysis. BNWL-B-452. Pacific Northwest Laboratory, Richland, WA.

Onishi, Y. and D. S. Trent. 1976. Mathematical and Experimental Investigations on Dispersion and Recirculation of Plumes from Dry Cooling Towers at Wyodak Power Plant in Wyoming. BNWL-1982, Pacific Northwest Laboratory, Richland, WA.

Onishi, Y. 1977a. Finite Element Models for Sediment and Contaminant Transport in Surface Waters -- Transport of Sediments and Radionuclides in the Clinch River. BNWL-2227. Pacific Northwest Laboratory, Richland, WA.

Onishi, Y. 1977b. Mathematical Simulation of Sediment and Radionuclide Transport in the Columbia River. BNWL-2228. Pacific Northwest Laboratory, Richland, WA.

- Patzer, R. G. 1976. Concentration Factors and Transport Models for Radionuclides in Aquatic Environments - A Literature Review. EPA-600/3-76-054.
- Pendleton, R. C. and W. C. Hanson. 1958. "Adsorption of Cesium-137 by Components of an Aquatic Community". In Proceedings of the Second U.N. International Conference on Peaceful Uses of Atomic Energy. 18:419-433.
- Stolzenbach, K. 1975. "Surface Discharges - Comparison of Alternative Schemes." Engineering Aspects of Heat Disposal from Power Generation. D. R. F. Harleman (ed.). R. M. Parsons Laboratory for Water Resources and Hydrodynamics, Dept. of Civil Eng., MIT, Cambridge, MA.
- Stolzenbach, K. 1972. "Heated Surface Discharges." Engineering Aspects of Heat Disposal from Power Generation. D. R. F. Harleman (ed.). R. M. Parsons Laboratory for Water Resources Hydrodynamics, Dept. of Civil Eng., MIT, Cambridge, MA.
- Stolzenbach, K., E. Adams and D. R. F. Harleman. 1972. A User's Manual for Three-Dimensional Heated Surface-Discharge Computations. Report No. 156, R. M. Parsons Laboratory for Water Resources and Hydrodynamics, Dept. of Civil Eng., MIT, Cambridge, MA.
- Stolzenbach, K. and D. R. F. Harleman. 1971. An Analytical and Experimental Investigation of Surface Discharges of Heated Water. Report No. 135, R. M. Parsons Laboratory for Water Resources and Hydrodynamics, Dept. of Civil Eng., MIT, Cambridge, MA.
- Stolzenbach, K. and D. R. F. Harleman. 1973. "Three-Dimensional Heated Surface Jets." Water Resources Research. 9(1).
- Trent, D. S. 1976. Mathematical Modeling of Transport Processes in Aquatic Systems. BNWL-SA-5374, Pacific Northwest Laboratory, Richland, WA.
- U.S. Nuclear Regulatory Commission. 1978. Liquid Pathway Generic Study. Impact of Accidental Radioactivity Releases to the Hydrosphere from Floating and Land-Based Nuclear Power Plant. NUREG-0440.*
- Vanderploeg, H. A., R. S. Booth and F. H. Clark. 1976. "A Specific Activity and Concentration Model Applied to Cesium-137 Movement in a Eutrophic Lake." Radioecology and Energy Resources. C. E. Cushing, Jr. (ed.) Dowden, Hutchinson & Sons, Inc.
- Westerdahl, H. E. 1973. A Study of Particulate Organic ³²P in a Simulated Sediment Water System. Ph.D. Thesis, University of Oklahoma.

*Available for purchase from the National Technical Information Service, Springfield, VA 22161.

8. RADIONUCLIDE ADSORPTION/DESORPTION

MECHANISMS

Before a fundamental understanding and generalized predictive capability for radionuclide transport in oceans, rivers and lakes can be obtained, the physical and chemical processes which control trace constituent adsorption/desorption must be described. To become quantitative the knowledge of processes must be such that mathematical relationships can be formulated. The mechanisms for which generalized mathematical relationships have been demonstrated are ion exchange, precipitation of pure mineral phases and complex formation.

Ion Exchange

Traditionally, most experimenters who have studied the interaction of soluble trace constituents such as radionuclides have used ion-exchange concepts to express their results. Classically, ion exchange is described as the chemical interaction which occurs when a charged solid matrix attracts oppositely charged solution species close enough to its surface to form electrostatic bonds. Because most geologic materials including soils, sediments and suspended solids have an inherent negative charge on their surface most interaction occurs with cations in solution. A measure of the geologic material's capacity to bind positively charged species is the cation-exchange capacity. Typical geologic materials show a variation of from 0.01 meq/g to 1.3 meq/g of cation-exchange capacity depending upon the mineralogy. There is a definite competition between soluble cations in solution for the exchange sites on the geologic media's surface.

The degree of competition is a measurable quantity and can be expressed mathematically. A simple ion exchange reaction is shown below:

where:

Cs^+ , Na^+ represent the cation in solution

Na-X , Cs-X represent the cation bound to the solid exchanger.

The competition between cesium and sodium can be determined quantitatively using thermodynamic constructs (mass-action)

$$K = \frac{\{Na^+\} \{Cs-X\}}{\{Cs^+\} \{Na-X\}} \quad (8.2)$$

where:

K = ion exchange constant

$\{$ = the activities of the aforementioned species.

The ion-exchange constant K can be determined from various experiments at variable cesium and sodium activities.

The ion-exchange equation for a general binary reaction is readily constructed from Equations (8.1) and (8.2).

$$K_{AB} = \frac{\{B^{+b}\}^a}{\{A^{+a}\}} \frac{\{A-X\}^b}{\{B-X\}^a} \quad (8.4)$$

where:

A, B = cations in solution

a, b = valence of the respective cations

$A-X, B-X$ = cations bound to solid exchanger

K_{A-B} = selectivity constant, ion exchange constant or equilibrium constant for the completion of cation A versus cation B .

Equations (8.3) and (8.4) are general and thus of great value in predicting the reaction of cations in solution with negatively charged solid matrices such as geologic media if the necessary constant and activities are known or can be measured. There are several complications in the direct application of these generalized ion-exchange equations to radionuclide sorption in oceans, estuaries, rivers and lakes.

In these environments there are many cations simultaneously competing for available exchange sites such that the binary exchange equation must be expanded greatly. The solid exchanger also now becomes a mixture of minerals with different affinities for various cations such that a unique value of K is not likely (although a weighted average, K, should be obtainable if the system is completely characterized). Finally, it is presently impossible to predict or measure the activities of solid phase components (i.e., A-X, B-X, etc.) and often difficult to predict or calculate solution species activities.

Several investigators have successfully quantified the adsorption of strontium using ion-exchange thermodynamic constructs. A Burns, Mississippi montmorillonite, with the composition shown in Table 8.1, was used in macroion systems of potassium, calcium and magnesium to obtain Kd values and calculated Kd values in mixed two and three ion systems (Baetsle et al., 1964). The selectivity coefficients given were

$$K_{Sr}^K = 0.096 (Sr_{mont.} + 2K^+ \rightleftharpoons 2K_{mont.} + Sr^{+2}), K_{Sr}^{Mg} = 1.08 (Sr_{mont.} + Mg^{+2} \rightleftharpoons Mg_{mont.} + Sr^{+2}) \text{ and } K_{Sr}^{Ca} = 0.98 (Sr_{mont.} + Ca^{+2} \rightleftharpoons Ca_{mont.} + Sr^{+2}).$$

The isotherms of the binary systems were obtained at several ionic strengths such as 0.1N, 0.01N and 0.001N. Kd values for strontium, for example, in a Ca-Mg system were then obtained by plotting the log of magnesium, calcium or some other macroion concentration versus the Kd to allow extrapolation of the resulting straight line relationship. Thus, the various binary system selectivity coefficients and Kd values determined for each macroion are used to determine a Kd in the binary macroion system.

Mercer (1966, 1967) has conducted similar studies on zeolite ion exchange from multicomponent systems and gave a table comparing his predicted strontium Kd results with those of Baetsle et al. (1964) on the Burns, Mississippi montmorillonite (Table 8.2). Clinoptilolite gave an experimental strontium Kd value of 733 ml/g from a macroion system 0.0104 meq NH_4^+ /ml + 0.0891 meq Na^+ /ml, and a strontium Kd value of 160 from a macrosystem of 0.0170 meq Na^+ /ml + 0.0830 meq Ca^{+2} /ml.

TABLE 8.1. Composition of Burns, Mississippi Montmorillonite.
Capacity was 1.04 meq/g (Baetsle et al., 1964).

Composition	Percent
SiO ₂	51.29
Al ₂ O ₃	15.96
Fe ₂ O ₃	2.46
FeO	0.14
TiO ₂	0.18
CaO	2.21
MgO	3.95
Na ₂ O	0.05
K ₂ O	0.13
H ₂ O ⁻	18.
H ₂ O ⁺	5.37

TABLE 8.2. Comparison of Experimental and Computed Strontium
Kd Values for Montmorillonite (Mercer 1966)

Solution Number	K ⁺ , M	Mg ²⁺ , M	Ca ²⁺ , M	Experimental Kd (ml/g)	Computed Kd (ml/g)
1	0.0855	0.01382		24.8	21
2	0.0404	0.00962		59.5	41
3	0.0143	0.00604		135.5	102
4	0.00702	0.00412		207.0	177
5	0.00240	0.00282		369.7	368
6		0.0180	0.0769	12.17	12.1
7		0.0146	0.0348	20.6	21.3
8		0.0106	0.0096	56.9	53.2
9		0.0068	0.0032	114.3	106.8
10		0.0043	0.0009	193.5	221.8
11	0.0895		0.0124	18.0	22.0
12	0.0411		0.00850	50.0	48.0
13	0.0155		0.00520	116.0	111.0
14	0.00612		0.00360	193.0	203.0
15	0.00582		0.00248	336.0	300.0
16		0.0852	0.0128	12.3	14.5
17		0.0388	0.0114	25.8	24.5
18		0.0100	0.0074	58.6	55.0
19		0.0046	0.0056	100.6	107.0
20		0.0015	0.0036	244.1	209.0

Wahlberg et al. (1965) studied the ion-exchange adsorption of strontium from calcium, magnesium, sodium and potassium solutions by kaolinite, montmorillonite and illite. The adsorption of strontium was described by the mass-action equilibrium equation. Calcium provided the greatest competition for strontium, and sodium the least. The data are presented in graphic form as Sr^{+2} normality (from 10^{-10}N to 10^{-1}N) versus strontium distribution coefficient (K_d). The clays used were American Petroleum Institute standards, well-characterized in the clay literature.

Hawkins and Short (1965) completed an experimental design to allow multiple regression analysis of the effects on strontium and cesium K_d values of the following ions and their concentration ranges: Ca^{+2} , 5-500 ppm; Na^{+} , 6-650 ppm; K^{+} , 1-100 ppm; NH_4^{+} , 1-100 ppm; Mg^{+2} , 1-125 ppm; Cs^{+} , 0.05-5 ppm; PO_4^{-3} , 0.1-10 ppm; and pH 4-9. The equation for strontium adsorption may be applicable to other soils besides INEL, Idaho soils, if they do not contain abundant sesquioxides.

Wahlberg and Dewar (1965) studied ion-exchange adsorption of trace concentration strontium (10^{-10}N ^{85}Sr) as affected by two competing cations. The K_d values calculated with the mass-action equation agreed most closely with high exchange montmorillonite than with lower capacity kaolinite.

Another article by Orcutt et al. (1957) includes experimental work on ion exchange in columns and its theoretical treatment. Several theories are presented that quantitatively describe hydraulic dispersion, ion-exchange equilibria and ion-exchange kinetics as they apply to the movement of radionuclides through natural porous media. In the opinion of the authors, the theoretical models, used in conjunction with field tests, served to reduce the uncertainties of ground disposal operations.

In general, enough scientists have found the ion exchange constructs useful to perpetuate their usage in the quantification of radionuclide sorption/desorption.

Precipitation-Mineral Formation

The processes of mineral formation and precipitation are quantifiable using the thermodynamic construct known as the solubility product rule (see

Stumm and Morgan, 1970, Chapter 6; Butler, 1964). When two or more species are present which can interact to form an insoluble compound, one can determine whether the compound should form by comparing the solubility equilibrium constant with the product of the solution species. An example follows:

where:

Sr^{+2} , SO_4^{-2} = solution species

SrSO_4 = an insoluble crystalline material.

At equilibrium $\{\text{SrSO}_4(+)\} = \{\text{Sr}^{+2}\} \{\text{SO}_4^{-2}\}$ and using the convention that the activity of the solid phase is one:

$$K_{\text{So}} = \{\text{Sr}^{+2}\} \{\text{SO}_4^{-2}\} \quad (8.6)$$

where:

K_{So} = the solubility product or equilibrium constant.

If the product of the strontium and sulfate activities in solution is greater than K_{So} precipitation should occur. If the product is less than K_{So} and the mineral SrSO_4 is present in the system it should dissolve until the activity product in solution equals K_{So} . Equations (8.5) and (8.6) can be generalized for any precipitate as follows:

and

$$K_{\text{So}} = \{\text{A}^{+a}\}^b \{\text{B}^{-b}\}^a \quad (8.8)$$

If K_{So} is known or can be measured it is thus possible to predict the formation (precipitation) or dissolution of mineral phases. Traditionally in the study of radionuclide sorption, precipitation was not considered important because of the extremely low concentration of radionuclide usually present in solution. However, the formation of metal

hydroxide precipitates of rare earths and actinides may occur at environmental pH's due to the extremely low K_{SO} . Such events are quite probable when acidic nuclear wastes contact geologic environments which typically neutralize the waste stream, thus increasing the activity of the OH^- species. For rare earths, M^{3+} , $K_{SO} = \{M^{3+}\} \{OH^-\}^3$ and small increases in OH^- activity may allow K_{SO} to be exceeded. Under reducing conditions often found in the organic-laden sediments of certain lakes and estuaries, the precipitation of sulfide minerals is common even for trace constituents.

Again, the direct application of precipitation-dissolution theories and quantification through the K_{SO} of pure minerals to the fate of trace amounts of radionuclides in rivers, lakes, estuaries and oceans is often obscured. Some of the complications are co-precipitation or scavenging of trace constituents during the formation of precipitates of major components of the system (i.e., $CaCO_3$, hydrous Fe, Mn, Al oxides), lattice substitution of trace constituents into existing mineral phases (i.e., a Sr atom replacing a Ca atom in an existing $CaCO_3$ or $CaSO_4$ mineral). These scavenging or substitution reactions are difficult to quantify (Stumm and Morgan, 1970, Chapter 10), yet they have been proposed frequently as being a major mechanism of sorption of trace constituents. Articles pertinent to co-precipitation and lattice substitution of radionuclides include: Ames, 1959a; Ames, 1960a; Ames, 1960b; Ames, 1961a; Ames, 1961b; Ames, 1961c; Belousdva and Melikhov, 1972; and Bernovskaya and Bogdanov, 1971.

Complexation-Hydrolysis

The fundamental concept of chemical reactivity is based on the quest to improve stability in the configuration of the outer electron shells. Ionic species in solution, including trace radionuclides will react with other species in solution and form a complex if there is a large increase in stability. Typically, cations or metal ions combine with anions (also known as ligands). Preference for one ligand over another depends on the cations electronic structure and size and can become rather selective.

The stability of a complex can be measured and is represented by an equilibrium constant, K . For example:

$$K = \frac{\{\text{Co SO}_4\}}{\{\text{Co}^{+2}\} \{\text{SO}_4^{-2}\}} \quad (8.10)$$

or in general:

$$K_i = \frac{\{\text{ML}_i\}}{\{\text{ML}_{i-1}\} \{\text{L}\}} \quad (8.11)$$

where:

M = a metal or cation

L = a ligand or anion

ML_i, ML_{i-1} = complexes.

Hydrolysis reactions are a specialized type of complex formation in which the OH⁻ anion acts as the ligand. As the hydroxyl anion is ubiquitous in waters, hydrolysis reactions with cationic radionuclides are quite common. Hydrolysis reactions are also quite sensitive to pH changes. Besides being common the hydrolysis of metallic radionuclides is important because hydrolysis species are readily absorbed by solid surfaces. No thorough explanation for the enhanced sorption is available, but it is hypothesized that changes in the hydration-sphere size and charge allow more covalent bonding between solid surfaces and the complex. Some data pertinent to hydrolysis of radionuclides can be found in the following references: Baes and Mesmer, 1976; Davydov and Bogatyreva, 1972; Grebenshchikova et al., 1972; Grebenshchikova et al., 1975.

In most instances the formation of complexes increases solubility and would thus be expected to retard incorporation of radionuclides into sediments. On the other hand, as just mentioned, hydrolysis often increases adsorption by ill-defined processes. Therefore, it is difficult to a priori state what the effect of complexation will be on radionuclide sorption. The inorganic

ligands, SO_4^{2-} , HCO_3^- , CO_3^{2-} and Cl^- are present in high concentrations in sea water compared with fresh waters and may retard the sorption of radionuclides through soluble complex formation.

The complexation of metals with soluble organic ligands in natural waters is frequently postulated to explain the occurrence of metal ions at concentrations higher than those calculated from existing solubility product constants. Analytical extraction schemes also often lend credence to the importance of such natural organic complexes but direct evidence is scarce. There are very few thermodynamic values available for organic ligand-metal complex stability constants such that quantification at present is impossible. A pertinent article on the importance of organic matter in radionuclide movement is Faure et al., 1972.

Oxidation-Reduction

This mechanism is conceptually analogous to acid-base reactions. Just as acids and bases may be interpreted as proton (H^+) donors and acceptors, respectively, reductants and oxidants are defined as electron donors and acceptors. The measure of electron activity analogous to pH is $\text{pe} = -\log \{e^-\}$ or a common Eh which is proportional to pe. The oxidation-reduction potential is important in that it may control the valence state and ultimately the species present in solution for many radionuclides and major constituents such as Fe, Mn, S and C. The stability fields of the various valence states possible for elements as a function of pH are often portrayed in Eh-pH diagrams. Some pertinent references explaining the usage and construction of Eh-pH diagrams include: Baes and Mesmer, 1976; Garrels and Christ, 1965; Lindsay, 1972; Pourbaix, 1966; Rai and Serne, 1977; and Rai and Serne, 1978.

Such diagrams show how electrons and protons can simultaneously shift the predominant soluble species or stable mineral from one moiety to another for an element. The oxidation-reduction reactions used to construct diagrams can be expressed quantitatively in the form of mass action equations as expressed earlier for precipitation and ion exchange with the resultant equilibrium constant, K, related to stability. In natural systems the use of thermodynamically derived oxidation-reduction reactions is not straightforward. Because

many redox reactions are slow, the concentrations of some species may be far from those predicted thermodynamically. Also, marked differences in redox potential may occur over small spatial areas near the sediment-water interface. Therefore, the use of theoretical redox constructs to predict the fate of sensitive constituents including radionuclides will depend upon kinetic hindrances and systems approach to equilibria. The fate of Sb, Nb, Pu, U and Tc in aqueous environments and the important scavenging mechanism of hydrous iron and manganese oxides for trace metals are directly affected by redox conditions.

Colloid and Polymer Formation

A final sorption mechanism on which there is scant quantitative data is the formation of colloids and polymers. This process involves the combination of atoms of trace constituents with themselves until a large entity (sub micron) with possible surface charge is formed. Colloids behave intermediately between small soluble and larger suspended particulates. Oftentimes the radionuclide will be bound to a very fine particle of clay or other geologic material and is often designated as a "pseudo colloid." The colloid usually exhibits a smaller charge/surface area ratio and is thus less chemically reactive. Its movement, especially if neutrally charged, is most dictated by physical laws (gravity settling, filtration, etc.) much like suspended sediments. Although quantitative mathematical expressions of this phenomenon are not readily available, highly charged metal ions such as Pu, Th, U, Zr and to a lesser extent Am, Cm, Sb and Ru are believed to commonly migrate as colloids or polymers under certain conditions. Several articles pertinent to radiocolloid formation, adsorption properties and transport properties were identified during this literature review: Benes, 1969; Betenekov et al., 1973; Eichholz et al., 1967; Feldman, 1976; Folsom and Hodge, 1975; Kaufman and Klingerman, 1963; Kepak, 1974; Kuznetsov et al., 1973; Lindenbaum and Westfall, 1965.

Existing Computer Codes

A quantitative description of nuclide transport requires development of models of the above mechanisms and potential mechanisms not identified, or a

generalized model which describes the combined effects of such mechanisms. Travis (1978) reviews numerous equilibrium and kinetic mathematical models which describe solute transport in porous media. These models are based on empirical observations and can be considered as functional relationships which describe the net effect of sorption-retardation mechanisms described above such as ion exchange, pure mineral precipitation, complexation, etc. These empirical mathematical relationships do not rely on descriptions on the physico-chemical processes controlling sorption; instead they describe the relationships between the amount of solute observed in solution and the amount of solute adsorbed on the solid matrix. Commonly used equilibrium empirical models include linear adsorption isotherms ($S = kC$), Freundlich isotherms ($S = kC^n$) and Langmuir isotherms ($S = \frac{k_b C}{1 + k_b C}$) where S = amount of solute sorbed on solid phase, C = amount of solute in solution and k , b and n are constants. Again it should be stressed that such equilibrium models are based on empirical observations on the distribution of solute between solid and liquid as opposed to physico-chemical description of mechanisms and processes. Kinetic adsorption models are also reviewed by Travis (1978). Most of the kinetic models have been constructed from first order kinetic constructs, i.e.

$$\frac{dS}{dt} = k_1 C - k_2 S$$

Chemical models of mineral precipitation, complexation, oxidation-reduction and ion exchange based on physico-chemical laws, usually thermodynamics and mass action relationships, do exist. The models' strengths lie in description of the major elements such as Si, Al, Ca, Mg, K, etc. as opposed to trace constituents such as nuclides. Also most of these models do not include transport (hydrodynamics, advection, dispersion, etc). These models which combine the chemistry with transport typically rely on simplified one-dimensional flow algorithms. An excellent recent review of chemical models can be found in Jenne, 1979. Several other references to chemical codes are: Ahlstrom and Foote, 1976; Cameron and Klute, 1977; Dutt et al., 1972; Frissel and Reiniger,

1974; Helgeson, 1968; Helgeson et al., 1970; Helgeson, 1969; Morel and Morgan, 1972; Rai and Franklin, 1973; Routson and Serne, 1972a, b; Tanji and Doneen, 1966; Tanji et al., 1967a; Tanji et al., 1967b; van Genuchten and Wierenga, 1974; and Wolery, 1978.

In the next section the most common way of quantifying the chemical interaction of trace radionuclides with geologic media is addressed. The distribution coefficient, K_d , concept is identical to a linear adsorption isotherm model.

DEFINITION OF K_d AND RATE DEPENDENCY

The quantification of radionuclide adsorption is usually expressed in terms of a distribution coefficient, K_d . There is some confusion and difficulty in the use of the K_d concept because to strict chemists it has a rigorous definition and can only be used properly when certain assumptions are met. To the engineer and waste management technician, K_d is often used in a broader sense and is defined as:

$$K_d = \frac{\text{amount of radionuclide sorbed on solid phase}}{\text{amount of radionuclide left in solution}} \quad (8.12)$$

Typically K_d has the SI units $\text{length}^3/\text{mass}$ (i.e., ml/g) as it is convenient to measure the ratio amount/g of sediment/amount/ml of solution. Some users measure the amount of radionuclide on the solid phase in terms of volume of solid phase and thus calculate a unitless ratio often designated, K . If one can determine the bulk density of the solid phase, a conversion from K to K_d is possible.

In the strictest sense the concept of K_d was developed from ion-exchange theory to represent the equilibrium distribution of a trace constituent between the solid exchanger and solution. Referring to Equation (8.3), the generalized binary ion-exchange expression, and making the following assumptions:

- (a) the component A^{+a} is present in very trace amounts and thus cannot displace a significant (measurable) amount of B^{+b} from the solid exchanger, and

- (b) the ratio of the activity coefficients of A^{+a} on the exchanger and in solution is constant (oftentimes assumed to equal 1)

then the terms $\{B^{+b}\}$ and $\{B-X\}$ are essentially constant. Thus the ion-exchange equation becomes:

$$K_{AB} \frac{\{B-X\}^a}{\{B^{+b}\}^a} \frac{\{\gamma A^{+a}\}^b}{\{\gamma A-X\}^b} = \frac{(A-X)}{(A^{+a})} \quad (8.13)$$

where:

γ = activity coefficients

() = concentrations.

The left-hand side of Equation (8.13) with the aforementioned assumptions is a constant, therefore:

$$K_d = \frac{A-X}{A^{+a}} \text{ which is equivalent to Equation (8.12).}$$

Key points to the correct usage of K_d include:

- (a) the necessity of trace concentrations of component A
- (b) the constancy of the activity coefficient ratio of component A
- (c) the satisfaction of system equilibrium.

The third point is often treated lightly in the popular usage of K_d for radionuclide migration calculations. Also as described in the previous section, reactions such as precipitation, mineral formation, and non-ideality of ion exchange in natural systems make the correct usage of K_d difficult.

To avoid confusion it would have been nice if engineers and scientists involved in nuclear waste management had chosen another symbol for the distribution of radionuclides between the solid and liquid phase. It might be difficult and just as confusing to suggest a new symbol after 20 years of familiarity. At any rate the K_d concept has proved invaluable to the prediction of radionuclide migration as long as the qualifying assumptions are met and an

understanding of the studied system is available. The K_d is typically inserted into a retardation term in the transport equation and the movement of the radio-nuclide is expressed in terms of the bulk water:

$$v_{\text{water}} = \left(1 + \frac{B_d}{\phi} K_d\right) v_{\text{nuclide}} \quad (8.14)$$

where:

v = velocity

B_d = bulk density of solid ($\frac{B_d}{\phi}$ also equals solids/solution ratio)

ϕ = porosity

As K_d increases, the water moves faster than the nuclide, thus indicating nuclide retardation. The assumption of system equilibrium is often tacitly assumed. In the systems under study the rapid movement of water and suspended sediments in rivers, estuaries and coastal waters may not satisfy the assumption of system equilibrium at all times and over all space. The low solids to solution ratio present in natural environments of interest as compared to laboratory systems usually studied may also complicate the interpretation of the applicability of K_d time-dependent data which are available. On the other hand, the high surface area and exchange capacity commonly found for suspended sediments might allow more rapid attainment of equilibrium sorption.

The few references which included K_d determinations as a function of time are addressed in the following sections on individual elements. Again it must be stressed that usage of laboratory time-dependent sorption results to predict sorption at field conditions cannot be readily performed. There is no data on sorption dependence on time under actual field conditions.

Another factor, until recently not given adequate study, was the area of reversibility. In the correct derivation of K_d from ion-exchange principles, K_d is equivalent to the ratio of the rate of adsorption to rate of desorption at steady state. For ideal ion exchange the binding of a charged ion and replacement with another requires equal energy. This leads to an equal rate of adsorption and desorption or the derived K_d value being correct for loading

or leaching. In natural systems it is becoming apparent that many radionuclides appear to desorb at slower rates and at steady state show a stronger affinity for the solid phase. This results in K_d 's measured in the desorption direction to be greater than when measured in the adsorption direction (i.e., some degree of irreversibility is apparent). It thus looks, besides incorporating a time dependency for K_d into the transport equation, as though the direction of approach must also be considered. A transport equation, including both a time-dependent adsorption K_d and a time-dependent desorption K_d , may be necessary.

FUNCTIONAL RELATIONSHIPS

To the uninitiated the K_d for a given radioisotope is commonly thought to be a constant value for all environmental conditions. Thus, it is common to see tables listing the radioelements and one K_d value for each. Others with somewhat more sophistication realize the dependency of K_d on geologic media type or water composition and will list K_d s for each element for a given media such as western U.S. desert soil (Lester et al., 1975), or for fresh and seawater (Booth, 1975).

In reality the K_d may be dependent on many factors. Some investigators, Routson and Serne (1972a,b), Serne (1978), and Hawkins and Short (1965), have attempted to express K_d s as a function pertinent to geochemical variables such as water composition, pH and Eh.

From discussions in the previous two sections on mechanisms and rates, it is apparent that a complete description of the dependency of K_d on geologic media, water consumption, hydrologic variables, time and direction (adsorption/desorption) would be immensely complicated. This author feels that a statistical approach such as regression or adaptive learning networks could be used to empirically derive functional relationships for K_d to be used in transport equations. Simple attempts Routson and Serne (1972a,b) and Hawkins and Short (1965), have proven useful and current efforts, Serne (1978), are under way to increase the parameters included.

The incorporation of a statistical approach requires the characterization of many system parameters to allow the important variables to be identified. The added cost in characterization in the author's view is warranted because:

- It allows much more detailed predictor equations for K_d to be evolved.
- It adds data and insight which should allow scientists to hypothesize probable controlling mechanisms which ultimately would allow fundamental understanding of nuclide sorption/desorption.
- It forces good scientific methods to be employed.

A list of parameters which should be considered when describing the experimental or field environment present while determining K_d is found below. With this supporting information a systematic study of the correlation of the K_d for each valence state or species of each element can be performed. The type of function emanating from such a study would be a nonlinear multinomial such as:

$$K_d_{\text{nuclide species}} = f(\text{geologic parameters, water parameters, time})$$

$$K_d = a(\text{Montmorillonite}) + b(\text{Quartz}) + c(\text{Ca}^{+2}) + d(\text{Na}^{+}) + e(\text{pH}) \dots \\ + x(\text{Ca})(\text{pH})(\text{Eh}) + \text{etc.} \quad (8.15)$$

where $a, b, c, \dots x$ are statistically derived coefficients. Such complex-looking functions are readily incorporated into numerical computer transport models without increasing cost or complexity significantly. The use of these complex variable functions, however, are not amenable to many simple analytical computer transport models.

The degree of complexity can be reduced to any level by dropping out the lesser significant terms in Equation (8.15), once the user has a clear objective or understanding of the accuracy needed in his whole transport systems model.

Each mechanism previously discussed would be more sensitive to certain of the parameters listed than others. Thus, a study of the strength of correlation of certain parameters to a nuclide's K_d can provide insight as to which sorption mechanism may predominate.

SUPPORTING INFORMATION NECESSARY TO EVALUATE
FUNCTIONAL DEPENDENCY OF K_d

Geological Media Parameters

1. Qualitative and Quantitative mineralogy including primary and secondary crystalline materials
2. Amorphous Coatings including hydrous Fe, Mn, Al oxides
3. Carbonate content (Ca, Mg)
4. Sulfide-Sulfate content, especially for reduced sediments
5. Organic Content
6. Cation-Exchange Capacity
7. Anion-Exchange Capacity
8. Nitrogen and Phosphorous Content (Nutrients)
9. Particle size distribution
10. Surface Area
11. Distribution of major cations on exchange sites
12. Bacterial Status

Water/Geologic Media Slurry

1. pH
2. Eh
3. Dissolved O₂ content
4. Temperature

Water Parameters

1. Major cations (Ca, Mg, Na, K)
2. Major anions (Cl, HCO₃, CO₃, SO₄)
3. pH
4. Eh
5. Dissolved O₂
6. Dissolved organic content (fractionated into types)
7. Dissolved nutrients (N,P)
8. Dissolved SiO₂
9. Minor constituents, especially natural occurring stable isotopes of Sr, Cs, I, and other important radionuclides

Nuclide Properties

1. Tracer Concentration (at start and at each measurement time)
2. Tracer Valence State or Species distribution (at start and at each measurement time)

Experimental or Hydrologic Parameters

1. Contact Time
2. Solids/Solution ratio
3. Degree of agitation
4. Water velocities
5. Suspended load concentration
6. Eddy diffusivities, bed shear stress (description of hydrologic system in field or experimental methodology)
7. Desorption or Adsorption

SELECTION CRITERIA AND SOURCES OF RADIONUCLIDES IN THE ENVIRONMENT

For this study the fission and activation products that are present in wastes (including cooling water and atmospheric emissions) remaining after nuclear power generation and potential nuclear fuel reprocessing exhibiting long half-lives or biological hazards were selected. Using an approach similar to Wrenn and Jinks (1976) one finds the elements listed in Table 8.3 present the largest potential hazards for the entire nuclear fuel cycle. Sources of the projected inventory of nuclear materials being produced and/or discharged from existing or planned reactors and waste processing plants which were used to prepare Tables 8.3 to 8.6 are: Dames and Moore, 1976; Haury and Schikorski, 1977; Joseph et al., 1971; Magno et al., 1970; ORNL, 1970; Phillips et al., 1977; Schneider and Platt, 1974; USEPA, 1973; U.S. NRC, 1976; and Wrenn and Jinks, 1976

From the references cited the following potentially biologically hazardous elements were chosen for further study: Am, Sb, Ce, Co, Cm, Eu, I, Fe, Mn, Np, Pu, Pm, Ra, Ru, Sr, Tc, Th, ^3H , U and Zr. Carbon-14, Cr, P and Zn were also added for study.

It would have been interesting but beyond the scope of this study to include the amount of radionuclides present now and in the future from sources such as medical wastes, nuclear bomb testing and fossil fuel consumption in the selection process. Several elements which were more difficult to exclude from consideration include ^{79}Se and ^{151}Sm . ^{85}Kr was excluded because it is an inert gas and would not interact with sediments by adsorption/desorption reactions.

TABLE 8.3. Most Potentially Hazardous Elements

<u>Operation</u>	<u>Elements</u>
Mining	Ra > U > Th
Milling	Ra > U > Th
Fuel Fabrication	U
Reactor Effluents	³ H, I, Cs, Co, Fe, Mn > Sb, Tc, Ce, Zr, ¹⁴ C
Reprocessing	Sr, ³ H, Cs, Co, transuranics
Waste Storage	I, Tc, transuranics, Ra, ¹⁴ C

TABLE 8.4. 1975 Summary Liquid Release of Radionuclides from Commercial LWR and PWR Reactors in the United States

<u>Isotope</u>	<u>Curies</u>
¹³⁷ Cs	120
¹³⁴ Cs	81
¹³¹ I	23
⁵⁸ Co	23
⁶⁰ Co	22
⁹⁰ Sr	0.5

TABLE 8.5. Annual and Cumulated Releases and Production of Radionuclides from Nuclear Plants and Fuel Reprocessing Plants for the World from 1975 to 2000

Nuclide	Annual Release Into Atmosphere(a)				.. Into Waters(a)		Cumulated Releases, 1975-2000(b)			Cumulated Production Not Released 1975-2000 (Ci)
	Power Plants 1975 (Ci/a)	Repr. Plants 1975 (Ci/a)	Power Plants 2000 (Ci/a)	Repr. Plants 2000 (Ci/a)	Power Plants 1975 (Ci/a)	Power Plants 2000 (Ci/a)	Power Plants Atmosph. (Ci)	Repr. Plants Atmosph. (Ci)	Power Plants Water (Ci)	
^3H	1.7×10^3	1.1×10^6	6.3×10^4	4.2×10^7	5.1×10^4	1.9×10^6	1.3×10^5	8.8×10^7	3.9×10^6	-
^{85}Kr	4.0×10^4	1.1×10^7	1.5×10^6	4.2×10^8	-	-	2.8×10^6	8.0×10^8	-	-
^{14}C	6.2×10^2	9.8×10^2	2.2×10^4	3.6×10^4	-	-	1.6×10^5	2.4×10^5	-	-
^{129}I	-	46	-	1.7×10^3	-	-	-	1.2×10^4	-	-
^{90}Sr	-	3.4×10^{-1}	-	13	1.6×10^{-1}	5.9	-	48	22	3.4×10^{10}
^{60}Co	-	-	-	-	5.7	2.1×10^2	-	-	2.1×10^2 (c)	-
^{106}Ru	-	5.7	-	2.1×10^2	-	-	-	2.1×10^2 (c)	-	-
^{134}Cs	-	2.3	-	84	5.7	2.1×10^2	-	84(c)	2.1×10^2 (c)	-
^{137}Cs	-	1.1	-	42	13	4.9×10^2	-	1.7×10^2	1.9×10^3	4.7×10^6
^{241}Pu	-	1.7×10^{-1}	-	6.3	-	-	-	16	-	4.4×10^8 (d)
Other Pu	-	7.2×10^{-4}	-	2.6×10^{-2}	-	-	-	1.8×10^{-1}	-	4.9×10^8 (d)
Other Trans-uranics	-	1.5×10^{-1}	-	5.5	-	-	-	38	-	8.0×10^7

(a) Power plants in operation in the world, 1975: 57 GWe (2.27); equivalent reprocessing capacity: 1.4 standard plants (1500 t per year); planned power plants in the world in the year 2000: 2100 GWe (see text); equivalent reprocessing capacity: 42 standard plants (1500 t per year).

(b) Includes radioactive decay, 1975-2000.

(c) Increase of production rates slower than radioactive decay.

(d) Total production including Pu for recycling.

TABLE 8.6. Nuclide Source Inventory(a)

100	Time	0.00E+00	1.00E+02	1.00E+03	1.00E+04	1.00E+05	1.00E+06
110	³ H	7.23E+02	2.29E+06	0.	0.	0.	0.
120	⁹⁹ Tc	2.86E+06	2.83E+06	2.82E+06	2.74E+06	2.04E+06	1.08E+05
130	¹²⁹ I	8.04E+03	8.04E+03	8.04E+03	8.04E+03	8.01E+03	7.72E+03
140	¹⁴ C	1.03E+06	1.02E+06	9.15E+05	3.08E+05	5.77E+00	0.
150	⁹³ Mo	5.22E+03	5.18E+03	4.84E+03	2.42E+03	2.37E+00	0.
160	⁴¹ Ca	6.85E+02	6.85E+02	6.80E+02	6.29E+02	2.88E+02	1.19E-01
170	⁷⁹ Se	9.72E+04	9.71E+04	9.62E+04	8.74E+04	3.35E+04	2.28E+00
180	⁹⁰ Sr	1.29E+10	1.10E+09	2.52E-01	0.	0.	0.
190	¹⁰ Bf	4.04E+02	4.04E+02	4.04E+02	4.03E+02	3.93E+02	3.06E+02
200	⁶⁰ Cu	7.70E+07	1.46E+02	0.	0.	0.	0.
210	⁵⁹ Ni	2.07E+05	2.06E+05	2.05E+05	1.89E+05	8.69E+04	3.57E+01
220	⁶³ Ni	6.67E+06	3.14E+06	3.57E+03	0.	0.	0.
230	⁸⁷ Rb	4.67E+00	4.67E+00	4.67E+00	4.67E+00	4.67E+00	4.67E+00
240	¹³⁵ Cs	8.59E+04	8.59E+04	8.59E+04	8.57E+04	8.40E+04	6.82E+04
250	¹³⁷ Cs	1.85E+10	1.84E+09	1.72E+00	0.	0.	0.
260	¹⁰⁷ Pd	2.28E+04	2.28E+04	2.28E+04	2.28E+04	2.26E+04	2.06E+04
270	¹²⁶ Sn	1.28E+05	1.28E+05	1.27E+05	1.19E+05	6.39E+04	1.25E+02
280	¹⁵¹ Sm	3.10E+08	1.40E+08	1.08E+05	0.	0.	0.
290	^{166m} Ho	1.00E+02	9.47E+01	5.63E+01	3.11E-01	0.	0.
300	¹⁵² Eu	1.61E+06	5.00E+03	0.	0.	0.	0.
310	¹⁵⁴ Eu	8.32E+08	1.09E+07	1.29E-10	0.	0.	0.
320	⁹³ Zb	4.03E+05	4.03E+05	4.02E+05	4.00E+05	3.84E+05	2.53E+05
330	¹¹³ Cd	4.67E+06	3.31E+04	1.49E-15	0.	0.	0.
340	²⁴⁸ Cm	5.01E-01	5.01E-01	5.00E-01	4.91E-01	4.11E-01	6.99E-02
350	²⁴⁴ Pu	5.36E-05	5.40E-05	5.74E-05	9.16E-05	4.02E-04	1.72E-03
360	²⁴⁴ Cm	4.71E+08	1.02E+07	8.58E-08	1.19E-07	5.23E-07	2.24E-06
370	²⁴⁰ Pu	1.93E+06	3.13E+06	2.88E+06	1.15E+06	1.13E+02	1.72E-03
380	²³⁶ U	5.58E+03	5.59E+03	5.67E+03	6.16E+03	6.47E+03	6.30E+03
390	²³² Th	7.80E+00	7.80E+00	7.80E+00	7.80E+00	7.83E+00	8.11E+00
400	²³² U	2.50E+04	9.75E+03	1.69E+00	0.	0.	0.
410	²⁴⁵ Cm	1.38E+05	1.37E+05	1.27E+05	5.97E+04	3.15E+01	0.
420	²⁴¹ Pu	2.64E+08	2.58E+06	1.27E+05	5.98E+04	3.16E+01	0.
430	²⁴¹ Am	8.56E+07	8.08E+07	1.93E+07	5.98E+04	3.33E+01	0.
440	²³⁷ Np	8.07E+04	8.34E+04	9.59E+04	9.98E+04	9.71E+04	7.26E+04
450	²³³ U	1.88E+04	1.88E+04	1.91E+04	2.21E+04	4.65E+04	7.73E+04
460	²²⁹ Th	1.74E+01	1.95E+02	1.73E+03	1.27E+04	4.72E+04	7.73E+04
470	²⁴⁶ Cm	2.68E+04	2.64E+04	2.31E+04	6.15E+03	1.09E-02	3.84E-25
480	²⁴² Pu	9.26E+03	9.46E+03	9.82E+03	9.87E+03	8.44E+03	1.63E+03
490	²³⁸ U	2.44E+02	2.44E+02	2.44E+02	2.44E+02	2.44E+02	2.45E+02
500	²⁴² Cm	3.61E+08	3.87E+06	6.40E+04	9.71E-14	0.	0.
510	^{242m} Am	7.45E+06	4.72E+06	7.80E+04	1.18E-13	0.	0.
520	²³⁸ Pu	3.97E+08	1.86E+08	2.32E+05	2.34E-13	0.	0.
530	²³⁴ U	2.27E+04	1.01E+05	1.70E+05	1.65E+05	1.29E+05	1.05E+04

TABLE 8.6. (contd)

540	230Th	5.50E+00	6.33E+01	1.38E+03	1.38E+04	8.43E+04	1.55E+04
550	226Ra	3.47E-01	1.56E+00	2.47E+02	1.08E+04	8.44E+04	1.55E+04
560	247Cm	1.29E-01	1.29E-01	1.29E-01	1.29E-01	1.29E-01	1.24E-01
570	242Am	5.12E+06	5.07E-06	4.67E+06	2.07E+06	5.95E+02	1.24E-01
580	243Cm	4.03E+06	4.63E+05	1.59E-03	0.	0.	0.
590	239Pu	9.69E+05	9.86E+05	1.08E+06	1.55E+06	1.93E+05	1.24E-01
600	239U	2.26E+01	2.27E+01	2.36E+01	3.57E+01	1.15E+02	1.21E+02
610	231Pa	1.57E+04	1.57E+04	1.54E+04	1.27E+04	1.95E+03	1.21E+02
620	250Cm	5.59E-08	5.57E-08	5.37E-08	3.75E-08	1.04E-09	2.82E-25
630	250Cf	1.31E+01	6.53E-02	5.37E-08	3.75E-08	1.04E-09	2.83E-25
640	249Cf	7.86E+00	6.53E+00	1.11E+00	2.24E-08	0.	0.
650	251Cf	2.20E-01	2.04E-01	1.02E-01	9.98E-05	0.	0.
660	252Cf	3.73E+00	1.58E-11	0.	0.	0.	0.

(a) Includes all high-level waste from the U.S. nuclear power economy through Year 2000 plus all tritium, carbon, and iodine from spent fuel and activation products from the cladding. The columns show the inventories of each nuclide in curie units at various times after Year 2000. Thus, the first column shows the inventories at the Year 2000, the second column at the Year 2100, the third at the Year 3000, etc.

ELEMENT LITERATURE REVIEW

The chemistry and geochemistry of the elements chosen for review are examined in the following section from the standpoint of radionuclide migration and retention by suspended and bottom sediments. Literature reviews on the interaction of radionuclides with soils and rocks have recently been performed by investigators at Pacific Northwest Laboratory (PNL) for the Department of Energy (DOE) and the United States Environmental Protection Agency (EPA) [Rai and Serne (1978) and Ames and Rai (1978)].

Efforts were taken to use available thermodynamic data to predict the stable solid phases and dominant solution species. The authors, however, pointed out that these predictions should only be regarded as estimates because of the many limitations of this approach. They made the predictions for different assumed weathering environments (pO_2 , 0.68 to 80; pCO_2 , 1.52 to 3.52; pH, 4 to 10; $pCl^- = pNO_3^- = pSO_4^{2-} = 2.5$ to 3; $pF^- = 4.5$; and phosphate levels in equilibrium with variscite or dicalcium phosphate dihydrate or $pH_2PO_4^- = 5.0$). Their assumed solution composition is significantly different than seawater and river water only for the concentration of chloride in sea water as shown in Table 8.7.

TABLE 8.7. Average Activities of Solution Constituents
($pX = -\log$ of the activity of X)

<u>Component</u>	<u>Sea Water</u>	<u>River Water</u>	<u>Ground Water</u>
$p(SO_4^{2-})$	2.34	3.9	3.
$p(Cl^-)$	0.45	3.66	3.
$p(H_2PO_4^-)$	6.	6.	5.
$p(F^-)$	4.32	5.28	4.5
$p(NO_3^-)$	5.	5.	3.
$p(CO_2)$	3.40	3.40	3.52

For convenience the thermodynamic data presented by Ames and Rai (1978) under the sponsorship of EPA will be used to outline the nature of solution species that may be expected in sea water and river water. The

influence of the high chloride concentration in sea water versus terrestrial groundwaters will be discussed if this change drastically alters the type of the dominant solution species.

For several of the elements little or no data were found in the literature on adsorption/desorption onto suspended or bed sediments. Rather than present no information the authors elected to present element adsorption/desorption data from soil-groundwater regimes. In general as presented in Table 8.7 the compositions of groundwater complexing ligands are quite similar to marine and freshwaters excepting the Cl^- anion. Thus, the use of soil-groundwater data to predict the general fate of elements in marine and limnetic regimes is warranted. As the adsorption/desorption K_d values are also dependent upon the particle size or available surface area and mineralogy, one should consider data on sorption onto clay or fine particulate soil to better predict the sorption on suspended sediments. To predict sorption onto bed sediments one should consider the bed sediment particle size distribution and mineralogy and then choose available soils data of a similar nature. Finally, in all cases the amount of organic matter in the sediments should be measured and considered when comparisons with soils are being performed. In general, higher organic-laden geomedial exhibit larger sorption of trace constituents.

AMERICIUM

Natural Sediment and Rock Distributions

The element americium has not been reported to occur naturally in sediments or rocks.

Brief Chemistry

Americium exists in radioactive wastes as two radionuclides, ^{241}Am with a half-life of 433 years and ^{243}Am with a half-life of 7,370 years. It is found in the following four oxidation states: Am(III) , Am(IV) , Am(V) and Am(VI) . The most stable state of americium is the trivalent. The higher oxidation states are strong oxidizing agents and are therefore stable only in media that contain no oxidizable substances (Coleman, 1963). The ionic radius of Am^{+3} is 1.07 Å (Ahrens, 1952).

The stability constants and complex formation of Am(III) are probably more well known and studied than any of the other trivalent actinides. The tendency to complex ion formation is a function of factors such as ionic size and charge. In order of decreasing complexing tendency, the actinide series is generally $\text{M}^{+4} > \text{MO}_2^{+2} > \text{M}^{+3} > \text{MO}_2^{+}$. For univalent anions, complexing ability with Am(III) follows the order for $\text{F}^- > \text{NO}_3^- > \text{Cl}^- > \text{ClO}_4^-$, and for bivalent anions, $\text{CO}_3^{2-} > \text{oxalate}^{2-} > \text{SO}_4^{2-}$ (Keller, 1971).

Solution Equilibria

The activity of various americium species in solution in equilibrium with $\text{AmO}_2(\text{s})$ in an oxidizing environment ($p\text{O}_2 = 0.68 \text{ atm}$) is given in Figure 8.1. The thermodynamic data for all the species except AmOH^{2+} and $\text{AmH}_2\text{PO}_4^{2+}$ were selected from Sillen and Martell (1964). The AmOH^{2+} and $\text{AmH}_2\text{PO}_4^{2+}$ data were selected from Keller (1971). In the normal fresh water environment the dominant solution species of Am at $\text{pH} < 6.5$ and > 6.5 would be AmSO_4^+ and Am(OH)^{2+} , respectively. Am^{3+} would be of lesser importance. In the high chloride environment of sea water, AmCl^{2+} and AmSO_4^+ would dominate at $\text{pH} < 6.5$ and again Am(OH)^{2+} would predominate at $\text{pH} > 6.5$.

With an increase in $p\text{O}_2$ (more reducing environment) and the concentration of anions, the curves given in Figure 8.1 would move upwards. However,

FIGURE 8.1. The Activity of Various Americium Species in Equilibrium with $\text{AmO}_2(\text{s})$ in an Oxidizing Soil Environment [$p\text{O}_2(\text{g}) = 0.68 \text{ atm}$], $p\text{SO}_4^{2-} = p\text{NO}_3^- = 3.0$ and $p\text{H}_2\text{PO}_4^- = 5.0$

the relative position of most of the isotherms would not change. The americium species are cationic in the pH range of from 4 to 8. It is to be expected, therefore, that ion exchange could be an important americium removal mechanism.

Americium found in the environment exists principally from ^{241}Pu decay in nuclear fallout and liquid and solid wastes from fuel reprocessing plants.

Laboratory Adsorption Studies

There have been a few laboratory studies which address the adsorption-desorption reactions of americium in sediments and soils.

Fukai and Murray (1974) studied the fate of americium in river water and sea water and its interactions with sediments. Their first experiment addressed the fate of americium added to waters devoid of suspended sediments. Tracer quantities of $^{241}\text{Am}(\text{III})$ were added to filtered water, the pH adjusted between 3 and 10, and were mechanically shaken for 4 days. The samples were

then filtered through 0.45 μm membranes and the fraction americium removed as particulate determined. Results are shown in Figures 8.2 and 8.3. More than 95% of the americium in both waters became associated with particles larger than 0.45 μm above pH 8.

In sorption experiments Am(III) was added to 100 ml of Var River water containing 1 g of river sediment and contacted for up to 250 hr. After adsorption the sediments were contacted with 100 ml of sea water. Both sorption and desorption reached equilibrium after 180 hr at pH 8 (see Figure 8.4). Adsorption was pH dependent as shown in Figure 8.5 where americium adsorption changes sharply between pH 6.5 to 8.5. Desorption of americium from Var River sediments by sea water was also slightly pH dependent as shown in Figure 8.6. In general desorption would be low (<20%). At pH 7 and 8 in fresh water the Var River sediment K_d_{Am} is approximately 85 and 900 ml/g given the experimental conditions. The desorption K_d_{Am} into sea water would be about 900 ml/g also.

Sanchez (1977), Seymour (1977), Schell et al. (1979) and Schell et al. (1980) report on batch K_d_{Am} experiments performed on the following sediment-water systems: a) anoxic marine sediment-sea water, b) oxic marine sediments-sea water, and c) lake sediments-fresh water. The particle size distribution, total carbon and total nitrogen contents are reported in Table 8.8.

Salinities, temperature, and nutrients were measured on the filtered water samples. Both sediment and water were frozen until laboratory experiments commenced. A portion of each sediment was irradiated with 10^6 rads of ^{60}Co to reduce if not destroy all microbial activity. ^{241}Am (0.5 $\mu\text{Ci/ml}$ in 4M HNO_3) was added to a slurry of sediment water, pH was adjusted and batch shaking experiments performed. An aliquot of the suspension was removed at set times and sediment separated by filtration (0.45 μm). Both filter and filtrate were counted. Various sediment concentrations (100 mg/l to 1000 mg/l), and pH's (4 to 10) were utilized at a total system ^{241}Am concentration of about 1 $\mu\text{Ci/l}$. After about 120 hr of contact the contaminated sediments were placed in unspiked water and desorption experiments performed.

FIGURE 8.2. Particulate Formation of Am(III) in Var River Water as a Function of Changes in pH

FIGURE 8.3. Particulate Formation of Am(III) in Sea Water as a Function of Changes in pH

FIGURE 3.4. Equilibrium Time for Particulate Formation and Adsorption on Sediments of Am(III) in Var River Water (pH = 8) and Its Desorption from Sediments in the Sea Water

FIGURE 8.5. Adsorption of Am(III) on Sediments in Var River Water at Different pH Values

FIGURE 8.6. Desorption of Am(III) from Sediments in the Sea Water Medium at Different pH Levels

TAB' 8.8. Sediment Characteristics and Average K_{dAm} Particle Size Distribution

	Sand, >62 μm	Silt	Clay, <2 μm	% Carbon	% N	K_{dAm} , ml/g ADSORB	K_{dAm} , ml/g DESORB
Fresh Water	2%	16%	82%	5.2	0.4	4×10^5	1.2×10^6
Anoxic Marine	4%	21%	75%	2.8	0.3	6.5×10^5	6.7×10^6
Oxic Marine	40%	21%	39%	1.8	0.1	2.6×10^5	1.8×10^5

The K_{dAm} versus sediment concentration for the unirradiated fresh water system is shown in Figure 8.7. As the sediment concentration increases the K_d decreases. A similar result was seen for an irradiated system except that the K_d for low sediment concentrations were an order of magnitude larger. The sorption of americium versus pH for both a fresh water and marine water system (not irradiated) are shown in Figures 8.8 and 8.9. At pH less than 7, americium adsorption appears to be rather sensitive to pH. Above pH 7 sorption

FIGURE 8.7. Distribution Coefficient for ^{241}Am as a Function of Sediment Concentration in Fresh Water. Bars indicate range in K_d values.

dependency on pH diminishes. Both the dependency on pH and sediment concentration suggest that precipitation is important. If ion exchange alone were causing the americium adsorption, the K_d should be independent of sediment concentration because there is not enough americium present in the system to significantly load exchange sites. On the other hand, if a certain fixed percentage of americium was forming radiocolloids or precipitates which are removed from the system by any amount of sediment, the calculated K_d would increase as sediment concentration decreases which is what was observed. As seen for the average $K_{d_{\text{Am}}}$ reported in Table 8.8, the coarser grained marine sediment has the lowest K_d whereas fine grained fresh and marine sediments have larger $K_{d_{\text{Am}}}$. In two cases the $K_{d_{\text{Am}}}$ measured on desorption is significantly

FIGURE 8.8. Distribution Coefficient for ^{241}Am as a Function of pH in Fresh Water Sediment System. Horizontal bars indicate range in pH values and vertical bars indicate the range in K_d .

FIGURE 8.9. Distribution Coefficients for ^{241}Am as a Function of pH in Marine Water-Sediment System. Horizontal bars indicate the range in pH values and vertical bars indicate the range of K_d .

significantly larger. The results of ^{60}Co irradiation are also presented in the cited papers but not addressed herein because interpretation of the total effect of irradiation on the system is obscure.

In a separate experiment Schell et al. (1979) found that 90% of the Am added to filtered seawater becomes filterable ($0.45\ \mu\text{m}$) rapidly ($<1\ \text{hr}$). A possible explanation is that Am is very insoluble at neutral pH and tracer addition exceeds the solubility limit.

In a continuing study of americium sorption a sandy sediment from the Skagit River estuary (Washington) was determined with 30.2% marine water by Schell et al. (1979). It was found by use of blank samples (traced water with no sediments) that 87 to 92% of the Am was filtered by $0.45\ \mu\text{m}$ membranes. Thus Kd values which were not corrected for blank particle formation $1\ \text{to}\ 2 \times 10^5\ \text{ml/g}$ would drop to $3\ \text{to}\ 7 \times 10^4\ \text{ml/g}$ upon blank correction. A second system, an anoxic marine sediment-anoxic water, gave essentially 100% removal of Am. The control (traced water by itself) led to 100% retention on a $0.45\ \mu\text{m}$ filter.

Sanchez (1977) used a dialysis membrane bag which permits particles the equivalent of 6000 to 8000/molecular weight (based on organic molecules) and lower to pass were filled with unspiked sea water and anoxic marine sediment. The bag was suspended in spiked sea water. After 10 days the spiked sea water and suspended sediment were analyzed. The resultant Kd was $97\ \text{ml/g}$ which is much lower than found previously. Also the americium outside the dialysis bag upon filtration ($0.22\ \mu\text{m}$) was distributed 50% in solution and 50% retained on the filter. Both results tend to support the hypothesis that americium forms colloids or precipitates in the laboratory systems used and that reported Kd values obtained from addition of acid americium spike may be unintentionally inflated.

In a dialysis experiment which lasted 11 days Schell et al. (1979) placed 3 liters of spiked seawater in a large glass beaker. They also added three dialysis sacs containing: (a) distilled water (control sac), (b) 765 mg of oxic marine sediment (see Table 8.8) and (c) plankton. Outside the sacs

and within the sacs, samples were filtered through 0.22 μm membranes. Results are presented in Table 8.9. The Am which entered the sediment sac became attached to sediment almost exclusively. Less Am was found outside the dialysis sacs than any other radionuclide studied. In a second dialysis experiment with estuarine water, dialysis sacs filled with: (a) unspiked estuarine water, (b) phytoplankton, (c) organic detritus and (d) montmorillonite clay were studied for 4 days. Again, samples outside and within the dialysis sacs were filtered through 0.45 μm membranes. Results are shown in Table 8.10. Americium predominantly is found bound to organic detritus, plankton and clay.

Schell et al. (1980) report on laboratory determinations of K_d_{Am} in numerous fresh and marine water environments with sediments. Table 8.11 summarizes the results. The K_d s for freshwater environments are at least 2 to 3 times larger than marine environments. Further desorption experiments yield higher K_d values than sorption experiments by factors of 3 to 5 suggesting that once bound Am is not easily resolubilized.

Schell et al. (1980) studied the effects of organic ligands on nuclide sorption from a fresh water onto a lake sediments in the laboratory. Table 8.12 summarizes results for four elements. Three organics significantly increased the K_d_{Am} while one EDTA decreased the K_d_{Am} . Caution is needed in interpretation of these results since the concentration of organics used is quite high. Figure 8.10 shows the effect of varying EDTA concentration on K_d_{Am} for a different freshwater/sediment system. There is no effect on K_d until the EDTA concentration is raised to 10^{-4} M, which is extremely high for natural environments.

Schell et al. (1980) continued dialysis experiments using a Lake Michigan freshwater system. A sediment slurry, phytoplankton slurry and organic detritus slurry were placed in dialysis sacs. Spiked Lake Michigan water surrounded the dialysis sacs. After 20 the Am was predominantly found bound to particulates.

TABLE 8.9. Percent Distribution of Radionuclides After 11 Days of Dialysis Experiment

Compartments		²⁴¹ Am	¹³⁷ Cs	²³⁸ Pu	²⁰⁴ Pb	⁶⁵ Zn	⁶⁰ Co
Spiked Water	<0.22 μ m	26.1	86.3	77.7	64.4	44.7	54.2
	>0.22 μ m	8.2	0.0	3.0	0.0	0.8	0.8
Control Sac	<0.22 μ m	0.7	2.2	0.5	0.0	1.0	8.4
	>0.22 μ m	0.5	0.1	0.1	0.6	0.1	0.1
Sediment Sac	<0.22 μ m	0.0	2.1	0.2	0.0	1.1	1.4
	>0.22 μ m	47.1	1.6	9.2	22.3	25.8	30.5
Plankton Sac	<0.22 μ m	0.8	2.2	0.4	1.9	2.4	1.7
	>0.22 μ m	12.4	0.3	2.7	11.5	16.9	0.3
Samples during experiment		4.5	0.7	2.5	2.8	7.3	4.5
Miscellaneous apparatus		0.5	0.0	3.8	0.6	0.0	0.0

TABLE 8.10. Distribution (%) of ²⁴¹Am, ¹³⁷Cs, ¹⁰⁶Ru, ⁶⁵Zn, ⁶⁰Co and ⁵⁹Fe After 96 hr in a Dialysis Experiment

Radio-nuclide		Spiked Seawater cpm/ml $\pm$ 2 S D, %	Dialysis Chambers			
			Blank cpm/ml $\pm$ 2 S D, %	Plankton cpm/ml $\pm$ 2 S D, %	Clay cpm/ml $\pm$ 2 S D, %	Detritus cpm/ml $\pm$ 2 S D, %
²⁴¹ Am	Soluble	9	2	3	2	8
	Particulate	4	4	23	9	35
¹³⁷ Cs	Soluble	19	19	19	21	21
	Particulate	<0.2	<0.2	<0.2	<0.1	<0.2
¹⁰⁶ Ru	Soluble	13	16	17	18	13.2
	Particulate	0.9	0.9	11	4	3
⁶⁵ Zn	Soluble	24.8	21.7	17	21	9
	Particulate	<0.2	0.5	1.6	2	2
⁶⁰ Co	Soluble	21.7	24.3	8.4	19.5	24.4
	Particulate	0.1	0.2	0.7	0.5	0.2
⁵⁹ Fe	Soluble	14.7	4.7	6.7	5.2	8.4
	Particulate	8.0	5.3	14.7	17.7	14.6

TABLE 8.11. Summary of Adsorption/Desorption Distribution Coefficients with Properties of the Sediment/Water Systems

Station	pH	Hardness mg/l	Salinity g/g	Surface Area m ² /g	C mg/g dry	N mg/g dry	K _d ml/g											
							137Cs		45Sr		60Co		239Pu		241Am			
							AOS K _d × 10 ⁻²	DES K _d × 10 ⁻²	AOS K _d × 10 ⁻²	DES K _d × 10 ⁻²	AOS K _d × 10 ⁻⁴	DES K _d × 10 ⁻⁶	AOS K _d × 10 ⁻⁴	DES K _d × 10 ⁻⁵	AOS K _d × 10 ⁻²	DES K _d × 10 ⁻⁶		
Lake Michigan	7.90	143	<1		62.0	1.8	5.09	5.57	82.2	1.41	6.23	2.79	14.1	4.79	5.40	No equil.		
Lake Washington	7.8	42	<1	31.4 ± 6.2									12.0	3.00	1.63	5.22		
Climax River	7.92	158	<1		14.0	1.8	13.6		124.4	0.046	6.75		4.71	1.94	7.33			
Cattaraugus Creek		200	<1		16.8	0.8	No equil.		62.3		1.39		2.00		2.96			
Hudson River																		
MP 40	7.90	171	<1		34.4	1.8	4.01	3.65	73.7	0.49	3.92	2.62	0.93	3.60	1.			
MP 30	7.82	378	2-3		23.0	1.1	8.78	3.34	36.8		5.15	3.35	3.12	2.98	2.37	8		
MP 0	7.70	2963	15		31.8	5.2	3.56	1.79			4.63	3.29	3.87	3.21	2.96	21.73		
Shogit Bay																		
No. 1	7.70	6662	29.62	2.6 ± 0.6			1.87				3.61				2.60			
No. 4	7.70	6325	31.06	7.0 ± 1.6	13.7	1.6	3.53				4.51		10.3		3.80			
Columbia R. Mouth	7.8	6250	32.566	8.7 ± 2														
Staslow Inlet	7.88	5606	28.88				1.24				5.42		1.62	0.25	1.03	0.70		
Seasick Inlet	7.89	6316	31.243								4.42		7.40	3.99	4.94			
Lake Hittslet	7.8	6188	31.217	40.3 ± 3											3.71			
Rockwall Inlet	7.70	5325	31.06				0.65						4.40	1.74	2.94	>10		
Granite Inlet															1.91			
Lake Michigan		143	<1.0						75.2 (4.1)				2.99					
Shogit Bay		6662	29.6						60.3 (4.4)				1.34					

AOS = K_d determined in adsorption direction
DES = K_d determined in desorption direction

TABLE 8.12. Sediment/Water K_d Values for Lake Washington System as a Function of Different Organic Compounds

Organic Compound Added, Concentration	K _d			
	²⁴¹ Am (x10 ⁻⁴) (a)	⁵⁷ Co (x10 ⁻⁴) (a)	¹⁰⁶ Ru (x10 ⁻⁴) (a)	¹³⁷ Cs (x10 ⁻²)
None (i.e., control) x ± s (b)	2.28 ± 0.71	0.32 ± 0.03	1.09 ± 0.39	4.15 ± 1.00
1-nitroso-2-naphthol (10 ⁻⁵ M) x ± s (b)	7.76 ± 3.01	35.82 ± 18.07	2.61 ± 1.03	5.04 ± 0.69
1,10-phenanthroline (10 ⁻⁴ M) x ± s (b)	25.30 ± 2.44	16.81 ± 4.18	3.78 ± 0.03	3.22 ± 0.39
acetic acid (10 ⁻⁴ M) x ± s (b)	5.60 ± 2.43	0.44 ± 0.04	2.30 ± 0.84	2.70 ± 0.77
Salicylic acid (10 ⁻⁴ M) x ± s (b)	2.94 ± 1.04	0.30 ± 0.07	1.23 ± 0.48	3.77 ± 0.61
EDTA (10 ⁻⁴ M) x ± s (b)	0.05 ± 0.01	0.01 ± 0.01	3.45 ± 0.54	3.47 ± 0.76

(a) Significant differences between groups at α = 0.05 level by Kruskal-Wallis statistical test
(b) x and s correspond to the mean and one standard deviation unit, respectively.

Van Dalen et al. (1975) determined the batch K_d_{Am} for four geologic materials; caprock (gypsum), river sand (quartz), sandstone and clay (illite-kaolinite mixture) with 90% saturated NaCl solution at pH 7 to 8 using a solids to solution ratio of 100 mg/15 ml and correcting for nuclide sorption on the walls of the test tubes. The following K_d_{Am} values were obtained 3,000, 400, 20,000, 50,000 ml/g, respectively. The pH dependence on sorption processes for americium between pH 5 to 8 was minor.

Routson et al. (1975) used batch adsorption experiments (10 g soil to 25 ml solution) and 24-hr equilibrations to determine the K_d for americium with desert sand and an eastern sandy clay. The K_d was determined as a function of solution calcium and sodium concentration at an initial pH of 2.5 to

FIGURE 8.10. Effect of Varying EDTA Concentration on Kd Values of ²⁴¹Am. Values at 0 M, 10⁻⁸ M and 10⁻⁴ M EDTA are single point measurements. Values at 10⁻¹⁰ M and 10⁻⁶ M EDTA are the mean + one standard deviation unit for triplicate sample measurements.

3.1. For the sandy clay, $K_{d,Am}$ decreased as the calcium concentration increased. At 0.002M Ca the americium Kd was 67 ml/g; at 0.20M Ca the Kd was 1 ml/g. For the Burbank sand the Kd was greater than 1200 for all concentrations of calcium. The americium Kd for the sandy clay also was a function of the sodium concentration in solution; 280 at 0.015M Na and 1.6 at 3.00M Na. Although a final pH was not given, the Burbank sand is known to be alkaline, suggesting that americium adsorption may be sensitive to pH.

Fried et al. (1974a, 1974b) determined the adsorption of americium onto a basalt. Addition of salts to the solution lowered the adsorption of americium.

La^{+3} and Zr^{+4} cations lowered the americium adsorption much more than Sr^{+2} and Na^{+} suggesting ion exchange as the mechanism controlling adsorption of americium.

Sheppard et al. (1976) reported distribution between 12 characterized soils from various locations and a solution containing $^{241}\text{Am}(\text{III})$. The locations included Muscatine, Illinois; Richland, Washington; Barnwell, South Carolina; and Idaho Falls, Idaho. Equilibrations were for up to 4 months with sampling of the solution at intervals. The distribution results are given in Table 8.13. The distribution values ranged from 43,500 ml/g for an Idaho soil

TABLE 8.13. Americium 50-Day Distribution (Calculated from the Data of Sheppard et al., 1976)

<u>Soil Identity</u>	<u>Am Distribution, ml/g</u>	<u>Monthly Change in Distribution Ratio, %</u>
Muscatine silt loam	4,830	+13%
Burbank loamy sand	714	-13%
Ritzville silt loam	971	+1%
Fuquay sand, 0-5 cm depth	476	+32%
Fuquay sand, 5-15 cm depth	417	+32%
Fuquay sand, 15-50 cm depth	249	+27%
Hanford A	125	0%
Hanford B	833	+34%
Idaho A	3,920	+30%
Idaho B	43,500	+86%
Idaho C	37,000	+81%
Idaho D	10,900	+53%

to 125 ml/g for a Washington soil. The distribution values were not constant with time, but steadily increased 1% to 86%/month. With Burbank soil, there was a 13% decrease/month. No change was detected for another Washington soil (Hanford). It was postulated that such adsorption behavior was consistent with the Am(III) being in the form of charged colloids or hydrolysis products including Am^{+3} , $\text{Am}(\text{OH})^{+2}$, $\text{Am}(\text{OH})_2^+$ and $\text{Am}_n(\text{OH})_{2n}^{n+}$ and removal by cation exchange and adsorption. It was reported that the removal of soil organics and raising the system temperature did not appreciably affect the rate of approach to equilibrium or the distribution values. Analysis of the soil cation exchange capacity data indicated a high correlation ($r = 0.96$) between soil cation exchange capacity and clay content. Correlation does not appear as marked between soil clay content and americium distribution.

Glover et al. (1977) also studied americium sorption by soils. Seventeen characterized soils from around the United States were equilibrated for 48 hr with distilled water solutions containing 10^{-10}M Am and 10^{-8}M Am. Eight replicates were run per soil at each americium concentration. Results were expressed as Kd values. Kd values ranged from 82 to 10,000 on the different soils. Generally, the Kd values for 10^{-10}M and 10^{-8}M Am were the same, or nearly so, with some exceptions. Regression analyses were performed on the americium sorption data to determine whether or not significant relationships existed between americium sorption and soil physical or chemical characteristics. Initial results indicated that a direct relationship existed between soil cation exchange capacity, clay content and americium Kd value.

Polzer and Miner (1977) relate americium adsorption data on the same soils to differences in the effective positive charge of americium (Korotkin, 1972) as influenced by system pH. Kd values for americium with several soils from around the United States are given in basic and acidic systems.

Field Studies

Fowler and Essington (1974) detected a possible difference in solubility between americium and plutonium fallout in soils. Americium may be more soluble than plutonium and may become the radionuclide of prime concern because it has a faster migration rate in soils. Several instances of decreasing Pu/Am ratios with depth in the soil profile could be explained by differential plutonium and americium solubilities.

Bowen (1975) reviewed the distribution of americium in the marine environment and suggested americium may be more mobile than plutonium. Hetherington et al. (1975) measured the americium and plutonium concentrations in the top two centimeters of marine sediments around the Windscale nuclear power facilities effluent. The Am/Pu ratio in the sediments did not vary and there was no evidence that the ratio changed with distance from the outfall. It was concluded that the behavior of americium was qualitatively similar to plutonium. One core taken to 25 centimeters also gave supporting evidence that both plutonium and americium become incorporated into the sediments and remained fixed to the same extent. Variable ratios of Am/Pu from month to month and year to year in the outfall effluent may mask small differences in the mobility of these transuranics.

Nevissi and Shell (1975) reports on the distribution of americium around Bikini Atoll. Inside Bikini Lagoon surficial sediments contain 0.3 to 77.0 pCi $^{241}\text{Am/g}$ while the waters contain 5.5 to 24 pCi/m³ (~ 5.5 to 24×10^{-6} pCi/ml) which give a K_d_{Am} assuming system equilibrium of $\sim 10^6$ to 10^7 . Murray and Kautsky (1975) report the waters in the North Sea contain ~ 0.09 to 1.60×10^{-3} pCi/l ^{241}Am from nuclear fallout. The ecological behavior of americium in a freshwater waste pond on the Hanford Site has been reported by Emery et al. (1975). Results pertinent to migration of americium include the fact that 93% of the americium in the ecosystem is tightly bound to sediment particles and transportable only with the particles. Americium in the water column is low and associated with fine particles. Algal detritus concentrates americium to twice the value of sediments on a dry weight basis. Americium in the interstitial waters appear to be cationic in form. The average sediment americium concentration is 83 pCi/g while the water contained 1.1 pCi/l which gives a $K_d_{\text{Am}} \sim 8.3 \times 10^4$.

Edgington et al. (1975) concluded after studies of the concentrations of ^{241}Am with depth in Lake Michigan that there was little or no preferential mobility of americium over plutonium.

Summary

Schell et al. (1980) summarize their work on Am sorption in fresh and marine environments. In general Am sorption is greater in freshwater by a factor of 2 to 3. Also Am sorption is dependent on pH especially for marine environments. At neutral pHs Kd_{Am} is quite large, 10^2 to 10^6 ml/g. Soil science studies tend to corroborate the above generalities. Americium adsorption (Kd values) on various soils and sediments have been correlated with: 1) cation exchange capacity of soils (Sheppard et al., 1976; Glover et al., 1977) and 2) the concentration of the competing cations (Na^+ , Ca^{2+} , Sr^{2+} , La^{3+} and Zr^{4+}), so that the adsorption of americium decreases with an increase in concentration of competing cations (Fried et al., 1974a; Fried et al., 1974b; Routson et al., 1975; Sheppard et al., 1976; Fried, 1977). Although none of the workers have tried to distinguish the contributions of polymer adsorption, cation exchange, hydrolysis and precipitation to the Kd value, the laboratory data indicate that americium removal from solution may be controlled by pH-dependent hydrolysis-colloidal formation and ion exchange.

ANTIMONY

Natural Sediment and Rock Distributions

The average concentrations of antimony found in igneous and sedimentary rocks and sediments are given in Table 8.14. Little is known about the behavior of antimony during weathering. Antimony may accumulate in shales by adsorption on clay minerals and hydrous oxides such as Mn and Fe precipitates. Antimony may be concentrated in sediments relative to igneous rocks.

TABLE 8.14. Antimony Concentrations in Rocks and Sediments
(Turekian and Wedepohl, 1961)

Igneous, ppm				Sedimentary, ppm		
<u>Ultramafic</u>	<u>Basaltic</u>	<u>Granitic</u>	<u>Syenite</u>	<u>Shale</u>	<u>Sandstone</u>	<u>Carbonate</u>
0.1	0.2	0.2	0.1	1.5	0.01	0.2

Sediments				
<u>Pacific</u>	<u>Atlantic</u>	<u>Indian</u>	<u>Carbonates</u>	<u>Clays</u>
3.0	0.8	1.1	0.2	1.0

Brief Chemistry

The stable isotopes of antimony found in nature are ^{121}Sb (57.25%) and ^{123}Sb (42.75%). The radionuclides of interest in waste disposal include ^{124}Sb (half-life = 60.3 days) and ^{125}Sb (half-life = 2.7 years).

Antimony may exist in (-III), (0), (III) and (V) oxidation states, readily losing its 2(s) and 3(p) electrons. Ionic radii are Sb^{-3} 2.45 Å, Sb^{+3} 0.76 Å and Sb^{+5} 0.62 Å (Ahrens, 1952). The important antimony minerals include native antimony (Sb), stibnite (Sb_2S_3), jamesonite ($2\text{PbS} \cdot \text{Sb}_2\text{S}_3$), boulangerite ($5\text{PbS} \cdot 2\text{Sb}_2\text{S}_3$), kermesite ($\text{Sb}_2\text{S}_2\text{O}$) and senarmontite (Sb_2O_3). Stibnite is the most common antimony mineral.

Antimony, in the form of Sb^{+3} , forms complexes such as $\text{Sb}(\text{OH})_2^+$, $\text{Sb}(\text{OH})_4^-$, SbCl_3OH^- , SbCl_5^{2-} and SbS_3^{3-} (Sillen and Martell, 1964). The existence of simple Sb^{+3} and Sb^{+5} is unlikely. Further, Sb is amphoteric.

Sb^{+3} , for example, reacts as $\text{Sb}_2\text{O}_3 + 3\text{H}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{Sb}(\text{OH})_4^-$ in bases, and in acids, $\text{Sb}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{H}^+ \rightarrow 2\text{Sb}(\text{OH})_2^+$. Sb^{+5} dissolves in strong acids forming complexes such as SbCl_6^- , and in strong bases forms complex antimonides such as $\text{Sb}(\text{OH})_6^-$ (Latimer, 1952). SbCl_3 dissolves in a limited amount of water to give a clear solution which, upon dilution, precipitates insoluble oxochlorides such as SbOCl and $\text{Sb}_4\text{O}_5\text{Cl}_2$ (Cotton and Wilkinson, 1962). Izrael et al. (1969) mentioned that ^{125}Sb was amphoteric, with a solubility minimum at pH 7.0.

Solution Equilibria

The relative activity of various solution species in equilibrium with $\text{Sb}_2\text{O}_3(\text{s})$ is given in Figure 8.10. If equilibrium with $\text{Sb}(\text{OH})_3(\text{s})$ is assumed, the activity of all the species would be approximately 2.9 log units lower with the lines still parallel to the lines given in Figure 8.11. Thermodynamic data for $\text{Sb}(\text{OH})_2^+$ were obtained from Baes and Mesmer (1976) and all the other data were selected from Wagman et al. (1968a,b). In the environmental pH range of interest (4 to 8), for either fresh or marine waters HSbO_2^0 and $\text{Sb}(\text{OH})_3^0$ are the species that would govern the total activity of antimony present in solution. The other species [SbOF^0 , $\text{Sb}(\text{OH})_2^+$, SbO^+ , $\text{Sb}(\text{OH})_4^-$ or SbO_2^- and $\text{NH}_4\text{SbO}_2^0$] do not contribute significantly to the total antimony present in the solution and hence can be ignored. Since the predominant solution species [HSbO_2^0 , $\text{Sb}(\text{OH})_3^0$] are neutral, ion exchange as an antimony adsorption mechanism is not expected to be important.

Laboratory Adsorption Studies

There have been no laboratory studies reported in the literature addressing antimony sorption onto aquatic sediments.

Field Studies

Cerrai et al. (1970) reported on the ^{125}Sb concentration of surface sediments in the Adriatic and Ligurian Seas. The sediments were separated into $<100 \mu\text{m}$ and $>100 \mu\text{m}$ fractions. The observed concentrations were <0.11 and $<0.15 \text{ pCi Sb/g dry sediment}$ for the Adriatic Sea and for the total

FIGURE 8.11. The Activity of Various Antimony Species in Equilibrium with $\text{Sb}_2\text{O}_3(\text{s})$ (cubic) with $\text{pH}_4^+ = 3.0$ and $\text{pF}^- = 4.5$. Oxidation-reduction changes do not affect the concentration of species reported in this figure.

Ligurian Sea sample 0.433 pCi/g. Unlike many metallic radionuclides (Eu, Cs, Ce, Sr) the coarse fraction did not exhibit much lower concentrations possibly suggesting Sb is not preferentially bound by clays.

Perkins et al. (1966) and Haushild et al. (1973b) report that most of the radionuclides introduced into the Columbia River at Hanford were in a dissolved state but quickly became associated with particulate phases such as suspended matter, aquatic biota and bottom sediments. At Vancouver, Washington, 425 km downstream the ^{124}Sb remaining was found to be >90% in the dissolved state. Evans (1973) found no suggestion that any Sb sorbed on suspended matter reaching the mouth of the Columbia River would desorb upon contacting sea water. His hypothesis was that antimony was basically present in the soluble phase and travelled without reacting through the estuarine region. Nelson et al. (1966) reports that antimony found in solution near the estuary is mainly uncharged (84%).

Robertson and Perkins (1975) report on the physicochemical states of antimony in a waste trench which directly receives N-Reactor cooling water (Hanford, Washington) and in spring seepage waters on the banks of the Columbia River. The trench water feeds the springs after a few hundred foot travel through coarse sands. The total concentration and percent of each antimony isotope found in the particulate (will not pass 0.3 μ m filter), cationic (sorbs on cation resin), anionic (sorbs on anion resin) and nonionic (passes through whole system) for trench and spring waters are shown in Table 8.15.

TABLE 8.15. Activity and Percentages of Antimony Isotopes

	Trench Water		Spring Water	
	dpm/l	%	dpm/l	%
^{122}Sb				
Particulate	410	>17.4	<0.03	—
Cationic	<270	<11.2	<0.2	—
Anionic	1160	>48.1	<1.0	—
Nonionic	<u>560</u>	>23.2	<u>0.2</u>	—
TOTAL	~2410		<1.43	
^{124}Sb				
Particulate	74	>29	<0.04	<0.09
Cationic	<90	<35	<0.2	<0.5
Anionic	59	>23	2.2	5.4
Nonionic	<u>34</u>	>13	<u>38.3</u>	94.5
TOTAL	<257		~40.7	
^{125}Sb				
Particulate	<100	---	<0.05	<0.06
Cationic	<200	---	<0.3	<0.3
Anionic	80	---	3.8	4.2
Nonionic	<u>55</u>	---	<u>86.4</u>	95.8
TOTAL	<435		~90.2	

In the trench water antimony is partitioned mainly as anionic and particulate; however, upon reaching the springs the nonionic form predominates, showing its mobility in soils. Overall, the antimony shows about 80% sorption in the soil.

Israel and Rovinskii (1970) measured the chemical states of fission products in bomb crater water and reported that ^{125}Sb was 85% anionic, 8.5% cationic, and 6.5% colloidal.

Movement of ^{125}Sb from trenches and seepage pits in the Melton and Bethel Valleys, Oak Ridge, Tennessee, to White Oak Creek was investigated by Duguid (1975, 1976). Typical results are given in Table 8.16. Relatively minor amounts of the ^{125}Sb are found in the ground water or seepage water compared to the amounts located on the soil. Similar ^{125}Sb values for burial ground 4 in Melton Valley showed a range of from 1.0 to 1.3×10^{-2} dpm/ml in the ground water and seepage water. This also represents a relatively minor antimony movement from the soil in the ground water. Computed antimony Kd values ranged from 10^3 to 10^6 ml/g.

Magno et al. (1970) investigated the fate of the radionuclides from the Nuclear Fuel Services plant in western New York state. The plant lagoon system waters and soils were sampled and analyzed. They estimated from these data that approximately 90% of the ^{125}Sb in the plant effluent passed through the lagoon system and into nearby surface streams. Ninety-eight percent of the ^{125}Sb was described as "dissolved" (in solution), exiting from the last lagoon. The antimony is not, therefore, associated with suspended solids, but is in solution, as Figure 8.11 postulates that it should be.

Saas and Grauby (1973) studied the transfer mechanisms of ^{124}Sb found in reactor cooling water and other wastes to river, irrigated soil and ground water. The river water contained organomineral pollution in the form of industrial and municipal sewage wastes that interacted with the ^{124}Sb to form chelates, an exchangeable fraction and hydrosoluble components defined as the totality of the organic and mineral components of a soil that are soluble in water. The percentage of the above hydrosoluble ^{124}Sb fraction was plotted versus depth in cm for an alluvial, calcareous soil column receiving

TABLE 8.16. ^{125}Sb Analysis of Water and Soil Samples from a Seep Near Trench 7 (Duguid, 1976)

<u>Sample Date</u>	<u>Water Samples Count Rate, dpm/ml</u>
3-5-73	≤ 2.0
3-19-73	≤ 4.0
5-11-73	6.7

<u>Depth</u>	<u>Soil Samples Count Rate, dpm/g</u>
0 to 3	≤ 690
3 to 6	≤ 240
6 to 9	≤ 120
9 to 12	≤ 41
12 to 15	≤ 18
15 to 18	< 13
18 to 21	< 9.7

^{124}Sb in river water. Ten to 30% of the ^{124}Sb was in the hydrosoluble form. The point of this work was the demonstration that interactions between pollutants in the river water and ^{124}Sb results in increased antimony migration. These pollution interactions with radionuclides should be addressed in nuclear reactor siting studies.

Summary

The principal aspect of antimony chemistry that governs its adsorption reactions with sediments and rocks over the pH range 4 to 8 is the prevalence of neutral and complexed species. Low K_d values are found with relatively rapid migration through soils (Robertson and Perkins, 1975) and surface waters

(Magno et al., 1970). In low redox conditions ($O_2 < 10^{-35}$ atmospheres), antimony trihydroxide may precipitate and may be a stable compound that controls antimony concentrations. Many of the antimony species associated with organopollutants are water soluble (Saas and Grauby, 1973) and migrate readily with the water. Thermodynamic data on the antimony complexes formed with soil organic materials do not exist at present because the complexes are chemically poorly defined and, in many cases, unknown. The high retention of Sb at Oak Ridge conflicts with the above information.

CARBON

Natural Sediment and Rock Distributions

Carbon is found in geologic materials in several forms: "elemental" as in graphite, diamond; "combined" as in carbonates; and "organic" as in plant and animal detritus. Carbon is unique in forming an almost infinite number of compounds, often linking carbonation to carbonation. In general, sedimentary materials contain 20 times as much carbon as magmatic material (Wedepohl, 1969).

Parker (1967) reports the following average concentrations of carbon in rocks: igneous, 320 ppm; sandstone, 13,800 ppm; shales, 15,300 ppm; and carbonates, 113,500 ppm. Most oceanic sediments also contain 2 to 3% organic matter which is high in carbon.

Brief Chemistry

There are two stable isotopes of carbon ^{12}C (98.89% abundance) and ^{13}C (1.11% abundance). Carbon-14 is the only radioactive isotope with a $t_{1/2}$ greater than 20 minutes. Its $t_{1/2}$ is 5730 years. Carbon-14 is produced naturally in the upper atmosphere by cosmic ray bombardment of ^{14}N . The steady-state ^{14}C budget on earth is 2.70×10^8 curies with 91% found residing in the ocean (Riley and Skirrow, 1965). Atmospheric bomb testing added 5×10^6 curies to the natural pool. For brief periods in 1962-63 this additional source increased the natural $^{14}\text{C}/^{12}\text{C}$ ratio in the atmosphere by two times. The annual production rate of ^{14}C by cosmic rays is 2.8×10^4 curies. The ocean is the great scavenger of ^{14}C by the gaseous exchange of CO_2 . Once in the ocean 90% of the ^{14}C becomes bicarbonate ions (Riley and Skirrow, 1965). A small portion of ^{14}C becomes entrapped in biological life. Wedepohl (1969) estimates the annual production of organic carbon to be 10^{11} metric tons. Carbon-14 has been measured in nuclear reactor effluent waters in low concentrations (<1 to 34 pCi/ml, Dames and Moore, 1978). Although the contribution from reactors is infinitesimal compared to natural sources a chronic release of this biologically active agent could potentially create an isolated hazard.

Solution Equilibria

Carbon can be found in all valence states from -4 to +5. In waters inorganic carbon is predominately found in the +4 valence state as HCO_3^- or CO_3^{2-} . The mean composition of river waters in North America contains 68 ppm bicarbonate (Wedepohl, 1969). Sea water contains 28 ppm inorganic carbon or 103 ppm bicarbonate (Riley and Skirrow, 1965). The range of organic carbon found in sea water is 0.2 to 2.7 ppm. Thus, most ^{14}C could be assumed to be present as carbonate species and be capable of escape to the atmosphere as $^{14}\text{CO}_2$ also. Reactor-derived ^{14}C formed by activation has not been studied in any detail to identify the speciation at production.

Laboratory Adsorption Studies

There were no experimental studies of ^{14}C sediment-suspended solids adsorption identified in the literature search.

Field Studies

Foster (1973) and Baranov and Khitrovi (1966) reported that the oceans contain on the average 0.1 pCi/l of ^{14}C .

Suess and Bien (1973) reported on the ^{14}C surveys of the oceans conducted by the Scripps Institution of Oceanography. As it takes 55 gallons of sea water to process one sample it is little wonder that few persons have studied ^{14}C in the environment.

Summary

Very little data are available on ^{14}C fate after release from nuclear power generation activities. It appears that the effluent levels are 10^3 to 10^4 times as large as natural sea-water values. As carbon can be assimilated into biological tissues, chronic releases in isolated areas could lead to biological concentration. Most likely the large amount of stable carbon would hold the bioconcentration at the specific activity level present in the area.

CERIUM

Natural Sediment and Rock Distributions

The abundance of cerium in rocks and sediments is given in Table 8.17. Cerium generally increases in concentration from basaltic to granitic rocks. In a study of Russian platform soils, it was found that the soils with highest cerium contents were alkaline, suggesting precipitation as the hydroxide. The acid soils were lower in cerium because cerium had been removed and had migrated. Sediments derived from granitic rocks could be expected to show the highest cerium contents if the weathering resulted in an alkaline environment. Vinogradov (1959) gave the average cerium content of soils as 50 ppm. Half, or more, of the cerium in rocks is found in accessory minerals such as apatite,

TABLE 8.17. Cerium Abundance in Rocks

Type	Ce, ppm	Reference
Continental basalts	59	Frey et al., 1968
Kimberlite	119	Burkov and Podporina, 1966
Ultramafic	0.1	Turekian and Wedepohl, 1961
Basaltic	48	Turekian and Wedepohl, 1961
Granitic, high Ca	81	Turekian and Wedepohl, 1961
Granitic, low Ca	92	Turekian and Wedepohl, 1961
Syenites	160	Turekian and Wedepohl, 1961
Shales	59	Turekian and Wedepohl, 1961
8616 Russian platform shales	67	Ronov et al., 1967
6051 Russian platform sandstones	33	Ronov et al., 1967
11205 Russian platform limestones	6.5	Ronov et al., 1967
Average of above	57	Ronov et al., 1967
Sandstones	92	Turekian and Wedepohl, 1961
Dolomite and limestones	11.5	Turekian and Wedepohl, 1961
Brown Clay SAM	56	Wildeman and Haskin, 1965
Manganese Nodule, Hawaii	518	Goldberg et al., 1963
Marine carbonates	35	Turekian and Wedepohl, 1961
Marine clays	345	Turekian and Wedepohl, 1961

while the remainder also substitutes for calcium but only in the main stage minerals such as plagioclase. Marine clays appear to concentrate cerium compared to parent rock material.

Brief Chemistry

Cerium occurs naturally in four stable isotopes shown in Table 8.18. The radioisotopes ^{141}Ce and ^{144}Ce are both present in radioactive wastes as fission products with half-lives of 33 days and 284 days, respectively. After 100 yr, little fission product cerium remains.

TABLE 8.18. Stable Isotopes of Cerium

<u>Isotope</u>	<u>Natural Abundance, %</u>
^{136}Ce	0.15
^{138}Ce	0.25
^{140}Ce	88.5
^{142}Ce	11.1

The usual oxidation state of cerium is tripositive with ionic radius of $1.03 \text{ \AA}$ (Ahrens, 1952).

The solubility product of Ce(III) hydroxide was given by Vickery (1953) as 1.5×10^{-20} . For comparison, the solubility products of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ are 3.7×10^{-5} and 3.8×10^{-38} , respectively (D'Ans and Lax, 1967).

In geologic environments, cerium forms weak complexes. The most important and the most common cerium minerals include monazite (light rare earths, Th) PO_4 and bastnaesite (light rare earths, Th) FCO_3 . Many other cerium-containing minerals exist but most are relatively rare.

Solution Equilibria

The activity of soluble cerium species assuming solid CePO_4 are shown in Figure 8.12. Trivalent cerium species in increasing order of importance are CeCl^{2+} , CeNO_3^{2+} , CeF^{2+} , Ce^{3+} , and CeSO_4^+ . Thus, CeSO_4^+ would be the most dominant solution species in the environmental pH range of interest (ph 4 to 8) for both fresh and marine waters.

FIGURE 8.12. The Activity of Various Cerium Species in Equilibrium with $\text{CePO}_4(\text{s})$ in an Oxidizing Soil Environment [$p\text{O}_2(\text{g}) = 0.68 \text{ atm}$], $p\text{F}^- = 4.5$, $p\text{Cl}^- = p\text{SO}_4^{2-} = 2.5$, $p\text{NO}_3^- = 3.0$ and $p\text{H}_2\text{PO}_4 = 5.0$

Laboratory Adsorption Studies

Baranova and Polikarpov (1966) studied the adsorption/desorption of cerium on sediments from the Black Sea. The sediments showed a large adsorptivity for cerium, cesium and zirconium when compared to strontium and ruthenium. Sea water desorbed little of the adsorbed cerium, but 0.2 M HCl removed much of the adsorbed cerium.

Collet et al. (1968) studied the adsorption of cerium on Rhine River silt. The sediments were separated into three fractions (sand, clay and organic material) to obtain conclusions on the effect of the individual constituents. Data are available in German.

Dawson and Duursma (1974), Duursma and Gross (1971), Duursma and Eisma (1973), and Duursma, Parsi and Statham (1974) determined the sorption/desorption of cerium onto marine sediments. Cerium added to sea water shows a great

affinity to adsorb onto sediments. In Appendix 4 Duursma and Eisma (1973) report log K (unitless) values and t 1/2 (half period of sorption) for numerous sediments. A summary of cerium results are included in Table 8.19.

TABLE 8.19. Cerium Data

<u>Sediment</u>	<u>log K</u>	<u>Kd (est), ml/g</u>	<u>t 1/2</u>
Atlantic Ocean	5.0 $\pm$ 0.4	1.5 $\times 10^5$	8.1 $\pm$ 6.5
Pacific Ocean	4.8 $\pm$ 0.3	9.5 $\times 10^4$	13 $\pm$ 8
Indian Ocean	4.5 $\pm$ 0.5	4.7 $\times 10^4$	
Baltic Sea	4.8 $\pm$ 0.1	9.5 $\times 10^4$	4.4
North Sea	4.8 $\pm$ 0.5	9.5 $\times 10^4$	
Mediterranean Sea	4.6 $\pm$ 0.3	6.6 $\times 10^4$	7.1 $\pm$ 3.5
Black Sea	4.5 $\pm$ 0.6	4.7 $\times 10^4$	
Red Sea	5.4	3.8 $\times 10^5$	

The cerium was not readily desorbed even with treatment in 1M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ at pH 5.4 (50% removed) but 1M acetic acid pH 2.3 removed 90%. The adsorption of cerium appears to involve precipitation (pH-dependent hydrolysis) more than ion exchange. In other studies of sorption onto Black Sea sediments under oxidizing and reducing conditions Duursma found Kd of 9×10^4 and 1×10^4 (unitless volume basis), respectively.

Doshi et al. (1973) studied the adsorption of cerium from sea water on manganese oxide precipitated in situ. All cerium present in solution co-precipitated.

Garder and Skulberg (1964) studied the adsorption of cerium onto post glacial marine clay taken from the Nitelva River (Norway). The clay fraction (20%) was mica and the remaining silt sized material 40% quartz and 40% feldspar. The cation-exchange capacity was 6.9 meq/100 g. The cerium (~ 1 pCi/ml) was added to distilled water. Ground sediment (<200 mesh) was shaken in the traced water at concentrations between 16 to 256 ppm sediment. The sorption of cerium versus time (1 to 9 days) was observed for the 64 ppm clay suspension. After 2 hr 60% of the cerium was adsorbed but after 1 and 9 days an

unexplained drop to 33% and 26% was observed. The K_d_{Ce} versus suspended sediment concentrations after 24 hr are shown in Table 8.20. The dependence on sediment concentration may indicate nucleation of cerium precipitation. For true ion exchange at trace cerium levels the K_d should be independent of sediment concentration. Hirano et al. (1973) performed extensive studies of the physicochemical behavior of cerium in sea water.

TABLE 8.20. K_d_{Ce} onto Post-Glacial Clay from Distilled Water

<u>Sediment Present,</u> <u>ppm</u>	<u>K_d, ml/g</u>
16	14,200
32	13,200
64	7,800
128	5,100
256	4,600

An investigation was performed on the nature of chemical species and existing states of radioactive cerium in sea water by means of filtration, ion exchange and solvent extraction with carrier-free ^{144}Ce as a tracer in pursuit of the physicochemical behavior and its effect on biological concentration. From the results of the experiments it was concluded that: radioactive cerium added into sea water exists mainly in dissolved forms and 20 to 25% of cerium becomes particulate forms having a diameter more than $0.01 \mu m$ after the aging for 40 days. Almost all of the radioactive cerium exists as ionic species in sea water or easily dissociated into ionic forms even after being associated with other anions present in sea water; although the ionic forms or easily dissociable species are the dominant existing states in the sea water with lowered pH below 6, radioactive cerium is hydrolyzed slowly when the pH is greater than 6 and forms complexes with hydroxide or chloride ions in sea water or changes to polymerized forms. It was reported that the residence time of natural cerium in the sea is about 80 years and the precipitate formed for natural cerium is CeO_2 . Therefore, it is inferred that the equilibrium between natural cerium and radioactive cerium added in sea water is achieved after a considerable time. Hirano et al. (1973) suggested that many of the

laboratory K_d values reported might be inflated because of outright precipitation of excess tracer. At any rate cerium concentrations in natural waters should be very small as predicted by the thermodynamic figure.

Kuznetsov and Schebetkovskii (1971) and Schebetkovskii and Kuznetsov (1971) determined the sorption/desorption of ^{144}Ce in sea water onto foraminiferal, diatomaceous, and iceberg silt and red shallow-water clays. The cerium added to sea water was allowed to equilibrate 24 hr before contact with sediments such that precipitates would settle. The $K_{d,\text{Ce}}$ values for the four sediments were 5×10^5 , 9×10^3 , 0.35 to 3.5×10^5 and 1 to 5×10^6 ml/g, respectively.

The sediment to water ratio was varied from 10^{-4} to 10^{-3} g/ml during this experiment. Leaching of cerium from the contaminated sediments showed a degree of irreversibility with each $K_{d,\text{Ce}}$ desorption being about twice as large.

Pirs (1974) determined the sorption capacity on humus material, calcite and dolomite for cesium, strontium, and cerium by static and dynamic measurements. The dependence of the equilibrium concentration on the solution pH, the presence of foreign salts and the stability of the fixation of the above-mentioned ions has been investigated. The elution curves for cesium, strontium and cerium from the humus material, sand, calcite and dolomite with water, salt solutions and acids were calculated.

Several investigations have been performed on the interaction of cerium with organic complexants [Bovard et al. (1968), Brown et al. (1969), Essington and Nishita (1966), Kulikov (1968), and Kulikov and Molchanova (1972)]. Bovard found cerium humic complexes formed more readily than iron, manganese, cobalt, ruthenium, strontium or cesium complexes and may be significant in the movement of fission products in geologic environments especially in light of the high retention of inorganic cerium by soils and sediments.

Brown et al. (1969) performed systematic studies on the formation of radiocolloids by ^{144}Ce and adsorption of Ce by humic acid-bentonite clay mixtures. Ionic strength, cerium concentration and pH were important factors affecting the distribution between colloids and monomeric cerium. At low ionic strength and cerium concentration and high pH more radiocolloids are

formed. At low ionic strength 10^{-3} M and pH 6.5, 90% of the cerium in a solution was found to be colloidal. Humic acids absorb more cerium than bentonite clay in a calcium dominated system but in a potassium-dominated system sorption was comparable. At environmental pH's most humic substances are insoluble and thus cerium bound to humate should remain immobile provided biological degradation of the organic matter is slow.

Nishita and Essington (1967) observed the effects on cerium movement of flushing 10^{-4} M solutions of organic chelators through contaminated soils. Cerium bound to soils is little affected by water or EDDHA flushing, and only slightly affected by EDTA and DTPA flushing, signifying strong sorption to soils. As the concentrations of organic chelators in nature seldom reach 10^{-4} M remobilization of sorbed cerium by organics may be minimal.

The adsorption capacity of the bottom deposits and surface suspension, collected in different portions of the Indian Ocean, was investigated by Gromov et al. (1972). It was established that various groups of sorbents studied can be arranged in the following series according to the degree of their adsorptive capacity: bottom deposits, Foraminifera > surface suspension > zooplankton. Regardless of the nature of the sorbent, radio-cerium is adsorbed most effectively from sea water ($K_d > 10^{-6} - 10^7$). Jenne and Wahlberg (1968) studied the adsorption of cerium identified as radiocolloid formation. Cerium sorption was not related to competing ion concentration in solution. As the sorption was more related to precipitation reactions the data could not be reduced to selectivity coefficients (see section on mechanisms) and was not reported. Nishiwaki et al. (1972) studied the adsorption of cerium onto estuarine sediments as a function of chlorosity and pH. Neither pH (5.3 to 8.12) nor chlorosity (0.1 to 19 g/l) significantly changed cerium sorption for sand. For silt and clay the low pH-low salinity water showed the lowest K_d . Most likely the pH 5.3 reduced cerium hydrolysis and precipitation. Figure 8.13 shows the $K_{d_{Ce}}$ for coarse material was $\sim 10^3$ and 10^4 for fine sediment. Taratani and Misumi (1962) studied the adsorption of cerium on suspended matter in river water and sea water. Between pH 6 to 8, 90% of the cerium

present in solution was adsorbed onto suspended sediments present at <1 g/l. For some materials, kaolinite and calcite, cerium adsorption increased with pH increases. Adsorption of cerium followed a Freundlich adsorption isotherm.

FIGURE 8.13. Distribution Coefficient of ^{144}Ce in Sediment

Nishita et al. (1966) studied five soils and two clay minerals in systems with ^{144}Ce . Pretreatment of bentonite with dilute acid gave much less cerium uptake by the clay than the untreated bentonite. The hydrogen ion was more strongly adsorbed than ^{144}Ce . The pH of the leaching solution had a profound effect on release of cerium by the soils. At pH values less than 5, 99.5% recoveries of ^{144}Ce were reported.

Rhodes (1957b) studied the uptake of ^{144}Ce on a Hanford soil as a function of pH. The K_d values rose steadily from 3.0 at pH 1.6 to >1980 at pH 6.1. The K_d then decreased to a minimum of about 100 at pH 10 and increased again to >1980 at pH 12 and above. The reduced uptake by soil of cerium between pH 7 to 12 did not occur in the presence of macroconcentrations (3M) of sodium

ions. Thus, the ^{144}Ce was present either as a radiocolloid in this region, which was flocculated by the high concentration of sodium ions, or as an ion species that was altered by the sodium ions to increase uptake by the soil. The complete removal of $4.2 \times 10^{-2}\text{M}$ cerium at pH 5.5 to 6 was reported, which at this concentration exceeded the capacity of the soil by ten times. The precipitation of cerium hydroxide was indicated.

Benson (1960) reported that cerium adsorbed on the soil could not be exchanged above pH 7.4 and was difficult to exchange at pH 5.5 to 7.4. The fraction of cerium exchanged by barium at pH 5.5 was 10% and virtually none at pH 7.4. All of the cerium could be removed by ion exchange at pH 2.2, with less removal as a function of pH to 7.4 when none of the cerium was exchangeable from the soil. Above pH 7.0, the presence of 0.5M alkali metal cations and 0.25M alkaline earth metal cations did not affect cerium removal from solution by soil. Below pH 3.0, the adsorption of cerium was depressed similarly by accompanying salts, implying that the cerium is ionic below pH 3.0 and removed by ion exchange on the soil.

Benson (1960) reported that the soil uptake of cerium added as Ce(III) was identical to that added as Ce(IV). However, when an oxidizing agent (NaBiO_3) was added, uptake of Ce(IV) increased to 99% at pH 1, while only 58% of the Ce(III) was adsorbed at this pH. Benson concluded that the absence of sufficient holding oxidant resulted in an immediate reduction of Ce(IV) to Ce(III) by contact with the soil.

Kampbell (1964) investigated ^{144}Ce uptake by colloidal suspensions of kaolinite, illite and montmorillonite type clays, all of which had a high affinity for ^{144}Ce . Only under very acid conditions did the cerium remain in solution. DPTA also was effective in keeping cerium in solution at trace levels.

Field Studies

Cerrai et al. (1965, 1967, 1970) reported on the concentration of fallout cerium isotopes in the Ligurian and North Adriatic Seas. The North Adriatic Sea sediments were split into two size fractions ($<100\ \mu\text{m}$ and $>100\ \mu\text{m}$). The amount of cerium in the fine fraction was significantly greater than the

coarser fraction, i.e., 2.31 to 3.61 pCi/g versus 0.16 pCi/g. The average ^{144}Ce concentrations in the North Adriatic and Ligurian Seas were 1.4 and 1.7 pCi/g, respectively.

Juguet et al. (1966) measured the concentration of radio cerium in waters and sediments in French rivers. The sediments were partitioned into sand, clay and organic matter. Cerium is almost totally fixed to sediments in the French river systems studied.

Nagaya and Saiki (1967) analyzed 19 samples of sediment from Tokyo Bay and found cerium content in fine mud to be much greater than in sand. Relative to strontium the distribution of cerium between sediment and water is much greater towards the sediment.

Ruf (1968) studied the concentration of fallout and reactor nuclides in fresh water within Bavaria. In sludge behind river dams Ruf found the ^{144}Ce activity reached 12,000 to 15,000 fold the concentration in water.

Spitsyn et al. (1973) studied the adsorption of ^{144}Ce in Indian Ocean bottom sediments. The best adsorbent for cerium was fine aleuritic radiolarium mud and the extraction mechanism was hypothesized to be trapping of colloids and true adsorption of dissolved cerium.

Magno et al. (1970) determined the forms and relative mobilities of radio-nuclides from the lagoon system of the Nuclear Fuel Services plant in western New York State. They reported that 0.02 Ci of ^{144}Ce were discharged from the last lagoon from May to October 1969. None of the discharged ^{144}Ce activity was dissolved in the water. All of the ^{144}Ce activity discharged was found in the suspended solids. Approximately 8.5 Ci of ^{144}Ce were discharged from the plant to the lagoon system over the same time period (May-October 1969). Thus, although all of the cerium was in particulate form, about 3% migrated through the lagoon system in the form of suspended solids.

Eichholz et al. (1967) studied the fractionation of several radioactive elements between several natural waters and the suspended solids contained in them. The results gave an indication of the ability of cerium to migrate as a suspended solid or adsorb on the suspended solids already present in most

natural waters. The suspended solids are characterized in Table 8.21. The most obvious relationship is a direct one between the suspended solids content and cerium adsorption. However, there also is a suggestion of an inverse relationship between cerium adsorption and solution pH. At the lower pH, more of the cerium should be present as cationic species and hence better able to adsorb on the suspended solids. It should also be pointed out that the Lodgepole Creek solids are largely montmorillonite, a high exchange capacity clay mineral.

TABLE 8.21. Adsorption of ^{144}Ce on Suspended Solids
(Eichholz et al., 1967)

<u>Water Source</u>	<u>^{144}Ce Removed, %</u>	<u>Suspended Solids, mg/l</u>	<u>Dissolved Solids, mg/l</u>	<u>pH</u>
Colorado River	72.0	299	350	7.5
Camp McCoy	44.6	12	60	6.9
Bayou Anacoco	36.9	24	63	6.2
Lodgepole Creek	96.9	965	200	6.8
Chattahoochee River	26.1	131	31	7.3

Summary

In all aquatic environments Ce(IV) and its complexes would have insignificant effects on cerium concentration (Figure 8.12). Thus, cerium would be expected to be present as Ce(III) (Figure 8.12 and Ahrens, 1952; Bensen, 1960). In the absence of strong complexing ligands, and especially in acidic environments, cerium would be expected to be present as Ce^{3+} (Figure 8.12; Bensen, 1960) and ion exchangeable. The increase in pH has been shown to increase the cerium adsorption. As expected, the presence of complexing ligands such as DTPA increases cerium concentration in solution and reduces adsorption. In slight acidic (pH 6.5) to alkaline conditions, cerium is thought to be present as radiocolloid which has been shown to increase adsorption. Cerium adsorbed on suspended solids has been shown to migrate in field and laboratory studies

(Magno et al., 1970; Eichholz et al., 1967). However, this type of movement would be expected to be dependent upon the particle size of the suspended solids and the pore size distribution of soils and rocks.

Adsorption experiments in general show high adsorption K_d (10^4 to 10^6) with precipitation and colloid formation probable mechanisms. Depression of K_d by high salt competition is not apparent or at least not significant.

CESIUM

Natural Sediments and Rock Distribution

The cesium content of several geologic media is given in Table 8.22. In general, cesium is enriched in the potassium minerals, although enrichment may only consist of a few hundred ppm cesium. The large size of the cesium cation makes it difficult for it to substitute in crystal positions normally occupied by potassium, its nearest geochemically abundant, alkali metal relative. Hence, cesium often becomes concentrated enough to form its own mineral phase (pollucite).

TABLE 8.22. Cesium Content of Rocks and Sediments

<u>Rock Type</u>	<u>Cs Content, ppm</u>	<u>Reference</u>
Basalt (estimated average)	1.1	Turekian and Wedepohl, 1961
Basalt (estimated average)	1.7	Heier and Adams, 1964
Basalt (estimated average)	1.0	Taylor, 1964
Basalt (estimated average)	1.0	Taylor and White, 1966
Granodiorite	3.0	Heier and Adams, 1964
Granite	6.8	Heier and Adams, 1964
Granite	5.0	Taylor, 1964
Granites, Russia	5.5	Beus and Fabrikova, 1961
Marine shales	5.0	Horstman, 1957
Sandstone	1.0	Horstman, 1957
Limestone	1.0	Horstman, 1957
Modern sediments	6.0	Horstman, 1957
U.S. stream sediments	2.6	Sreekumaran et al., 1968
Marine sands	1.0 to 3.2	Hirst, 1962
Marine clays	7.9 to 13	Hirst, 1962
Marine carbonates	0.4	Turekian and Wedepohl, 1961

Brief Chemistry

The only stable isotope of cesium is ^{133}Cs . Fission product cesium radioisotopes include four main cesium isotopes, with only ^{134}Cs , ^{135}Cs and ^{137}Cs (half-lives of 2.05 years, 3×10^6 years and 30.23 years, respectively) of significant concentrations 10 years after separation from PWR (Pressurized Water Reactor) fuels (Schneider and Platt, 1974). Pollucite, $(\text{Cs}, \text{Na}) (\text{AlSi}_2\text{O}_6) \times \text{H}_2\text{O}$ containing 22 to 36 wt% cesium, is the only independent cesium mineral of any importance.

In all its natural compounds, cesium occurs as a monovalent cation with a radius of $167 \text{ \AA}$ (Ahrens, 1952). There is little, if any, tendency for cesium to form complexes in natural environments, and the solubility of most cesium compounds in water is very high.

Solution Equilibria

Baes and Mesmer (1976) reported that cesium may be associated with OH^- ions in solution and that the extent of this association cannot be estimated accurately. Charlot (1957) reported that cesium rarely forms solution complexes. Therefore, cesium would be expected to appear in solutions predominantly as Cs^+ . Only 1.5% of the cesium from underground nuclear explosions was found (Izrael et al., 1970) to be colloidal with the rest cationic, which may have been adsorbed on other colloids. The main soil and rock reaction with cesium is expected to be ion exchange.

Laboratory Adsorption Studies

Aston and Duursma (1973) studied the adsorption of Cs onto sediments contacting spiked Mediterranean sea water ($1.125 \mu\text{g Cs/l}$). Stirred suspensions 20 to 2000 mg/l were studied at pH 8. Blank samples were run (without sediments) to study radionuclide precipitation and adsorption on reaction vessels. At several times an aliquot of suspension was filtered and the cesium distribution on sediment and in the filtrate determined. Only 2% of the spiked cesium sea water was observed to form particulates in the blank vessels. The equilibration of cesium was quite rapid (0.4 to 0.5 hr) and was not affected by the range of sediment concentrations studied. The K_d_{Cs} value was not dependent on sediment concentration below 200 mg/l and became

independent above 200 mg/l, but did not depend upon sediment mineralogy, thus suggesting particle formation rather than ion exchange as the predominant mechanism. At sediment concentrations of 500 mg/l K_d was a direct function of sediment illite content, which suggests ion exchange reactions. At the total cesium concentration expected in sea water and neglecting cesium which forms colloids, K_d s for two carbonate sediments were about 40 ml/g, but for two illitic fine grain sediments $K_{d_{Cs}}$ values were 450 and 900 ml/g. K_d was dependent on amount of stable cesium added as a carrier and data followed a Freundlich isotherm. Aston and Duursma concluded that at low sediment concentrations nucleation of colloids controls the $K_{d_{Cs}}$ but at higher sediment concentrations ion exchange predominates. They also warned that tracer results cannot show the behavior and distribution of the stable counterpart of the element. Radioisotope adsorption might be occurring while at the same time sedimentary particles are desorbing the stable element.

Baker et al. (1964) determined the $K_{d_{Cs}}$ on 17 samples collected in the vicinity of Cape Thompson, Alaska. Cesium adsorption, at 1 day, was found to be represented by the mass-action equation. The distribution coefficients for cesium adsorption were so large that, in all but a few cases, very little of this nuclide would remain long in solution in the natural waters of the area. Equilibrium was reached within 1 day.

Baranova and Polikarpov (1966) found that, among the sediments studied, a large adsorptivity for ^{137}Cs was exhibited by shallow-water silts (aleuritic silt with mussel biocoenosis and phaseoline silt). Despite differing mechanical and chemical properties, these silts have similar affinity coefficients for each isotope, an effect for which the size and fraction of particles of less than 90 μm is responsible. Phaseoline silt and aleuritic silt with mussel biocoenosis most effectively adsorb ^{91}Y , ^{95}Zr , ^{137}Cs and ^{144}Ce . Their affinity coefficients for ^{90}Sr and ^{106}Ru are low.

Of the radionuclides tested, ^{137}Cs is most strongly retained by the silts. None was desorbed by sea water or 0.2N HCl (within the limits of the experimental error), which seems to preclude ion exchange as the sorption mechanism.

Cheng and Hamaguchi (1968) studied the sorption of cesium on marine and terrigenous sediments. Batch experiments 0.03 g of sediment/30 mls solution were shaken overnight. Desorption was carried out by loading the contaminated sediments into columns and washing with water. Kd_{Cs} values in distilled water and sea water at pH 7 to 9 were constant. The Kd_{Cs} was dependent on the ratio of exchangeable potassium to total potassium and exchangeable magnesium to total magnesium. In other words, the competition of cesium for sites bound with potassium and magnesium obeys mass action law. Cesium sorption is most favorable on calcium based sediments, followed by magnesium, sodium and potassium. The Kd_{Cs} for marine red clay varied from 2 to 9×10^3 in distilled and sea water, depending on sediment characteristics.

Collet et al. (1968) determined the distribution of cesium between sediments and waters in the Rhine River basin. Duursma and coworkers have studied the adsorption of cesium onto sea sediments [Dawson and Duursma (1974), Duursma et al. (1974), Duursma and Eisma (1973), Duursma and Gross (1971), and Duursma (1973a)]. In general cesium was found to adsorb rapidly (half-time period of sorption $t_{1/2} = 0.7 \pm 0.4$ days) and appeared to be controlled by ion-exchange reactions. The higher the cation-exchange capacity of the sediment is, the larger will be the Kd_{Cs} . The Kd_{Cs} correlated very well with the exchangeable potassium content of the sediments. If the sediment had high concentrations of exchangeable potassium the Kd_{Cs} was large. The Kd_{Cs} was also dependent on the concentration of stable cesium in solution. For every $10 \mu\text{g/l}$ increase in cesium concentration, the observed Kd_{Cs} dropped 1 to 6%. As the average concentration of stable cesium is $1 \mu\text{g/l}$ in the marine environment, a change of $\pm 10 \mu\text{g/l}$ would be highly unlikely.

The log K (unitless volume Kd) values for sediments from various oceans and seas are shown in Table 8.23.

Gardner and Skulberg (1964) investigated the sorption of radionuclides on river sediments (post-glacial marine clay) from the Nidelva River, Norway. A description of the sediment and water is given in the cerium discussion. At a sediment concentration of 64 parts per million, cesium in distilled water was

found to reach adsorption steady state between 2 to 24 hr of contact. K_{dCs} values for various sediment concentrations contacting distilled water and river water after 1-day contact are shown in Table 8.24.

TABLE 8.23. K_{dCs} in Various Sediments from Durness and Eisaa (1973)

<u>Sediment</u>	<u>Log K</u>		<u>Estimated K_d Average (ml/g)</u>	<u>t 1/2 (days)</u>	
Atlantic Ocean	3.1	0.9	1,800	1.1	1.0
Pacific Ocean	3.1	0.8	1,800	0.8	1.3
Indian Ocean	3.3	0.4	3,000	0.6	0.2
Baltic Sea	3.3	0.4	3,000	0.6	
North Sea	3.5	0.2	4,275	1.0	
Mediterranean Sea	3.1	0.6	2,000	0.6	0.3
Black Sea	3.3	0.2	3,000	0.6	
Red Sea	2.4		380	0.6	

TABLE 8.24. K_{dCs} on Nitelva River Sediments

<u>Sediment Concentration (ppm)</u>	<u>K_{dCs} Distilled</u>	<u>K_{dCs} River</u>
16	15,600	8,900
32	13,600	7,300
64	11,800	5,500
128	10,800	5,000
256	7,300	3,900

Increased sediment concentration causes K_{dCs} to decrease and the dissolved salts in the river water compete with Cs for sorption sites and effectively half the observed K_d . It is also possible that container adsorption is causing part of the difference. The high K_{dCs} may be caused by the illite content of the sediments (15 to 30%).

Jenne and Wahlberg (1968) studied the adsorption of cesium onto Whiteoak Creek, Tennessee, sediments from stream water. Detailed mineralogy of various size fractions of stream sediments was performed. It was shown that illite present in the sediments controlled the sorption of cesium. K_d_{Cs} values for two particle size ranges (<60 mesh) and 9 to 60 mesh were 800 to 1000 and 650 to 790 ml/g, respectively.

Kawabata (1967) studied factors affecting the sorption of various radionuclides by a river sediment sample in the fresh or saline water. In addition, release of radionuclides in the sediments when it was exposed to the sea water was studied. Water and sediment samples were collected at several places along the Sagami River. Cation-exchange capacity of the river sediments (less than 120 mesh fraction) was 1 meq/100 g. Uptakes of radionuclides by the sediments were much affected by various competing cations, and the rate of inhibition depends not only on the cationic species but also concentration of cations. The higher in the concentration of a competing cation, the more inhibitive to the uptake of radionuclides by river sediments. Release of radionuclides which had been sorbed by the river sediments in the filtered sea water was examined during 12 days storage. Cesium-137 was released easily, and never was readsorbed.

Kuznetsov and Schebetkovskii (1971) and Schebetkovskii and Kuznetsov (1971) studied the distribution of ^{137}Cs in the sea water and major types of sediments covering the Pacific Ocean floor. The foraminiferal, diatomaceous, and iceberg silt and red shallow-water clays are favorable locales for the sorption of these isotopes. These sediments show a high affinity for ^{137}Cs . Results for four sediments are shown in Table 8.25.

Desorption of ^{137}Cs from the sediments into sea waters was studied. An empirical relation was established between the percentage of desorption and volume of water with $P = V/a + bV$, where V = volume of water, P = desorption percentage, and a and b are empirical constants. The distribution of ^{137}Cs between sea water and sediments occurs as a homogeneous sorbate, i.e., follows Henry's Law.

TABLE 8.25. Distribution of ^{137}Cs Between Sea Water and Sediments

<u>Sediment</u>	<u>Kd</u>		<u>Kd</u>	
	<u>Adsorption</u>		<u>Desorption</u>	
Iceberg Silt	559	21	590	20
Red Clay	42	5	54	11
Foraminiferan Silt	104	9	115	10
Diatom Silt	147	6	230	10

Mahmoud et al. (1968, 1973) studied the sorption of cesium by bottom sediments from Ismailia Canal adjacent to the United Arab Republic Atomic Energy Establishment. Laboratory studies, using slurry tests, on sorption of ^{134}Cs by bottom sediments were conducted. The affinity of these sediments for sorption of radionuclides was influenced by grain-size distribution, contact time and carrier concentration. Linear relationships were noticed between logarithm of capacity of bottom sediments for sorption of radionuclides versus logarithm of carrier concentration. A Freundlich sorption isotherm was identified.

Meeussen et al. (1975) studied the sorption of cesium on Belgium sediments. Using ^{60}Co , ^{85}Sr and ^{137}Cs as tracer ions, the sorption capacity of Scheldt sediments for Co^{2+} , Sr^{2+} , and Cs^{+} was studied and their distribution coefficients between sediment and Scheldt water were determined.

It is found that clay and silt samples show relatively high sorption capacities for cobalt and cesium, compared with the low fixation rate for strontium.

The selectivity of the sediments for a particular ion, in competition with other ions, was studied and the sequence found is in accordance with the distribution coefficients. From these experiments it may be concluded that the high salt concentrations, present in normal Scheldt water, will limit the risks of radioactive isotopes accumulation in the sediments.

Puschmann (1970) studied the sorption behavior of fine-grained sediments from the Weser, Donau and Elbe Rivers. The experiments with closed systems give the course of the sorption and the possible sorption rate after the

equilibrium has been established. The sorption rates are converted to grams of the element per m^3 sand as used in the laboratory experiment. The results are compared with the sorption rates dealt with by Weisflog (1968), which were made with low-terrace sediments from the river Rhine.

Schneider and Block (1968) studied the sorbability of deposits of the Rhine for several nuclides. The sorbability increases in the following order: I^- , $Sr(II)$, $Pu(IV)$, $Zn(II)$, $Cs(I)$. Saturation was reached by sediments after 24 hr at the latest for all nuclides. The sediment samples were taken from Oehningen (Upper Rhine), Koblenz (Middle Rhine), and Wesel (Lower Rhine). Data were compared with the organic content for each sample. The sorption of ^{137}Cs is dependent on grain size but not on organic material. A sudden release by living or dead organic material of radionuclides is not possible, though desorption from mineral suspended material is more rapid, often occurring within a few hours. Less than 1% of transported nuclides in the Rhine under any conceivable conditions would be bound to suspended material or sediments.

Seymour (1977) and Seymour et al. (1979) reported on batch experiments on three sediments: anoxic marine, oxic marine and fresh-water sediment in contact with ^{137}Cs traced waters in the overlying water. The observed Kd_{Cs} values were 52 ± 3 , 17 ± 1 and 50 ± 4 ml/g, respectively. Equilibrium was reached prior to the first counting period (48 hr). In a separate experiment anoxic marine sediment was placed in a dialysis bag suspended in traced sea water. After 10 days the sediment had accumulated some radioactivity as did the originally clean sea water within the dialysis bag. The apparent Kd_{Cs} by this method was 0.09 ml/g. The sea water originally spiked with cesium also showed 20% of the cesium had become filterable ($0.22 \mu m$), suggesting particulate formation of added tracer had occurred.

Schell et al. (1979) measured the sorption of cesium from 30.2% salinity water by a sandy sediment from the Skagit River estuary. The values obtained varied from 90 to 134 ml/g. In separate blank controls (traced water without sediment) 95% of the Cs remained in solution showing little problem with

colloid formation exists for Cs. A second sediment from an anoxic marine basin, Saanich Inlet, contacting a traced water from Saanich Inlet was found to yield a Kd_{Cs} of 61 ± 24 ml/g.

In two dialysis experiments on oxic marine sediments and montmorillonite contacting seawater Cs was found to remain almost exclusively in the soluble phase. Percentages of cesium in the various compartments can be found in Tables 8.9 and 8.10 in the Americium section.

Schell et al. (1980) report on laboratory determinations of Kd_{Cs} in numerous fresh and marine water environments with sediments. Table 8.11 summarizes the results. The cesium Kds for fresh waters exceed those for marine waters by about a factor of 5, suggesting ion competition by Na in seawater reduces cesium sorption. Kd_{Cs} for desorption exceeds the adsorption values and thus models which assume quantitative reversibility $Kd_{ADS} = Kd_{DES}$ will over-estimate cesium mobility.

Schell et al. (1980) studied sorption of cesium versus pH for a Clinch River, Tennessee sediment/freshwater slurry. From pH 4 to 9 there was no effect. Between pH 9 and 10 there appeared to be an order of magnitude increase in Kd.

Schell et al. (1980) studied the effects of five organics on cesium sorption in a freshwater environment. In no case did the organics significantly alter cesium sorption (see Table 8.12).

Schell et al. (1980) continued dialysis experiments using Lake Michigan sediments and water. Cesium remains primarily in solution, but some sorption onto the sediment is also observed within 1 day.

Dunigan and Francis (1972), Essington and Nishita (1966), Nishita and Essington (1967), Kulikov and Molchanova (1972), and Salo and Saxen (1974) investigated cesium interaction with humic substances and chelators. In general, organic complexes with cesium are not observed or not stable. Thus, soluble organic complexing of cesium has little effect on cesium movement.

Cerrai et al. (1969) contacted 200 mg sediments with 40 ml of traced sea water or distilled water for 1 hr. Resultant $K_{d_{Cs}}$ values for distilled water and sea water were 249 and 114 ml/g.

Wahlberg and Fishman (1962) determined cesium K_d values with kaolinite, illite, montmorillonite and halloysite over a large cesium concentration range and in competition with sodium, potassium, calcium or magnesium. The type and amount of competing ions and the cesium concentration determined the cesium K_d variation with potassium having the most depressing effect. Thirty-four figures showing $K_{d_{Cs}}$ versus cesium concentration (10^{-10} to 10^{-1} M) in NaCl, KCl, $MgCl_2$ and $CaCl_2$ solutions (0.002 N to 0.2 N) are presented for the above minerals. The logarithm of $K_{d_{Cs}}$ on a particular clay mineral, at very low cesium concentrations, is a linear function of the logarithm of the competing ion.

Tamura (1972) measured the $K_{d_{Cs}}$ versus sodium concentration in a pure brine system for several minerals. The $K_{d_{Cs}}$ decreased as a function of increasing sodium concentration and for the mineral order illite, biotite, hydrobiotite, montmorillonite, kaolinite (Figure 8.14).

FIGURE 8.14. Distribution Coefficient (K_d) of Several Minerals as a Function of Sodium Concentration

Field Studies

Alberts, Wahlgren and coworkers studied the distribution and transport of fallout cesium in Lake Michigan and its watersheds. The results showed ^{137}Cs from weapons testing is concentrated in the sediments. The mean half-life of cesium entering the lake water is 1.4 ± 0.3 years before incorporation into bottom sediments. Convection mixing causes resuspension of surface sediments during summer months. Residual fractions of ^{137}Cs in the water column (0.04 to 0.08 pCi/l) are homogeneously distributed throughout the lake primarily in particle size fractions less than $0.4 \mu\text{m}$ [Alberts et al. (1974b), Edgington et al. (1975), Wahlgren and Nelson (1973, 1974), and Wahlgren et al. (1976)].

Bowen and co-workers reported the concentrations of fallout cesium found in the Atlantic Ocean and Lake Ontario waters and sediment [Bowen (1971, 1974a) and Bowen et al. (1972)]. Cerrai et al. (1970) measured fallout concentrations of ^{137}Cs in Adriatic and Ligurian Sea sediments and found 0.17 and 0.38 pCi/g, respectively. All of the cesium in the Adriatic sediment was found on fine sediment ($<100 \mu\text{m}$).

Field and laboratory studies of cesium emanating from the Savannah River plant were performed by Brisbin et al. (1974), DuPont (1965) and Marter (1974). Brisbin sampled three transects across Steel Creek 15.5, 16.2 and 16.9 km downstream from the reactor effluent. Fine particle silt and clay sediments averaged 170.47 pCi/g (562 pCi/g maximum) while coarser sediments averaged 18.1 pCi/g. Differential distribution of fine and coarse sediments in the stream channel have resulted in a complex mosaic of radiocontamination. Samples collected 1 m apart differed in radiocesium content by as much as 190%. Radiocesium was correlated with both available potassium and organic matter. In desorption experiments (24 hr) distilled water removed 0.9%, in NaCl 12.0%, Steel Creek water 6.3%, Savannah River water 6.0 to 6.7% of the cesium bound to the sediments. The desorption experiments suggest cation competition of high ionic strength waters can remove some of the bound cesium. • •

Brungs (1963, 1964) reported on the distribution of cesium added to a 30,000 gallon pond with a sand substrate over an 80-day period. The disappearance of cesium was rapid, 95% after 4 days. At the end of 80 days the

sediments contained about 400 pCi/g while the water contained 86 pCi/l for an apparent $K_{d_{Cs}} = 4.6 \times 10^3$. At day 80, 0.25% of the cesium was in the dissolved state, 0.33% on suspended material, 0.03% on biota and 99.39% on the sediment. The pond water contained 10 ppm Na, 8 ppm K, 24 ppm Ca, 22 ppm Mg, 31 ppm SO_4 , 8 ppm Cl, 72 ppm HCO_3-CO_3 and pH 8.8.

Comprehensive field and laboratory studies of radionuclides in the stream and river leaving Oak Ridge National Lab were performed by Carrigan, Pickering and coworkers [Carrigan et al. (1967), Carrigan (1968, 1969), Lammers (1968), Lomenick and Tamura (1965), Pickering et al. (1965, 1966), and Pickering (1969, 1970)]. A comprehensive inventory of radionuclides over a 21-mile reach of the Clinch River shows 21% of the cesium released remains bound to bottom sediments. High adsorption of cesium is related to the illite clay present in the sediments. Complete sediment and water characterization is provided such that the functional dependency of sorption can be addressed. For a clay bed sediment (60% illite, 15% kaolinite, 10 to 15% vermiculite, 10 to 15% quartz) contacting tap water, the following $K_{d_{Cs}}$ values were obtained (Table 8.26).

TABLE 8.26. Cs Sorption by Clinch River Sediment

<u>Contact Time</u>	<u>pH 6</u>	<u>pH 9</u>
1 hour	2,326	3,169
3 days	50,152	50,152
7 days	88,048	82,769

Most of the cesium in solution in the Clinch River is bound to suspended sediment with a particle size greater than $0.7 \mu m$ (69 to 92% depending upon location). Cesium content in water correlates with suspended solids, turbidity, color, iron and manganese, all of which relate to suspended solids content. Lammers (1968) and Lomenick and Tamura (1965) studied the distribution of cesium in White Oak Lake. More than 80% of the ^{137}Cs is associated with the clay fraction of the material, which was found to be predominantly illite. Significant quantities of ^{137}Cs were removed from the material only

by treatment with strong acids. Studies of several selected clays showed illite to have a high affinity for ^{137}Cs at levels of the same order of magnitude as those observed in lake bed sediment and that desorption is only accomplished after disruption of the lattice structure. The desorption behavior of the sediments and the corroborative behavior of the reference minerals are evidence that cesium in the sediment will not be leached by percolating ground water to any appreciable degree. However, movement of cesium can occur by erosion of the sediment.

Cushing and Watson (1974) studied the biotic and abiotic components of a cooling water pond ecosystem at Hanford. Most of the ^{137}Cs in the pond is associated with the sediments which are probably the main source of ^{137}Cs for uptake by the biota. Generally, highest concentrations of ^{137}Cs and other radioisotopes were found in the upper 2 in. of sediments in the northwest end of the pond and in the deeper areas along the long-axis of the pond. Sediment could be a source of high concentrations of radioactivity or radioactive contamination concern if the concentration of radiocontaminants increased and/or the pond dries up, and the contaminated sediments become windborne.

DeBortoli and Gaglione (1970) surveyed the ^{137}Cs in Lake Maggiore to evaluate the amount and distribution of the contamination in bottom sediments. Through these measurements the vertical profile of the contamination has been also determined and found very irregular. The contamination in the bay is confined to an area of approximately 0.03 km^2 and the activity levels found are very low, as expected on the basis of the activity released.

Eyman and Kevern (1975) studied the distribution of cesium in a hyper-eutrophic lake. The inputs of ^{137}Cs and stable cesium and their distribution among the water, sediments, macrophytes, filamentous algae, zooplankton, and several species of fish were studied in a lake exhibiting an advanced stage of eutrophy. Most of the cesium pool (97% ^{137}Cs , 98% stable cesium) was found to be associated with the sediments. Stable cesium enters the lake primarily in a bound state as migratory waterfowl excreta and is deposited to the sediments. Cesium-137 is associated with fine particulates in the

inorganic form as it enters the lake. This results in a longer residence time in the water column with distribution throughout the lake. Specific activity (pCi ^{137}Cs /ng stable cesium) of the sediments was lower than other components of the system due to the different modes of entry for the two cesium isotopes.

Gloyna and co-workers studied the movement of radiocesium in model rivers (flumes) and in the field (Guadalupe River) [Clanton (1968), Gloyna et al. (1966, 1971), Kudo (1969), Kudo and Gloyna (1971), Purushothaman (1968, 1971), Purushothaman and Gloyna (1968), Reynolds (1963), Reynolds and Gloyna (1963), Texas University (1968), and Yousef et al. (1970)]. A fully-instrumented flume and reservoir complex was used to simulate typical ecological environments. A model river as represented by the flume has been used to develop more fully a comprehensive transport equation, thereby defining the transport coefficients needed to satisfy any prediction model. This system has been used to evaluate the effect of various environmental conditions on the net transport of the radionuclides. Rates of radiocesium sorption and desorption were highest during the first few moments of contact, but total mass adsorbed continued to increase slowly throughout 7-day experiments. Organic fractions in sediments increased cesium sorption substantially. When the contaminated sediments were placed in conditions simulating a marine environment, 43% of the ^{137}Cs was released because of competition for the exchange sites from the more abundant ions in sea water. Even though fluvial releases are considered an acceptable means of radionuclide disposal, it should be emphasized that all stream systems are dynamic, and this disposal is at best temporary. The distribution of the radionuclides in the bottom sediment, plants, algae, and water was determined. Under the conditions of the release, less than maximum permissible concentration, the radioactivity continued to increase on the surface of bottom sediments until a quasi-equilibrium level was reached at approximately 25 days after initiation of release. At this condition or saturation, the specific activity of bottom sediments associated with ^{134}Cs approached $55 \mu\text{Ci}/\text{cm}^2$ and sediment K_d was 275 ($K_d \sim 410 \text{ ml/g}$).

The delay in transport of radionuclides caused by the interaction between flowing water and bed sediments was determined. This interaction phenomenon for ^{137}Cs was observed by using a set of flumes, each 50 ft in length and a model river which was 200 ft long. The greatest uptake rate, K_{st} , by bed sediment was $88.7 \times 10^{-4} [(\text{cpm}/\text{cm}^2)/(\text{cpm}/\text{cm}^3)]/(\text{sec})$ with a velocity of 1.65 fps and a flow rate of 0.345 cfs/ft. In this case the sediment transport rate was 0.0795 lb/sec-ft. A mathematical model was developed describing the migration of radionuclides into the sediments. The relative concentration of radionuclides on the surface of the bottom sediments to that in the bed sediment was found to be a function of $z/(2\sqrt{Dt})$, where z , D , and T , respectively, are the depth of bed sediment from the surface, diffusion coefficient of ^{137}Cs in water, and time after migration started.

Hakonson (1972), Hakonson and Whicker (1975), Hubbard (1968) and Hubbard and Striffler (1973) studied cesium transport in mountain lakes and streams. For the mountain lake to which 0.2 Kg_{Cs} /hectare were added, the loss of ^{137}Cs from water occurred in two phases. The rapid phase, which resulted in the loss of 60% of the cesium from water, had a loss half-time of 0.5 days while the slow phase had a loss half-time of 130 days. The seston fraction of each water sample contained from 25 to 80% of the ^{137}Cs present in each liter of unfiltered water. Bottom sediments were identified as the major site of deposition of the ^{137}Cs dose. The sediment, at 393 days post-dosing, accounted for 82% of the ^{137}Cs inventory in the lake whereas water and seston accounted for only 3 and 14%, respectively.

The stream study showed the distribution of the fallout radionuclide ^{137}Cs on the surface and in the stream channel of an alpine watershed in the Colorado Front Range. Cesium-137 activities of the surface (mean = $222 \text{ nCi}/\text{m}^2$) were considerably higher than at Fort Collins, Colorado. The effects of snow-accumulation, soil-vegetation complexes, and the hydrologic surface were studied in relation to ^{137}Cs activity. Snow-accumulation areas contained significantly more ^{137}Cs than snow-free areas. Alpine bog contained significantly more ^{137}Cs than did Alpine turf and Alpine meadow soils. Micro-channels and micro-depressions had significantly higher levels of ^{137}Cs activity than areas characterized as surface runoff. Concentrations

of ^{137}Cs in stream bottom sediments and stream vegetation decreased exponentially downstream with distance from a permanent snowfield at the headwaters. There is some evidence that ^{137}Cs in sediments is accumulating in a marshy area where the stream flows across the morrain of a former mountain glacier. ^{137}Cs activities of the sediments were not highly related to percent silt + clay. Evidence did not support the hypothesis that most ^{137}Cs would concentrate in the silt + clay as it moved downstream. Significant quantities of ^{137}Cs were not found in stream water or the 1967 or 1968 snowpack. Measurable ^{137}Cs activities were found in litter and inorganic materials in and about the permanent snowfield, and in moss on rocks in the stream channel.

Lerman (1971), Lerman and Taniguchi (1971), and Lerman and Lietzke (1975) have studied the uptake and migration of tracers in the Great Lakes. For modeling efforts, field observations and a few laboratory experiments have been performed on the sorption of cesium. K_d_{Cs} values of 5,200 to 15,000 ml/g have been obtained, depending upon sediment characteristics.

Nakamura and Nagaya (1975) studied the concentration of ^{137}Cs in the marine sediment of Tokyo Bay and of the coastal seas of Ibaraki, Fukushima and Fukui prefectures. The radiocesium ranged from 5.3 to 220 pCi/kg dry sediment. The degree of radionuclide enrichment versus sea water was in the hundreds for ^{137}Cs .

Wrenn et al. (1971, 1974) have studied the distribution of ^{134}Cs and ^{137}Cs in the Hudson River estuary. The spatial and temporal distribution of ^{137}Cs and ^{134}Cs was measured in fish, plants, water, and sediments of the Hudson River Estuary along an 80-mile stretch of the river, encompassing salinities from one-fifth sea water to fresh water, in order to better understand the cycling of this radionuclide in an estuarine environment. Although the ^{137}Cs content of Hudson River water has dropped tenfold since 1964, the average content in fish and sediments has remained relatively constant. This implies that the ^{137}Cs content of fish residing in the river has depended primarily on the cumulative deposit in the sediments. The major source of this ^{137}Cs has been fallout, although in a limited section of the river an

elevation of ^{137}Cs in sediments from the Indian Point nuclear plant can be seen. In order of decreasing content, ^{137}Cs was found in sediments, aquatic plants, and fish, roughly in the ratios of 30:1:1.

Magno et al. (1970) determined radionuclide migration through the effluent lagooning system of the Nuclear Fuel Services plant in Western New York. From their analytical data, they estimated that 75% of the ^{134}Cs and ^{137}Cs discharged from the plant was deposited in the sediments in the lagoon system. From 40 to 95% of the cesium at the lagoon system exit was associated with suspended solids.

Eichholz et al. (1967) investigated the partitioning of dissolved radionuclides between suspended sediment particles and aqueous solutions. Their work does not necessarily have a direct application to particulate migration through sediment, but it does give a feeling for the types and amounts of radionuclides that can be transported on suspended solids. Several bodies of water were sampled and utilized by the authors in the adsorption study as sources of suspended solids. Some of the properties of the natural water samples are listed in Table 8.27. A fission product mixture was added; the system allowed to come to equilibrium; and the water was recovered and passed through a mixed-bed ion-exchange resin. The resin and sediment were then counted with the radionuclides extraction results shown in Table 8.28. It is noteworthy that a large portion (80 to 90%) of the radionuclides was associated and traveled with the particulate matter in a highly concentrated form. There is a direct correlation between cesium adsorption and the suspended solids concentration, with some effect of dissolved solids in the water.

Summary

Cesium mainly exists in solutions as Cs^+ . Schell et al. (1979) found very little tendency for Cs to form colloids or to be unstable in solution. Therefore, the principal reaction mechanism of cesium adsorption on sediments, soils and rocks is expected to be cation exchange. In fact, some researchers have determined adsorption isotherms on several natural materials, and from the isotherms, derived thermodynamic functions for the specific cation exchange reactions. Some of the thermodynamic studies include Thomas (1967),

TABLE 8.27. Properties of Natural Water Samples (Eichholz et al., 1967)

Source	Suspended Solids, ppm	Dissolved Solids, ppm	pH	Conductivity μ mhos	Solids Composition
Colorado River, Utah	229	350	7.5	540	95% quartz, 5% calcite, feldspar, illite, kaolinite
Camp McCoy, Wisconsin	12	60	6.9	80	30% quartz + feldspar, 6% kaolinite, 24% illite
Bayou Anacoco, Louisiana	24	63	6.2	60	30% quartz, 2% kaolinite, 6% smectite
Lodgepole Creek Nebraska	965	200	6.8	300	20% illite, 80% smectite
Chattahoochee River, Georgia	131	31	7.3	45	33% quartz, 44% kaolinite, 23% illite
Billy's Lake Georgia (swamp)	8	68	4.2	45	2% quartz, balance was amorphous and/or organic

TABLE 8.28. Adsorption of Radionuclides on Suspended Solids (Eichholz et al., 1967)

Source	^{137}Cs , %
Colorado River	83.9
Camp McCoy	3.3
Bayou Anacoco	16.2
Lodgepole Creek	96.3
Chattahoochee River	26.1
Billy's Lake	0.3

Tamers and Thomas (1960), Merriam and Thomas (1956), Gaines and Thomas (1953), Lewis and Thomas (1963), and Eliason (1966) on cesium ion exchange on systems of cations with clays. Ames (1959b), Frysinger (1962) and Howery and Thomas (1965) studied ion exchange and cesium thermodynamics on the natural zeolite clinoptilolite. Ion exchange reactions are rapid, thus in most instances sorption of cesium is observed to reach steady state rapidly (within hours).

There is the tendency for cesium to become "fixed" or preferentially sorb on 10 Å mica, illitic-like minerals as witnessed by the tenacious adsorption of cesium on clays around Oak Ridge National Lab. Most field studies show cesium becomes rapidly associated with bottom and suspended sediments.

Schell et al. 1980 show data which supports ion exchange like processes control cesium sorption in aquatic environments. In general Kd_{Cs} for fresh-water environments is about five times greater than Kd_{Cs} for sea water. Organic ligands appear to have little effect on cesium sorption.

CHROMIUM

Natural Sediment and Rock Distribution

Some average values for chromium content of sediments are found in Table 8.29.

TABLE 8.29. Chromium Concentrations (ppm)

Type	Range	Average	Reference
Atlantic Ocean Sediment	8 to 190	65	Duursma, 1974
Pacific Ocean Sediment	7 to 93	52	Duursma, 1974
Indian Ocean Sediment	84 to 160	116	Duursma, 1974
Pelagic Carbonate		11	Turekian and Wedepohl, 1961
Pelagic Clays		90	Turekian and Wedepohl, 1961
Red Clay		55	El Wakeel and Riley, 1961
All Ocean Sediments		93	El Wakeel and Riley, 1961
Manganese Nodule		10	Riley and Sinhaseni, 1958

Brief Chemistry

Chromium is a metallic element, resembling iron, occurring chiefly in chrome iron ore $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. There are four stable isotopes with the following abundances: ^{50}Cr (4.41%), ^{52}Cr (83.46%), ^{53}Cr (9.54%) and ^{54}Cr (2.61%). The only radioactive isotope of consequence is ^{51}Cr with a 26-day half-life.

Solution Equilibria

Chromium occurs in the +2, +3, and +6 oxidation states in water. The trivalent state is the only one that has a broad stability with pH and Eh (Pourbaix, 1966). The divalent state is unstable with respect to evolution of hydrogen (Baes and Mesmer, 1976). The hexavalent chromium occurs in strongly oxidizing conditions only. Pourbaix (1966) and Baes and Mesmer (1976) disagree as to the most predominant solution species of Cr(III) in solution. According to Pourbaix the dominances of Cr^{3+} , CrOH^{2+} , $\text{Cr}(\text{OH})_2^+$ are pH < 4, 4 to 6 pH, and 6 to 9 pH, respectively. According to Baes and Mesmer (1976), the

predominant solution species in solutions of pH < 7.5 is $\text{Cr}(\text{OH})_4^{5+}$, and in solutions of 7.5 to 9 is $\text{Cr}(\text{OH})_2^+$. Nevertheless it is obvious that the hydrolysis species of Cr(III) will predominate above pH 6.

Laboratory Adsorption Studies

Bartlett and Kimble (1976a, 1976b) studied the behavior of Cr(III) and Cr(VI) in three acid soils with relatively high organic matter content 5% and a neutral clay soil without organic matter. The soils were shaken at various pHs in contact with 5 μm Cr(III)/m/solution for 24 hours. As pH in blank tubes (no soil) was raised above 4 the solubility of Cr(III) decreased with apparent complete precipitation at pH 5.5. When acidic organic soils were added to the system Cr(III) was adsorbed totally when pH exceeded 4.5. Below pH 2.5 less than 20% of the Cr(III) was adsorbed.

Soil organic complexes of Cr(III) formed at low pH and appeared to remain stable and soluble even when soil pH's were raised to levels where the Cr would be expected to precipitate. Adsorption and solubility behavior of Cr(III) as it varied with pH and P treatment was similar to that of Al.

Oxidation of Cr(III) to Cr(VI) was not demonstrated at all, even under conditions of maximum aeration and high pH.

Adsorption and reduction of added Cr(VI) were characterized in soils with contrasting pH's, organic matter contents, and chemical and mineralogical properties.

Presence of soil organic matter brought about spontaneous reduction of Cr(VI) to Cr(III), even at pH's above neutrality. Reduction did not occur in soils very low in organic matter unless an energy source was added. Cow manure added to practically organic-free Cecil B2 reduced Cr(VI) only after the pH had been lowered below 3 with HCl.

The solubility of Cr(VI) in the presence of excess Al changed in a pattern remindful of orthophosphate. All of the soils, except a pH 7.8 Cca horizontal material, adsorbed Cr(VI). Presence of orthophosphate prevented the adsorption of Cr(VI), presumably by competition for the adsorption sites. Consistent with this finding, KH_2PO_4 was found to be the best extracting agent for Cr(VI).

It was concluded that behavior of Cr(VI), if it remains in soils, is similar to that of orthophosphate. However, unlike phosphate, Cr(VI) is quickly reduced by soil organic matter. Thus, Cr(VI) added to a soil will remain mobile only if its concentration exceeds both the adsorbing and the reducing capacities of the soil.

Kawabata (1967) studied factors affecting the sorption of various radionuclides by a river sediment sample in the fresh or saline water. In addition, release of radionuclides in the sediments when it was exposed to the sea water was studied. Water and sediment samples were collected at several places along the Sagami River, and radionuclides employed in these experiments were ^{90}Sr , ^{137}Cs , ^{54}Mn , ^{60}Co , ^{51}Cr and ^{59}Fe . Cation-exchange capacity of the river sediments less than 120 mesh fraction was 1 meq/100 g. Uptakes of radionuclides by the sediments were much affected by various competing cations, and the rate of inhibition depends not only on the cationic species but also on concentrations of cations. The higher in the concentration of a competing cation, the more inhibitive to the uptake of radionuclides by river sediments. Release of radionuclides which had been sorbed by the river sediments in the filtered sea water was examined during 12 days storage. Both ^{60}Co and ^{137}Cs were released easily, and never were re-adsorbed. The release of ^{90}Sr , however, increased for the first 2 days, then gradually decreased, which might be due to the re-adsorption of the nuclide by sediments in the sea water. The rate of release of ^{54}Mn was rather low, in addition, the amount released in the sea water decreased gradually, which might be due to the precipitation in the form of MnO_2 .

Nelson et al. (1966) studied the uptake of Cr(III) and Cr(VI) onto Columbia River sediment both untreated and oxidized with hydrogen peroxide. Cr(III) was taken up rapidly. For Cr(VI) contacting "oxidized" sediment uptake was much slower suggesting that in nature reducing material in sediments will reduce chromium to the +3 valence state and will substantially increase sorption.

Field Studies

Armstrong et al. (1968) and Eromiec and Gloyna (1973) studied the movement of chromium in model flumes. The design of the model river system, its

instrumentation, and its uses are described in detail. The ground water supply, depth control, and aquatic life environment are itemized. The instruments installed measure several environmental factors, such as pH, dissolved O, temperature, sunlight, and oxidation-reduction potential. To measure sunlight energy, two pyrheliometers were used ~ midway between the inlet and outlet. The digital data acquisition system and its operation are described briefly. The dispersions of 8 radionuclide tracers at various velocities, water depths, and bed slopes were studied to determine how their transport is affected by environmental conditions. Transport data were obtained by conducting laboratory, model river, and field tests. Canal, river, and estuarine environments provided the necessary field information on hydrodynamic dispersion and on uptake and release of radionuclides by sediments.

The dispersion of $^{51}\text{Cr(III)}$ is illustrated. The approximately Gaussian curves at each station indicated typical dispersion, but the long tails were the result of uptake and subsequent release of radioactivity by sediments and plants showing the effects of one environmental condition on radionuclide transport and also indicating the importance of geochemical and biochemical relations in transport. The effect of organic pollution on sediment uptake of $^{51}\text{Cr(VI)}$ is shown. On the control side of the model river, where no organic load was added, the percentage rise in the sediment was only moderate, whereas on the polluted side, the rise was rapid to a level 3 times that of the control side, because of ^{51}Cr sorbing onto settling particles. Sediment transport and its role in radionuclide transport is being considered now for study in the model river. Mathematical models are being developed to describe and predict radionuclide transport and the manner in which it is affected by environmental conditions.

The release of radiochromium to the Columbia River from Hanford reactors has been extensively studied [Cutshall (1967), Evans (1973), Evans and Cutshall (1973), Forster and Hanson (1969), Glenn (1971), Gross (1966, 1967, 1972), Gross et al. (1963), Hanson (1967), Haushild et al. (1971a, 1971b, 1973a, 1973b), Hubbel and Glenn (1973), Perkins et al. (1966), Nelson and

Haushild (1970), Nelson et al. (1966), Renfro (1971) and Robertson and Perkins (1975)]. In summary, ^{51}Cr found in water at various locations between the reactors and the mouth of the Columbia River (375 miles) is predominantly in the soluble form ($<0.3\ \mu\text{m}$), 98% at the reactor site and 90% at Vancouver 275 miles downstream. That which is soluble is predominantly anionic 93 to 99% regardless of location. Most of the chromium passing Pasco, Washington, (50 miles downstream from the reactor) reaches Vancouver, Washington, (275 miles downstream from the reactor) except in the fall when some chromium is stored in the bed sediments. Upon mixture with sea water, chromium, bound to suspended matter or bed sediments found in the river, does not desorb even after 11 weeks of contact in some instances. Thus, the small fraction of chromium bound to particulates is tightly held. Nelson et al. (1966) leached Columbia River sediments with various extractants and found chromium to be non-exchangeable but apparently resolubilized partially by sodium hyposulfite treatment which removes hydrous oxides.

Robertson and Perkins (1975) sampled water directly leaving N Reactor at Hanford and water seeping from springs on the Columbia River bank nearby which are fed by the cooling water. The cooling water itself contains greater than 85% particulate ^{51}Cr ($>0.3\ \mu\text{m}$). The ^{51}Cr which reaches the spring is greater than 98 anionic and is 0.4% of the original cooling water concentration.

Summary

Chromium exhibits two valence states in aqueous environments: Cr(III) as Cr^{+3} and Cr(VI) as CrO_4^{-2} . The Cr(VI) species in water probably do not sorb readily but do appear to reduce readily to Cr(III) upon contact with sediments, especially those containing organic or other reducing agents. Once adsorbed, chromium is not easily removed via ion competition. Chromium adsorption/desorption will be sensitive to Eh and pH.

COBALT

Natural Sediment and Rock Distributions

The average cobalt concentrations found in igneous and sedimentary rocks and sediments are listed in Table 8.30. As can be seen, the cobalt content of rocks steadily decreases from the dark ultramafic rocks to the light-colored granitic rocks. The ultrabasic rocks usually contain the bulk of the cobalt in olivines and pyroxenes, but an occasional sulfide body in these rocks provides a workable ore deposit (Young, 1957). Cobalt normally is enriched in areas of low redox potential in the environment.

TABLE 8.30. Cobalt Concentrations in Igneous and Sedimentary Rocks and Sediments in ppm

<u>Igneous</u>					<u>Sedimentary</u>			
<u>Ultra- mafic</u>	<u>Basaltic</u>	<u>Granitic</u> <u>High Ca</u>	<u>Low Ca</u>	<u>Syenite</u>	<u>Shale</u>	<u>Sand- stone</u>	<u>Lime- stone</u>	<u>Reference</u>
150	48	7	1	1	19	0.3	0.1	Young (1957)
<u>Marine Carbonates</u>		<u>Marine Clays</u>			<u>Reference</u>			
	7	74 to 160			Turekian and Wedepohl (1961) El Wakeel and Riley (1961)			
<u>Nearshore Marine</u>		<u>Manganese Nodules</u>			<u>Reference</u>			
	13	3400			Wedepohl (1960)			

During weathering processes, cobalt is separated from manganese and iron because its (III) oxidation state is normally unstable unless complexed. However, certain bacteria are known to liberate chelated Co(III), as stable amino acid complexes from soil. Little is known, as yet, of these reactions, but the technique of predicting mineral solubilities for cobalt based on thermodynamic data may not be entirely applicable if the bacterial reactions are ignored (Moore, 1964). Vinogradov (1959) reported the average soils content of cobalt as 8 ppm. Cobalt contents of up to 1.96 wt% CoO have been reported for calcite (Hacquaert, 1925).

Brief Chemistry

Only one stable cobalt nuclide, ^{59}Co , is known to exist in nature. Cobalt-60 is the principal cobalt activation product radionuclide with a half-life over 1 yr. Reactor effluents also contain significant quantities of short-lived ^{58}Co . Cobalt oxidation states include Co(II) and Co(III). Cobalt is geochemically similar to the other ferromagnetic and closely related transition metals, iron and nickel.

Sulfides of nickel and cobalt constitute the chief cobalt ore minerals. Co^{+2} ionic radius in octahedral coordination is 0.74 Å, intermediate between Ni^{+2} (0.70 Å) and Fe^{+2} (0.77 Å) (Shannon and Prewitt, 1969). The relative stabilities of the Co(II) and Co(III) states are greatly affected by complexing in aqueous solutions (Latimer, 1952a,b). Although Co^{+3} cannot exist in aqueous solution, complexing can stabilize the trivalent state which would normally decompose in water.

Solution Equilibria

Cobalt exists as Co^{2+} and Co^{3+} and forms solution complexes with common anions (OH^- , Cl^- , SO_4^{2-} , NO_3^-). The relative concentration of these solution species in equilibrium with CoCO_3 and in an oxidizing environment ($\text{O}_2 = 10^{-0.68}$) is depicted in Figure 8.15. If a solid phase other than CoCO_3 or a constant concentration of cobalt is chosen for the diagram, the lines will shift up and down, while the relative concentration of various solution species would stay the same. The thermodynamic data for CoSO_4^+ were obtained from Sillen and Martell (1964) and the hydrolysis species data were obtained from Baes and Mesmer (1976). Data for all the other species were obtained from Wagman et al. (1968, 1969).

It can be seen from the figure that cobaltinuous ion (Co^{2+}) and its solution complexes are the most stable and dominant solution species in the oxidizing environment. The most dominant solution species up to a pH value of approximately 9.5 is Co^{2+} .

Beyond pH 9.5, $\text{Co}(\text{OH})_2^0$ becomes dominant. The activity of Co^{2+} ion in solution decreases 100-fold with an increase of a pH unit, whereas the activity

FIGURE 8.15. The Activity of Various Cobalt Ions in Equilibrium with $\text{CoCO}_3(\text{s})$ in an Oxidizing Soil Environment [$p\text{O}_2(\text{g}) = 0.68 \text{ atm}$], $p\text{CO}_2(\text{g}) = 1.52 \text{ atm}$, $p\text{Cl}^- = p\text{SO}_4^{2-} = 2.5$, $p\text{ML}_3 = 3.0$ and $p\text{H}_2\text{PO}_4 = 5.0$

of Co(OH)_2^0 does not change with the pH. These predictions are similar to Baes and Mesmer (1976). If CoCO_3 was the solid phase that controlled the solubility, the total cobalt concentration in solution at pH 7 would be approximately 10^{-7} M and approximately 10^{-12} M at pH 9.5.

Laboratory Adsorption Studies

Aston and Duursma (1973) studied the adsorption of cobalt onto marine sediment from sea water. Factors such as sediment and carrier concentrations and contact time were varied. Only 0.9% of the ^{60}Co was precipitated from sea water samples which were filtered 50 hr after spike addition. In adsorption experiments the cobalt remaining in solution reached steady state as early as 5 hr and as long as 20 hr for different sediments regardless of sediment concentration (100 to 2000 mg/l). As the stable carrier cobalt concentration was increased from 0.5 to 4 $\mu\text{g/l}$ (natural sea water contains 0.05 $\mu\text{g/l}$ Co) the $K_{\text{d}_{\text{Co}}}$ increased contrary to ion exchange theory. For fine grain sediments K_{d} increased from about 1×10^5 to $3 \times 10^5 \text{ ml/g}$. At sediment concentrations below 50 mg/l, $K_{\text{d}_{\text{Co}}}$ for carbonaceous sediments is relatively high 1 to 3 x

10^4 and drops to 1 to 5×10^3 at sediment concentrations above 50 mg/l. For clay sediments no consistent trend was observed for K_d_{Co} versus sediment concentration. The extreme dependency of carbonaceous sediments at low concentration may reflect a cobalt substitution for calcium in lattice sites or $CoCO_3$ precipitation. There was no direct relationship between K_d_{Co} and sediment mineralogy, exchange capacity or particle size. The mechanism controlling cobalt sorption could not be identified.

In other studies Duursma and coworkers found the adsorption of cobalt perplexing [Dawson and Duursma (1974), Duursma and Eisma (1973), and Duursma and Gross (1971)]. Using the same sediment at various agitations (quiescent, vigorous stirring, slight stirring) and various time sequences, variable cobalt sorption and desorption results were obtained. For Black Sea sediments cobalt appears to be less mobile under anoxic conditions than oxic (K_d 2.1×10^4 versus 9×10^3); yet Bonatti et al. (1971) finds natural cobalt to be enriched in oxidizing layers of cores from the Pacific Ocean when compared to reduced layers. Results of K_d_{Co} for various sediments and the rate at which cobalt is adsorbed are shown in Table 8.31.

TABLE 8.31. K_d_{Co} in Various Sediments from Duursma and Eisma (1973)

Sediment	log K, Unitless	$K_{d_{avg}}$ (est), ml/g	$t_{1/2}$, days
Atlantic Ocean	3.9 ± 1.1	1.2 ± 10^4	6.9 ± 7.2
Pacific Ocean	4.9 ± 0.9	1.5 ± 10^4	7.8 ± 6.7
Indian Ocean	3.9 ± 0.4	1.2 ± 10^4	5.8 ± 2.6
Baltic Ocean	4.8 ± 0.4	9.5 ± 10^4	12.6
North Sea	4.7 ± 0.6	7.0 ± 10^4	25
Mediterranean Sea	3.7 ± 1.0	7.3 ± 10^4	4.9 ± 5.4
Black Sea	4.0 ± 0.3	1.4 ± 10^4	8
Red Sea	3.6	6.7 ± 10^3	6

Fukai and Lang (1968) and Fukai and Murray (1973) report on the stability of tracer ^{60}Co added to sea water versus pH. Results indicated that most of the cobaltinuous ions stay in solution within the pH range 7 to 9 in sea water and that the formation of a solid phase, if any, is not due to $\text{Co}(\text{OH})_2$. They hypothesized that the geochemical behavior of cobalt in marine environments is closely related to that of manganese. Doshi et al. (1973) confirm the quantitative removal of trace cobalt by manganese oxide.

Murray and Murray (1973) studied the adsorption of ^{60}Co by sediments in fresh water and desorption of ^{60}Co from the sediments when contacted with sea water. More than 80% of ^{60}Co was adsorbed within 48 hr at pH 8.0 but only 30% of the ^{60}Co was desorbed at pH 8.0 by sea water in 24 hr. Cobalt sorption/desorption was very dependent on pH. For fresh waters at pH 7 sorption dropped to 20% (versus 80% at pH 8) as shown in Figure 8.16. For 250 mg/l sediment the K_d would be 1000 at pH 7 and 16,000 at pH 8.

FIGURE 8.16. Variation of Adsorption of ^{60}Co at Constant Carrier Concentration and Sediment Load with Varying pH

In a similar fashion desorption in sea water is dependent on pH as seen in Figure 8.17. The adsorption/desorption reactions reached equilibrium within 72 hr. Cobalt adsorption from fresh water onto Var River sediments decreased with increasing concentration of soluble organic matter, but desorption in sea water of adsorbed cobalt was not affected by soluble organic content of sea water. Also investigated was the possibility of scavenging of cobalt by iron hydroxide at 50 $\mu\text{g/l}$ iron. The results showed little scavenging (<3%) of soluble ^{60}Co .

FIGURE 8.17. Variation of Desorption of Trace Elements at Constant Adsorbed Trace-Element Concentration and Sediment Load with Varying pH

Jenne and Wahlberg (1968) found cobalt bound to Whiteoak Creek, Tennessee, sediments to be unremovable with ammonium extractants which typically replace exchangeable elements from sediments. The less than 60-mesh bed sediments had a K_d_{Co} between 1400 to 2400 ml/g. The adsorption of ^{60}Co was attributed to scavenging by iron and manganese oxides.

Kawabata (1967) studied factors affecting the sorption of various radionuclides by a river sediment in fresh and saline waters. In addition, release of radionuclides from the sediments when they were exposed to sea water was studied. Water and sediment samples were collected at several places along the Sagami River. Cation exchange capacity of the river sediments less than 120 mesh fraction was 1 meq/100 g. Uptakes of radionuclides by the sediments were much affected by various competing cations and the rate of inhibition depends not only on the cationic species but also on concentration of cations. The higher the concentration of a competing cation, the more inhibitive was the uptake of radionuclides by river sediments. Release of radionuclides which had been sorbed by the river sediments in filtered sea water was examined over 12 days. Cobalt-60 was released easily, and never was re-absorbed.

Mahmoud et al. (1968, 1973) performed laboratory and field tests on cobalt uptake by sediments and biota from the Ismailia Canal. Affinity of these sediments for sorption of radionuclides was influenced by grain-size distribution, contact time and carrier concentration. Linear relationships were noted between the logarithm of capacity of bottom sediments for sorption of radionuclides versus logarithm of carrier concentration. A Freundlich sorption isotherm was identified. Possible applications of the experimental laboratory data to the natural conditions prevailing in the Ismailia Canal are also discussed.

Meeussen et al. (1975), using ^{60}Co , ^{85}Sr and ^{137}Cs as tracer ions, studied the sorption capacity of Scheldt sediments for Co^{2+} , Sr^{2+} and Cs^{+} and their distribution coefficients between sediment and Scheldt water.

It is found that clay and silt samples show relatively high sorption capacities for cobalt and cesium, compared with the low fixation rate for strontium.

The selectivity of the sediments for a particular ion, in competition with other ions, was studied and the sequence found is in accordance with the distribution coefficients. From these experiments it may be concluded that the high salt concentrations, present in normal Scheldt water, will limit the risks of radioactive isotopes accumulation in the sediments.

Ojima et al. (1965) studied the physico-chemical behavior of ^{89}Sr , ^{90}Sr , ^{137}Cs and ^{60}Co ions in relation to pH of marine water, trace elements dissolved in it, fragments of marine organisms living in it, and sea sediments.

Radosavtjevic and Tasovac (1970) studied, as a part of the program for the control of the radioactivity of the Danube, the behavior of different radionuclides and the fixation of ^{60}Co by suspensions. The influence of different parameters on fixation was determined.

Schell et al. (1979) studied the fate of Co in seawater via dialysis experiments which have been described in the section on americium. Table 8.9 shows that any Co which passed through the dialysis bag into the sediment slurry became associated with particulate matter. Plankton did not adsorb Co to any extent. A second experiment with montmorillonite clay as the adsorbent showed very little sorption on $>0.45\ \mu\text{m}$ particles. Perhaps the montmorillonite was smaller than the filter membrane used and appears with the soluble fraction (see Table 8.10, Americium section). Schell et al. (1980) performed laboratory experiments to determine the effect of pH on cobalt sorption for the Clinch River (Tennessee) freshwater system. The K_d_{Co} increases by more than two orders of magnitude between pH 6 and 7.5. Above pH 7.5 to pH 10 there is no further change. Cobalt sorption at neutral pH needs further study to understand this dramatic increase in sorption.

Schell et al. (1980) studied the effect of five organics on cobalt sorption in a freshwater environment. Two organics caused K_d_{Co} to increase significantly and one (EDTA) caused a significant decrease (see Table 8.12). Care must be exercised in interpreting the significance of these results as rather high concentrations of organic ligands were utilized.

Schell et al. (1980) performed dialysis experiments using Lake Michigan fresh water and sediments. Much of the cobalt remains soluble but the sediment adsorbs a significant percentage. Cobalt does not associate strongly with phytoplankton or organic detritus.

Tiller et al. (1963) studied sorption of Co^{+2} from very dilute solutions by soil clays in the presence of a 0.1N CaCl_2 and compared with the sorption by pure minerals (mica, montmorillonite, vermiculite, kaolinite, quartz, hematite, goethite) under similar conditions. The cobalt sorption results were not very different. Organic matter in soils containing small to moderate amounts did not seem to affect cobalt adsorption.

Dunigan and Francis (1972) and Fukai and Murray (1973) described the interaction of cobalt with humic acids, EDTA and natural organic decomposition products. Although interaction may be slow, nonionic and anionic complexes of cobalt with natural organics form in sea water and fresh water. At the low concentrations found in natural waters for both chelating agents and cobalt, formation of complexes would be slow but if formed could greatly increase the mobility of cobalt.

Friend (1963) reported that suspended solids in a pond environment took up ^{60}Co rapidly, with suspended illite having the most selectivity for cobalt removal of the clay minerals. Wilding and Rhodes (1963) studied the effects of 100 ppm citrate and EDTA on cobalt equilibrium distribution coefficients with the zeolite clinoptilolite and Well-81 sediments. At pH 6.5, citrate enhanced cobalt adsorption on clinoptilolite, the K_d value being 48 with no treatment and 102 with 100 ppm citrate added. With EDTA addition at pH 6.5, the cobalt K_d value fell from 100 to 1 ml/g. Well-81 sediments adsorbed about the same amounts with and without citrate. At pH 7.7, the cobalt K_d was 30 ml/g with no citrate and 26 ml/g with citrate. At 7.7, the cobalt K_d was 1000 ml/g with no EDTA and 1.2 ml/g with EDTA. Tiller et al. (1963) found no correlation between cobalt adsorption and soil mineralogy. Hawkins (1964) described a process of cobalt removal from waste solutions by scavenging on manganese dioxide precipitate and removal of the remaining cobalt by ion exchange on lignite, soil and the natural zeolite clinoptilolite. Distribution coefficients for cobalt were 56, 800 and 24 ml/g for Idaho soil, lignite and clinoptilolite, respectively.

Gonzalez and Gomez (1961) found that most of the cobalt in Andalusian soils was found in oxide and hydroxide gels associated with clays. There was a positive correlation between cobalt content of the soil and Fe_2O_3 content.

James and Healy (1972) showed the adsorption isotherm for $1.2 \times 10^{-4} \text{M}$ Co^{+2} on silica at 25 C as a function of pH. Adsorption is 10% at pH 6 and greater than 90% at pH 8. Computed hydrolysis data at this cobalt concentration are also shown.

Tewari et al. (1972) investigated the adsorption of Co^{+2} by Fe_3O_4 , Al_2O_3 and MnO_2 as a function of concentration, solution pH and temperature in connection with the transport of cobalt adsorbed on corrosion product oxides. Hydrolysis of Co^{+2} was suggested as a possible mechanism for the marked dependence of cobalt adsorption on pH and temperature.

Field Studies

Brungs (1963, 1974) studied the fate of ^{60}Co added to a 30,000 gallon pond with a sand substrate for 80 days after addition of tracers. Sorption was rapid; after 4 days, only 10% of the cobalt remained in solution, 31% was found on suspended sediments and 59% in the bed sediments. After 80 days the distribution was as follows: dissolved 0.68%, suspended particulate 0.33%, bed sediment 98.94%.

Parker (1966) described a study of the distribution of cobalt between the liquid and solid (suspended particles) portions in 8 lakes in Wisconsin. Samples were taken from various depths. Seasonal changes in distribution, differences in distribution in various lakes, and evaluation of the causes of various distributions are presented.

Carrigan (1969), Carrigan et al. (1967), Pickering (1969, 1970) and Pickering et al. (1965) indicated only 9% of the total ^{60}Co released from Oak Ridge National Lab remains in the Clinch River with 21 miles of the discharge. The bulk of cobalt reached the bottom sediments as particulate matter. Sorption of cobalt by Whiteoak Creek sediments showed higher sorption at pH 6 than 9 probably because colloidal cobalt was not as readily centrifuged out at the higher pH due to hydroxyl ion stabilization. Equilibrium was not reached within the 7-day experiment. At pH 6 K_d_{Co} increased from 1,734 (1 hr) to 28,017 (3 days) and 71,567 (7 days). At pH 9 K_d_{Co} was 5,120 (1 hr), 9,354 (3 days) and 11,445 (7 days). The distribution of cobalt in water samples from Whiteoak Creek, Clinch River and the Tennessee River showed most of the

cobalt in a dissolved ($<0.7 \mu\text{m}$) form (70 to 98%) and very little bound to suspended solids. The cobalt that does reach the bed sediments does not desorb upon contact with competitive salt solutions but will readily desorb if acid solutions are introduced. This suggests hydrous oxide scavenging or colloid formation as a key mechanism.

Duguid (1976, 1977) and Means et al. (1976) have shown ^{60}Co movement from shallow land burial grounds to Whiteoak Creek and the Clinch River is mainly caused by soluble organic complexation (85% by EDTA present for waste disposal and 15% by natural organic acids). Truly inorganic cobalt is found to be quite immobile $K_{d_{\text{Co}}} \sim 10^4$. At 10^{-5}M EDTA the $K_{d_{\text{Co}}}$ was reduced to ~ 3 a reduction of four orders of magnitude.

Delaplane et al. (1969), Glenn (1971), Gross (1966), Gross et al. (1963), Haushild et al. (1971, 1973a), Hubbell and Glenn (1973), Perkins et al. (1966), Robertson (1974), Robertson and Perkins (1974, 1975) and Robertson et al. (1973) have studied the distribution and fate of radiocobalt produced at Hanford, Washington, and discharged into the Columbia River and Pacific Ocean. The cobalt found in the Columbia River is 98% particulate ($>3 \mu\text{m}$) and bound to suspended matter. Upon reaching the ocean, the high salt content only leaches about 10% of the cobalt bound to fine bed sediment behind a dam. During high runoff periods much of this fine material is resuspended and could be carried to the Pacific Ocean. The cobalt does not appear to be bound to readily exchangeable sites. Cobalt-60 present in cooling water emanating from the Hanford N reactor is about evenly split between particulate ($>0.3 \mu\text{m}$) and cationic with only traces of nonionic or anionic forms but after percolation through soil the cobalt reaching the Columbia River is 73% anionic, 17% cationic and 9% nonionic. The soil effectively removes particulate and cationic forms. The fate of the anionic and nonionic forms once in the river have not been determined, but assuming their fate is similar to previous studies of cobalt produced by now idle weapons reactors, the cobalt should rapidly become sorbed on particles.

Gloyna et al. (1966), Gromiec and Gloyna (1973) and Yousef et al. (1970) investigated the dynamics of cobalt transport in model rivers (flumes). The most significant factors influencing sorption of cobalt by bottom sediments

were contact time and pH. Cobalt was not removed by exchange competitive salts but was readily acid soluble at pH 4. Probably sorption mechanisms are precipitation of hydroxides and carbonates.

Ophel and Fraser (1971) studied the fate of cobalt in a fresh water lake on the property of Atomic Energy of Canada (Chalk River, Ontario). Most of the nuclide is confined to the upper few centimeters of the sediment.

Magno et al. (1970) reported that ^{60}Co constituted only <0.1% of the beta activity in surface drainage from the Nuclear Fuel Services plant lagoon system in Western New York State. The ^{60}Co in the effluent was relatively small, but was all in solution and thus able to travel with the surface water. The implication is that the "soluble" ^{60}Co was migrating as a complexed species. The implication is that the ^{60}Co is complexed by low molecular weight natural organics. Migration of ^{60}Co would be negligible in the absence of organic complexation because the soil adsorption capacity for inorganic forms of ^{60}Co was reported to be extremely high. Manganese oxides in the Conasauga shale were the principal adsorbents of ionic and weakly complexed ^{60}Co .

Saas and Grauby (1973) studied the migration of cobalt and its transfer mechanisms from nuclear reactor to river water, irrigation water, and finally ground water. Three fractions of ^{60}Co were differentiated including a chelated fraction, an exchangeable fraction and a hydrosoluble fraction. The hydrosoluble fraction was defined as the totality of the organic and mineral components of the soil that are water soluble. The different fractions in a brown, calcareous soil were given. The hydrosoluble fraction constituted about 70%, the exchangeable fraction about 20% and about 10% was chelated from river water containing ^{60}Co . The hydrosoluble form on an alluvial calcareous soil column varied from 10% at the point of input to 60% at 17 cm depth. The water soluble material was only slightly biodegradeable, eventually migrating to the ground water through application in irrigation water. The pollutants in the river water, including industrial wastes and municipal sewage, are responsible for the rapidly migrating hydrosoluble fraction. The authors suggest that the quality of surface drainage water will have to be taken into account during nuclear reaction siting.

Summary

Among the various sediment components, MnO_2 , Fe_2O_3 and illite have been shown to have a strong affinity for cobalt. With the increase in pH (especially 6 to 9) the adsorption of cobalt increases. This increase in adsorption with pH has generally been explained as due to the formation of cobalt colloids and hydrolysis of Co^{2+} . The presence of various complexing ions such as EDTA, cyanide, and fulvic acids has been shown to reduce the adsorption by sediments. These laboratory results are consistent with the theoretical predictions (Figure 8.15) which indicate that in acidic pH values cobalt would predominantly exist as Co^{+2} and with the increase in pH it hydrolyzes to CoOH^+ and Co(OH)_2^0 .

Discrete cobalt minerals have not been identified in sediments. High concentrations of cobalt are required to precipitate cobalt minerals and thus it is not likely that any of the minerals would exist in the environment. However, in highly alkaline conditions, CoCO_3 would maintain fairly low concentrations of cobalt in solution and thus might exist.

Cobalt is apparently relatively easily complexed by natural organics and by synthetically-produced organics and as such is able to migrate with relative ease through the geologic media with which it would normally react by adsorption.

CURIUM

Natural Sediment and Rock Distributions

The element curium has not been reported to occur naturally in sediments or rocks.

Brief Chemistry

Thirteen isotopes of curium are known from ^{238}Cm to ^{250}Cm , most with relatively short half-lives. There are no naturally-occurring curium isotopes. The curium isotopes are produced in reactors by n reactions on ^{239}Pu or by decay of californium isotopes (Keller, 1971). The LWR reprocessing waste isotopes include: ^{243}Cm (32 years), ^{244}Cm (18.1 years), ^{245}Cm (8,265 years), ^{246}Cm (4,711 years), ^{247}Cm (1.6×10^7 years) and ^{248}Cm (3.84×10^5 years). Curium-250 also has a long half-life, but yields are normally very low. Curium can exist in Cm(III) or Cm(IV) oxidation states, but stabilization of Cm(IV) requires high concentrations of fluoride ions to form the anionic complexes CmF_5^- and CmF_6^{2-} (Keller, 1971). Only trivalent curium is normally stable in aqueous solutions. The ionic radius of Cm^{3+} in coordination number 6 is 0.986 Å. Trivalent curium forms many complexes with inorganic ligands found in wastes and in ground waters.

Solution Equilibria

Curium (IV) is not stable in solutions because of self-radiation, and it rapidly changes to Cm(III). Only trivalent curium is stable in aqueous solutions. Keller (1971) reported that the behavior of Cm^{3+} in solution is similar to lanthanide elements. Most of the lanthanides form trivalent hydroxides in natural waters with solubility products of $<10^{-19}$ (Vickery, 1953). Thomas and Jacobs (1969) found that the activity of curium in 0.1M NaCl solutions which contained approximately 10^{-11} M/l of curium decreased at pH values above 3. They attributed this decrease in activity in pure solutions to either precipitation or adsorption on walls. If this is assumed to be due to precipitation, the solubility product of curium hydroxide would be at least as low as the lanthanides, and probably much lower.

Since thermodynamic data for the curium compounds are not available, it was decided to plot the solution species in equilibrium with $\text{Cm}(\text{OH})_3$ with an

assumed $\log K^\circ$ of 2 for the dissolution of $\text{Cm}(\text{OH})_3$ [$\text{Cm}(\text{OH})_3 + 3\text{H}^+ \rightleftharpoons \text{Cm}^{3+} + 3\text{H}_2\text{O}$] in order to show the relative activity of various solution species of curium with the changes in pH. Keller (1971) reviewed the curium data and stated that little work has been performed on the complex chemistry of curium and since a wide variation occurs in stability constants determined by various authors, these values should be regarded as relative rather than absolute. The thermodynamic data used to develop Figure 8.18 were obtained from the following sources: Trotman-Dickinson (1973), CmCl^{2+} , CmF^{2+} , CmSO_4^+ ; Jones and Choppin (1969), CmNO_3^{2+} ; Shalinets and Stepanov (1972), CmOH^{2+} , $\text{Cm}(\text{OH})_2^+$; and Moskin (1969), $\text{CmH}_2\text{PO}_4^{2+}$.

FIGURE 8.18. The Activity of Various Curium Ion Species in Equilibrium with $\text{Cm}(\text{OH})_3(\text{s})$ with $\text{pF}^- = 4.5$, $\text{pCl}^- = \text{pSO}_4^{2-} = 2.5$, $\text{pNO}_3^- = 3.0$ and $\text{pH}_2\text{PO}_4 = 5.0$

It can be seen from Figure 8.18 that curium forms various solution complexes with OH^- , F^- , Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} . The activity of all the complexes decreases with the increase in pH. The solution complexes of PO_4^{3-} , Cl^- , NO_3^- do not contribute significantly to the total curium concentration in solutions. The most dominant solution species in pH ranges of 3.3, 3.3-5.7, 5.7 and up are Cm^{3+} , $\text{Cm}(\text{OH})^{2+}$, and $\text{Cm}(\text{OH})_2^+$, respectively.

Laboratory Adsorption Studies

No studies have been performed on curium adsorption with aquatic sediments.

The adsorption characteristics of ^{242}Cm on several clays were measured in distilled water and 0.1M NaCl by Thomas and Jacobs (1969). Adsorption was not a function of ion-exchange capacity because greater adsorption occurred in 0.1M NaCl solutions (Jacobs et al., 1966) than in distilled water solutions. When adsorption studies were made as a function of pH, some curium was removed from solution even without the addition of clay at pH values above 3. This was due to precipitation or to adsorption on glass walls. Addition of clay caused a considerable increase in adsorption possibly because increased surface area was available for deposition. Column-loading studies of ^{242}Cm tagged 0.1M NaCl showed normal ion-exchange chromatographic breakthrough at pH 1. Above pH 1, the effluent deviated from normal chromatographic curves and remained constant during the entire run. The effluent/influent ^{242}Cm concentration ratio at pH 3 was about 0.008; at pH 7 the ratio was 0.028; and at pH 10 the ratio was 0.150. Although ^{242}Cm precipitated from stock solution at pH values above 3, the column leakage of curium increased with increasing pH. The leakage is probably caused by hydroxy and oxo-complexes forming radiocolloids. Movement of curium through soil is probably restricted by filtration and surface adsorption of radiocolloids rather than by ion exchange.

Sheppard et al. (1976) investigated the distribution values of ^{244}Cm on several Washington and South Carolina soils. The 50-day distribution results for trace ^{244}Cm in a distilled water solution are given in Table 8.32. The distribution for curium between soil and solution increased with time. The distribution values were computed in the same manner as a K_d value. However, K_d values are defined as obtained at soil-solution equilibrium which these values did not attain. The slow increase in distribution values was interpreted by the authors as due to the presence of colloids. It was also shown that iron and manganese oxides were effective scavengers for curium.

TABLE 8.32. Curium 50-day Distribution Computed from Sheppard et al. (1976)

<u>Soil Identity</u>	<u>Distribution ml/g</u>	<u>Monthly Change in Distribution, %</u>
Muscatine Silt Loam	1330	+8
Burbank Loamy Sand	106	+27
Ritzville Silt Loam	704	+40
Fuquay Sand 0 to 5 cm Depth	1850	+26
Fuquay Sand 5 to 15 cm Depth	1850	+28
Fuquay Sand 15 to 50 cm Depth	1240	+18

Nishita et al. (1976) determined the extractability of plutonium and curium from a contaminated soil as a function of pH and soil components. The organic matter and pH influenced hydrolysis, precipitation, coprecipitation and adsorption of the radionuclides. In the work, 2 g of soil were suspended in 25 ml of extracting water, in duplicate, and the pH adjusted with NaOH or HNO₃. The K_d values computed from Nishita et al. (1976) are given in Table 8.33 for the untreated Aiken clay loam, a kaolinitic soil, at several pH values. The Aiken clay loam also was treated sequentially with progressive treatments to remove salts, organic matter, carbonates, manganese oxides, iron oxides, free silica and alumina and amorphous alumino-silicates. The organic matter was shown to have the greatest ability to retain curium, but this was a function of pH as well. Below pH 4.5, curium was less strongly adsorbed whether organic matter was present or not.

Field Studies

Duguid (1976) reported that Bondietti had shown that the alpha contamination in water from seep S-4 along the south side of burial ground 5, Oak Ridge,

TABLE 8.33. Kd Values for ^{242}Cm in Untreated Arken Clay Loam (Nishita et al., 1976)

pH	^{242}Cm Kd, ml/g	pH	^{242}Cm Kd, ml/g
1.21	85.7 $\pm$ 12	8.54	4608 $\pm$ 1635
2.12	2,457 $\pm$ 6	9.43	1776 $\pm$ 142
2.56	6,803 $\pm$ 46	10.31	690 $\pm$ 38
4.69	100,000 $\pm$ 30,000	11.25	358 $\pm$ 2.7
5.55	100,000 $\pm$ 10,000	12.22	190 $\pm$ 3.3
7.08	71,429 $\pm$ 10,204	13.25	272 $\pm$ 23

Tennessee, was due to 3.2×10^{-7} $\mu\text{Ci/ml}$ of ^{244}Cm and 3.2×10^{-8} $\mu\text{Ci/ml}$ of ^{238}Pu . The trenches in burial ground 5 were overflowing because precipitation infiltrated the trenches, reached the less permeable trench bottom and flowed out the lower end of the trench in a seep. The ^{244}Cm and ^{238}Pu were presumably picked up by the water in its passage through the waste-filled burial trench. Bondietti and Reynolds (1977) reported that seepage water, presumably from burial ground 5, contained 0.3 to 3.2×10^{-7} $\mu\text{Ci/ml}$ of ^{244}Cm in the filtrate from a $0.45 \mu\text{m}$ filter sampled at two yearly intervals. White Oak Lake water contained 0.3 to 1×10^{-9} $\mu\text{Ci/ml}$ with about 50 passing through a $0.45 \mu\text{m}$ filter. Sedlet (1977) reported on the average concentration of curium in surface water near Argonne, Illinois, in 1975. Wastes from Argonne National Laboratory enter Sawmill Creek which flows into the Des Plaines River. The ^{244}Cm - ^{252}Cf concentration was $<1.2 \times 10^{-15}$ Ci/l and the ^{244}Cm - ^{249}Cf concentration was $4.5 \pm 0.8 \times 10^{-15}$ Ci/l in Sawmill Creek. No detectable (5×10^{-16} Ci/l) curium was found in the Des Plaines River.

Summary

No information is available on possible curium compounds in soils and sediments. It appears that curium precipitation as $\text{Cm}(\text{OH})_3$ in alkaline solutions may control curium concentrations in those solutions. Theoretical calculations (Figure 8.18) indicate that Cm^{3+} hydrolyzes even in acidic solutions (pH 3.3 and above). Very little reliable information is available on interactions of curium with soils and sediments, and none on curium

interactions with rocks. What little data are available indicate that curium adsorption is not a function of ion-exchange capacity of the soil (Thomas and Jacobs, 1969; Jacobs et al., 1966), and that precipitation and/or formation of radiocolloids may predominately influence curium adsorption reactions (Thomas and Jacobs, 1969; Sheppard et al., 1976).

EUROPIUM

Natural Sediment and Rock Distributions

The europium content of several common rock types and sediments are given in Table 8.34.

TABLE 8.34. Europium Content of Sediments and Igneous Rocks in ppm

<u>Pelagic Carbonates</u>	<u>Pelagic Clays</u>	<u>Fresh Water Clays</u>	<u>Manganese Nodule</u>	<u>Reference</u>			
0.6	1.6	1.8	10.4	Turekian and Wedgepohl (1961) Wildeman and Haskin (1965) Goldberg et al. (1963) Duursma (1974)			
Igneous Rocks							
<u>Perido- tite</u>	<u>Low K Tholeiite</u>	<u>Hawaiian Tholeiite</u>	<u>Ande- site</u>	<u>Grano- diorite</u>	<u>Leuco- granite</u>	<u>Nepheline Syenite</u>	<u>Reference</u>
0.2	1.9	1.3	1.0	1.2	0.17	10	Haskin and Schmitt (1967)
Sedimentary Rocks							
<u>Shale</u>	<u>Quartzite</u>	<u>Limestone</u>	<u>Subgraywacke</u>	<u>Reference</u>			
2.0	0.09	0.14	1.3	Haskin et al. (1966)			

In a study of rare earths in Russian platform soils, Balashov et al. (1964) reported high europium contents in alkaline soils, the europium precipitating as hydroxide. Acidic soils probably allow complexing and removal of the europium and other rare earths.

Brief Chemistry

Europium occurs in two stable isotopes out of a total of 17 isotopes, ^{151}Eu (47.8%) and ^{153}Eu (52.2%). The two radionuclides of interest are ^{152}Eu (13 yr) and ^{154}Eu (16 yr). The oxidation states of europium are trivalent with radius 0.95 Å and divalent with radius 1.09 Å (Ahrens, 1952). The divalent state is typical of europium occurrence, substituting for Ca^{+2} and K^{+} in main stage feldspars (plagioclases, microcline, orthoclase). The

potential of the Eu(III)/Eu(II) couple is -0.43 volts (Latimer, 1952). Europous ions are stable in water solution at low hydrogen ion concentrations (basic pH), and can be formed from Eu^{3+} by zinc reduction. However, the europium in interstitial solutions is more apt to be in the trivalent than divalent state.

Solution Equilibria

Europium can exist as Eu^{2+} and Eu^{3+} . However, Eu^{3+} is the only state which is stable in water (Baes and Mesmer, 1976). The activity of various solution species of europium in equilibrium with Eu(OH)_3 and at assumed concentrations of various anions commonly found in ground water is given in Figure 8.19. The thermodynamic data of all the species except EuOH^{2+} and EuF^{2+} were obtained from Schumm et al. (1973). The data for EuOH^{2+} and EuF^{2+} were obtained from Baes and Mesmer (1976) and Walker and Choppin (1967), respectively.

FIGURE 8.19. The Activity of Various Europium Species in Equilibrium with $\text{Eu(OH)}_3(\text{s})$. Other soil solution conditions included $\text{pSO}_4^{2-} = \text{pCl}^- = 2.5$, $\text{pNO}_3^- = \text{pF}^- = 4.5$ and phosphate levels were from Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP).

In a general way the solution complexes of europium in decreasing order of importance can be arranged as follows: $\text{Eu}_2\text{P}_2\text{O}_7^{2+}$, EuSO_4^+ , $\text{Eu}(\text{SO}_4)_2^+$, EuF^{2+} , EuCl^{2+} , and EuNO_2^+ . Under the conditions assumed in Figure 8.18, the predominant solution species in pH ranges of <4.5, 4.5 to 7.75, 7.5 to 8.85, and >8.85 will be EuSO_4 , $\text{Eu}_2\text{P}_2\text{O}_7^{2+}$, EuSO_4 , and EuOH^{2+} , respectively. Thus, significant quantities of uncomplexed europium (Eu^{3+}) can only be expected in solutions with very low levels of sulfate and phosphate. The solution complexes of europium with fluoride, chloride, and nitrate do not contribute significantly to total europium concentration in solution even for sea water.

Laboratory Adsorption Studies

Benson (1960) reported that the uptake of rare earths (cerium, promethium and europium) was virtually complete and unaffected by accompanying 0.5M alkali metal and 0.25M alkaline earth metal chlorides at a pH above 7. Below pH 3, however, the adsorption of all rare earths was depressed similarly by the accompanying salts. These results were interpreted to mean that the rare earths, including europium, are ionic at pH below 3 and that they are taken up principally by ion exchange on the geologic media. Above pH 7, they are precipitated.

Baetsle and Dejonghe (1962) gave a europium Kd range in Mol soil (mostly quartz sand) at pH 7.7 as 228 to 705, and reported that at pH >3, europium hydrolyzed. Therefore, above pH 3, the authors did not consider that adsorption was an ion exchange phenomenon.

Baetsle et al. (1964) gave Kd values for trace europium in three different waters. The compositions of these waters were not given. Kd results are shown in Table 8.35. The europium Kd values are much larger than the cesium and strontium Kd values for the same soils.

Serne and Rai (1976) studied the adsorption/precipitation behavior of europium in soils and pure solutions. The pH of the various europium solutions (0.15M CaCl_2 plus trace to 50 mg Eu/l) was increased in 0.05 pH increments until precipitation was observed by the Tyndall Beam method. At the point of $\text{Eu}(\text{OH})_3$ precipitation, the europium activity and pH was

TABLE 8.35. Variation of Trace Europium Kd Values on Mol Soils (Baetsle et al., 1964)

Soil Type	Kd, ml/g		
	Deionized Water, pH 3	Tap Water, pH 7.7	Ground Water, pH 3
Eolian Sand			
Horizon A	214 to 244	705	130 to 380
Horizon B	61 to 75	430	---
Horizon C	69 to 89	384	---
Mol White Sand	---	801	165 to 315
Mol Lignitic Sand	---	---	27 to 1830

determined. The results are plotted in Figure 8.20 along with the theoretical $\text{Eu}(\text{OH})_3$ solubility line. The results indicate that:

1. the kinetics of precipitation of $\text{Eu}(\text{OH})_3$ is rapid.
2. the laboratory results agree well with the theoretical $\text{Eu}(\text{OH})_3$ solubility.
3. Eu^{3+} does not appear to hydrolyze appreciably because total europium activity in equilibrium with $\text{Eu}(\text{OH})_3$ is similar to the calculated Eu^{3+} activity.
4. for meaningful Kd values, the theoretical solubility of $\text{Eu}(\text{OH})_3$ should not be exceeded.

Europium adsorption experiments where $\text{Eu}(\text{OH})_3$ did not precipitate were conducted and results shown in Table 8.36. The results show that the europium Kd increases with an increase in pH and decreases with increasing europium concentration, below the point of $\text{Eu}(\text{OH})_3$ precipitation. These reactions suggest that ion exchange is an active mechanism below the point of $\text{Eu}(\text{OH})_3$ precipitation.

Cerrai et al. (1969) looked at ^{152}Eu uptake by marine sediments. Sediment (up to 200 mg) was contacted with 40 ml of sea water (pH 8.1) traced in europium. The contact time was 1 hr. Leach experiments with clean water in

FIGURE 8.20. The Influence of pH on the Activity of Europium in Solution (Serne and Rai, 1976)

contact with the sediment lasted up to 15 hr. One experiment was performed with ^{152}Eu and $0.02 \mu\text{g/l}$ carrier europium in distilled water contacting the sediment. Above a sediment/solution ratio of 1000 mg/l the $K_{d_{\text{Eu}}}$ remained constant for the seawater case at a value between 4.9×10^3 to $1.3 \times 10^4 \text{ ml/g}$. For one sediment as the sediment to solution ratio dropped below 1000 mg/l , the K_d also dropped. For another sediment there was no decrease in K_d as sediment concentration dropped. The $K_{d_{\text{Eu}}}$ for the sediment contacting distilled water showed no increase over the seawater case. Thus, the high salt concentration does not affect europium sorption. Europium leach experiments showed only 5% of the sorbed ^{152}Eu was released in the first hour of contact with fresh sea water regardless of sediment concentration (700 to 5000 mg/l). The percentaged leach rises to 14% after 15 hr. The $K_{d_{\text{Eu}}}$ desorption after 1 hr was 4.8×10^3 to $2.8 \times 10^4 \text{ ml/g}$, depending upon sediment.

Field Studies

Cerrai et al. (1970) measured the concentration of ^{155}Eu in sediments from the Adriatic and Ligurian Seas. The finer fraction of Adriatic Sea

TABLE 8.36. Effect of pH and Europium Concentration on Europium Kd by Burbank Sand^(a) (Serne and Rai, 1976)

<u>Eu, ppm(b)</u>	<u>Final pH</u>	<u>Kd, mg/l</u>	<u>Eu, ppm(b)</u>	<u>Final pH</u>	<u>Kd, mg/l</u>	<u>Eu, ppm(b)</u>	<u>Final pH</u>	<u>Kd, mg/l</u>
0	4.82	46	0.05	5.25	73	5.0	5.20	17.7
0	4.82	48	0.05	5.30	83	5.0	5.20	15.9
0	4.90	51	0.05	5.30	82	5.0	5.25	17.0
0	5.00	75	0.05	5.30	84	5.0	5.32	20.0
0	5.05	70	0.05	5.35	98	50.0	4.70	6.9
0	5.05	69	0.5	4.75	28	50.0	4.70	6.9
0	5.08	75	0.5	4.80	26	50.0	4.73	6.5
0	5.10	84	0.5	4.80	27	50.0	4.88	5.8
0	5.10	78	0.5	5.00	35	50.0	4.90	5.8
0	5.10	78	0.5	5.05	35	50.0	4.90	5.9
0	5.10	82	0.5	5.05	41	50.0	4.90	6.3
0	5.10	75	0.5	5.10	42	50.0	4.90	6.2
0	5.15	93	0.5	5.10	41	50.0	4.90	6.2
0	5.15	90	0.5	5.10	42	50.0	5.00	7.2
0	5.15	81	0.5	5.15	43	50.0	5.00	7.0
0	5.15	93	0.5	5.15	45	50.0	5.00	7.1
0	5.20	94	0.5	5.20	53	50.0	5.15	8.2
0	5.20	98	0.5	5.20	48	50.0	5.15	8.2
0	5.20	98	0.5	5.20	45	50.0	5.20	7.9
0	5.25	107	0.5	5.25	48			
0	5.30	106	0.5	5.25	57			
0	5.30	97	0.5	5.30	54			
0	5.50	153	0.5	5.35	60			
0.05	4.75	32	5.0	4.80	12.4			
0.05	4.75	38	5.0	4.80	11.3			
0.05	4.80	38	5.0	4.80	12.4			
0.05	5.00	63	5.0	4.95	16.9			
0.05	5.00	53	5.0	5.00	18.4			
0.05	5.00	53	5.0	5.05	15.7			
0.05	5.08	56	5.0	5.05	14.8			
0.05	5.08	62	5.0	5.10	15.9			
0.05	5.10	67	5.0	5.10	18.7			
0.05	5.25	71	5.0	5.15	16.4			

(a) One gram samples free of CaCO₃ and soluble salts were used.

(b) Various concentrations of europium were added to 0.15M CaCl₂ solutions spiked with ¹⁵²Eu. Samples were equilibrated first for 48 hr and then for 24 hr after adjusting the pH.

sediment (<100 μm) contained significantly more europium, 0.36 pCi/g versus 0.02 pCi/g for coarser fractions (<100 μm). The total concentration of ¹⁵⁵Eu in Adriatic and Ligurian sediments was 0.23 and 0.24 pCi/g.

Robertson et al. (1973) studied the distribution of ^{155}Eu in the Columbia River. Water samples were filtered ($<0.3\ \mu\text{m}$) and then run through cation and anion exchange resins. The europium was predominately found on suspended particulates 97 and 98 with the rest being soluble cationic and nonionic species. Europium bound to bed sediments are not easily leached by sea water. Only 5% of the sediment bound europium was removable from 30 g eluted with 8 l of sea water.

Summary

Serne and Rai (1976) have shown that the kinetics of precipitation of $\text{Eu}(\text{OH})_3$ from pure solutions is rapid. The concentration of europium in equilibrium with $\text{Eu}(\text{OH})_3$ decreases 1000-fold with an increase of one pH unit. The activity of europium in equilibrium with $\text{Eu}(\text{OH})_3$ is low under highly alkaline conditions and $\text{Eu}(\text{OH})_3$ may control europium concentration in alkaline soils and sediments.

Bensen (1960) and Baetsle and Dejonghe (1962) reported that europium appears to be taken up principally by ion exchange below pH 3. Baetsle and Dejonghe (1962) suggested that ion exchange was not the adsorption mechanism above pH 3 because of europium hydrolysis. Serne and Rai (1976) have shown that for meaningful determination of K_d values in soils, one must be below the solubility line of $\text{Eu}(\text{OH})_3$. Their results, thus obtained, showed that between pH 4.7 and 5.5 the K_d increases with an increase in pH and K_d decreases as europium concentration increases, which suggests an ion exchange as an adsorption mechanism.

Europium in rivers and oceans is found associated almost exclusively with sediments and suspended particulates. Desorption by ion exchange is small.

IODINE

Natural Sediment and Rock Distributions

The iodine content of rocks and sediments is given in Table 8.37. Yoshida et al. (1971) tried leaching the iodine from volcanic rocks, and usually removed less than 20% of the total iodine in the rock. The average iodine value for igneous rocks probably falls within the range of 75 to 150 ppb. Nearly the same average value also would be applicable to metamorphic rocks.

While the iodine content of marine sediments depends on the carbon to a large extent, marine sediments are much richer in iodine than sedimentary rocks.

There is a marked increase in the soil iodine content compared to the rocks they are derived from. For example, the average iodine content of soils was noted as 5 ppm by Vinogradov (1959), who also suggested that much of the soil iodine is atmospherically derived.

Many of the iodine studies have noted the correlation of iodine content and humus in the soil (Sinitskaya, 1969; Irinevich et al., 1970; Pennington and Lishman, 1971).

Brief Chemistry

There are 24 known isotopes with 18 of these isotopes having half-lives of less than 1 day. The only stable isotope is ^{127}I . Only ^{129}I , with a half-life of 1.7×10^7 years is of long-term interest in high-level waste disposal. The fission product ^{131}I with a half-life of 8.07 days, and ^{125}I with a half-life of 60 days, are often a short-term disposal hazard because of their anionic character and resulting lack of adsorption.

Although iodine is known in the (-I), (I), (III), (V) and (VII) oxidation states, its usual occurrence is as the (-I) (iodide) state in fresh waters with a radius of 2.20 Å (Goldschmidt et al., 1926) and as iodate-iodine in marine or similar aqueous environments (Sugawara and Terada, 1958). I^- tends to be a dispersed element in many environments as a result of its large size in comparison with fluorine, chlorine, bromine and hydroxyl ions. Oxidation of

TABLE 8.37. Iodine Concentration in Sediments and Rocks

<u>Rock Type</u>	<u>I, ppb</u>	<u>Reference</u>
<u>Volcanic</u>		
Basalt (BCR-1), Columbia River, WA	160	Becker and Manuel (1972)
Basalts, Japan, 15	29 to 140	"
Andesites, Japan, 10	22 to 260	"
Dacites, Japan, 3	43 to 220	"
Rhyolite, Japan, 2	26 to 320	"
Obsidians, Japan, 3	20 to 65	"
Obsidian, US	540 to 730	"
Obsidian, Mexico	1900	"
<u>Sedimentary</u>		
Sandstones, 11, Bashkiria, USSR	0.5 to 1.5	Itkina and Lygalova (1964)
Sandstone, white, Klondyke, MO	0.068	Becker et al. (1972)
Sandstone, red, Potsdam, NY	0.14	"
Argillaceous Sandstone, Portageville, NY	37.6	"
Argillaceous Shale, Rochester, NY	13.0	"
Calcareous Shale, Lima, NY	38.0	"
Limestones, 6, Paleozoic, OK	4.2	Collins et al. (1972)
Sediments, SW Barents Sea	68 to 828	Price et al. (1970)
Deep Sea	11 to 46	Bennett and Manuel (1968)
<u>Calcareous Ooze</u>		
(All Oceans)	16 to 40	Shishkima and Pavlova (1965)
<u>Deep Sea Clays</u>		
	30 to 250	

iodide ions to produce the iodate ion (IO_3^-) is easily accomplished in basic solution by the reaction: $3\text{I}_2 + 6\text{OH}^- \rightarrow 5\text{I}^- + \text{IO}_3^- + 3\text{H}_2\text{O}$ (Cotton and Wilkinson, 1962). Iodine can form complexes with metal ions, but these are generally the least stable of all the halide complexes, with a few exceptions. Iodine also is a volatile element, subliming at atmospheric pressures without melting.

Examples of iodine minerals include marshite (CuI), iodargyrite (AgI) and coccinite (HgI_2), bellingerite [$\text{Cu}(\text{IO}_3)_2$], salesite [$\text{CuIO}_3(\text{OH})$] and lautarite [$\text{Ca}(\text{IO}_3)_2$] (Fleischer, 1966). Most such iodine minerals are confined to unusual environments such as the Chilean nitrate deposits.

Solution Equilibria

Iodine can exist in (-I), (I), (III), (V) and (VII) oxidation states. Out of all of these oxidation states, (-I), (I^- , iodide) is the most important and its domain of predominance extends all along the pH scale, almost completely covering a large part of the stability domain of water (Pourbaix, 1966). Thus, it is not surprising that iodine in aqueous solutions free from oxidizing agents generally exists as iodide.

Laboratory Adsorption Studies

Baker et al. (1964) determined distribution coefficients for carrier-free cesium, strontium, and iodine on 17 samples of earth materials collected during July, 1961, in the vicinity of Cape Thompson, northwestern Alaska. Iodine sorption varied with percent organic matter in the samples. If the iodine remained in contact with organic matter for several days, a substantial part of it probably would be removed from solution in the natural waters.

Collet et al. (1968) studied the fixation capacities of river silt for radioactive material in order to draw conclusions on the deposition of fission products and other radioisotopes in the river bed. The distribution coefficient C_p between river silt and river water (the ratio of the absorbed mass of the element studied per gram silt to the concentration of the same element in the water in equilibrium with the silt) was determined in the laboratory for the elements ^{141}Ce , ^{137}Cs , ^{131}I , ^{32}P , ^{103}Ru , and ^{89}Sr . Altogether

756 individual samples were processed. These samples were separated by a centrifuge method into the three fractions sand, clay, and organic material, in order to obtain conclusions on the effect of the individual constituents of the silt. The methods were outlined, the results were reported, and the fixation capacities found were related to the activity of the individual fallout nuclides present in the silt.

Hamid and Warkentin (1967) evaluated ^{131}I retention in marine-deposited clay soils. Adsorption was measured with different competing anions at different salt concentrations and at varying pH values. The ^{131}I was assayed for γ radiation with a spectrometer using a solid NaI crystal scintillator. Keeping the pH value above 7 or the addition of stable iodide salt prevents the adsorption of ^{131}I on the clay particles. The ^{131}I can be used as a tracer in acid soils only in the presence of stable I^- carrier.

Juguet et al. (1966) investigated the fixation capacity of French River mud and its various components for radioisotopes cesium, strontium, ruthenium, plutonium and iodine. The purifying role of mud is confirmed by the results of measurement of fixation capacities. Depending on their nature and chemical form radioisotopes may be only slightly fixed (iodine), or may be almost totally fixed (cerium). A large part of the activity transported by surface waters is thus eliminated by deposition of mud or by filtration plants.

Knaelmann (1970) found among the fission products, ^{131}I is relatively easily transported in the soil. Therefore, its uncontrolled spreading in the soil constitutes a hazard. The sorption of iodine by 59 different soils was therefore investigated. Iodine was supplied in the form of aqueous iodide solutions of different concentrations. Differences in the relative sorption were noted among the various soils; however, the plot of concentration supplied versus relative sorption gave similar shaped curves for all soils.

Puschmann (1970) examined fine-grained sediments from the Weser, Donau, and Elbe Rivers for their sorption behavior in respect to ^{85}Sr , ^{137}Cs , and ^{131}I . The experiments with closed systems give the course of the sorption and the possible sorption rate after the equilibrium has been established. The sorption rates are converted to grams of the element per m^3 sand as used

in the laboratory experiment. The results are compared with the sorption rates dealt with by Weisflog (1968), which were made with low-terrace sediments from the River Rhine.

Schneider and Block (1968) determined the sorbability of deposits of the Rhine for several nuclides; the sorbability increases in the following order: I^- , Sr(II), Pu(IV), Zn(II), Cs(I). Saturation was reached by sediments after 24 hr at the latest for all nuclides. The sediment samples were taken from Oehningen (Upper Rhine), Koblenz (Middle Rhine), and Wesel (Lower Rhine). Data were compared with the organic content for each sample. Less than 1% of transported nuclides in the Rhine under any conceivable conditions would be bound to suspended material or sediments.

Schneider (1970) investigated the sorptive properties of artificial monomineralic fine sands of uniform grain size. Montmorillonite, kaolinite, muscovite, and biotite have a high sorptive power. The sorptive power of quartz oxides, microcline and albite is low. Hornblende and augite occupy a medium position. The highest affinity for the minerals is found for the cations ^{137}Cs , ^{90}Sr , and ^{65}Zn . Phosphorus-32, as complex phosphate anion, is less highly absorbed. The sorption of ^{131}I is negligible.

Szabova (1976) followed the sorption of radioiodine by soils under static conditions at different pH values of the initial solution in five soil types. Sorption of radioiodine by soils is affected by the amount of the organic mass and by the pH of solutions. With the same pH, soils containing a higher amount of the organic mass adsorb more radioiodine. The highest sorption percentage of $^{131}I^-$ for all pH values was found in the meadow chernozem soil and the lowest in the rendzina and in carboniferous meadow soils. The highest sorption of ^{131}I for degraded chernozem, meadow chernozem soils and brown soil was recorded at pH 5 and for carboniferous meadow soil and rendzina at pH 7.

De et al. (1971) contacted soils and soil clays with iodide solutions at 20, 30 and 40°C containing 0.127, 0.635 and 1.269 g I^-/l . Only the clay minerals showed iodide uptake, with illite absorbing more iodide than kaolinite or montmorillonite.

Goldberg et al. (1962) determined iodide absorption on Rainier tuff ground to 100 to 200 mesh from simulated ground water. The value obtained using ^{131}I was 1.10 ml/g.

Kepak (1965, 1966) studied the sorption of ^{131}I on hydrated aluminum and ferric oxide. One weight percent silver oxide was added to the ferric oxide adsorbent. The adsorbent of ferric oxide was 0.06 to 0.1 mm grain size and the influent solution contained 0.1M NaNO_3 at pH 6.9. Slow column breakthrough of the ^{131}I began immediately even from a ^{131}I -distilled water solution. Sixty-six free column volumes (void fraction = 0.66) were loaded to 1% column breakthrough and 758 free column volumes to 90% ^{131}I breakthrough.

Raja and Babcock (1961) examined the behavior of ^{131}I with two California soils, kaolinite and bentonite. Results of pretreatment by autoclaving, peroxide oxidation, alcohol digestion and extraction of ^{131}I with various salt solutions indicated that the bulk of the iodide retained by soils was due to reaction with organic matter.

Walters and Winchester (1971) examined iodine binding in dry marine sediments and found that most of the iodine was surface-adsorbed or covalent bonded to carbon. About 23% could be extracted with organic solvents.

The most extensive study of iodine retention by soils was made by Wildung et al. (1975). Iodine was applied to the soils as iodide (I^-) and methyl iodide (CH_3I), a colorless transparent liquid when fresh, with one part soluble in 50 parts of water. The solution normally remained nonionic during the distribution studies. Twenty-two soil types were collected for use in the study in Oregon, Washington and Minnesota with a range of properties as listed in Table 8.38. The $^{131}\text{I}^-$ and $\text{CH}_3^{131}\text{I}$ were used in trace quantities in 0.01M CaCl_2 solution.

TABLE 8.38. Range of Surface Soil Properties Used in the Methyl Iodide and Iodide Sorptions (Wildung et al., 1975)

	Particle Size, μ						
	10-20	5-10	2-4	1-0.5	0.5-0.25	0.25-0.1	0.1-0.05
Cation Exchange Capacity, meq/100 g	2.4	2.6	3.6	3.8	3.9	5.4	9.5

The equilibrium distribution coefficients were treated statistically. Methyl iodide retention by soils was largely a function of organic carbon and clay content, while iodide adsorption was a partial function of silt content. The mechanisms and causal relationship between the silt and iodide were under further study but were not covered in the report. The mechanisms underlying the cation exchange capacity/methyl iodide relationship are difficult to envision. Regression equations were listed to obtain iodide and methyl iodide Kd values over the soil parameter ranges studied.

Jacobs (1955) studied the desorption of radioiodine from clays. The clays and Clinch River (Oak Ridge) flood plain sediment were contaminated with iodine vapor from the oxidation of ^{131}I -tagged KI. Desorption studies indicated that the adsorbed iodine was in the form of a mixture of HI and I_2 . The rate of desorption decreased with decreased surface concentration, and after 24 hr, the iodine remaining was proportional to the reciprocal of the absolute air temperature. Desorption occurs most rapidly in high humidity air. Most of the iodine was readily removed with tap water. After ten 25-ml increments of Oak Ridge tap water through a 10-g, iodine-contaminated Clinch River floodplain sediment, less than 5% of the iodine remained on the sediment. However, removal from 10% to 5% required 60% of the water leach volume, indicating that part of the iodine is relatively tightly held. Some preliminary work with methyl iodide suggested that this chemical form of iodine would move readily through the ground without being adsorbed.

Field Studies

Mun and Bazilevich (1964) determined the abundance and distribution of iodine in lacustrine muds and pore solutions in seven fresh and salt lakes in central Kazakhstan. Iodine accumulates in the muds of fresh and salt lakes, and especially in the pore solutions of bottom muds regardless of the salinity of the lakes. The concentration of iodine increases with depth below the surface of the muds, possibly as the result of anaerobic decomposition of iodine-bearing organic matter. The content of water-soluble iodine always decreases with depth in the mud. Both fresh and salt lakes are much richer in iodine than sea water, but the iodine content of lacustrine sediments is not necessarily distinguishable from that of marine sediments because the organisms in

lakes may concentrate less iodine than marine organisms, and there is a direct correlation between content of organic carbon and iodine content.

Pennington and Lishman (1971) studied lake sediments in northern England and Scotland. Their conclusions follow:

1. In these profiles there is no evidence for changes in iodine content due to diagenesis after burial of the source material in the sediments.
2. The iodine content shows a very close correlation with the carbon content, indicating association of iodine with organic matter in the sediments.
3. This association is not, however, quite complete, for some late-glacial clays of very low carbon content contain appreciable amounts of iodine. The evidence indicates that these clays originated from soils during cold periods with freeze-thaw cycles. The iodine content can be explained by the power of clay colloids to adsorb iodine while present in soils. Varied clays, originating by fresh glacial erosion of coarse rock, contain only very small traces of iodine.
4. These facts can be explained by the hypothesis that lake sediments which are richer in iodine than the source rocks of the region must be derived from soils in the catchment area, where iodine from the atmosphere, washed down by rain and absorbed by plants, accumulated in association with humus and with clay colloids.
5. Differences from lake to lake in the iodine content of the sediments and in the ratio of iodine to carbon did not show any correlation with differences in the present annual rainfall; that is, with the supposed rate of supply of iodine from rain.
6. Changes in the iodine content and in the iodine:carbon ratio from one horizon to another in the profiles, and differences between the sites in their iodine contents and in their iodine:carbon ratios, have been shown to correlate well with changes in soils on the catchments as deduced from pollen analysis and qualitative changes in the organic fraction of the sediment.

Price et al. (1970) found in 42 surface sediments from the southwestern Barents Sea that both I and Br are related to organic matter; the dependence of halogens on the grain size of the sediment is small. With depth, all sediments showed a marked decrease in I and Br and in I/C and Br/C ratios; the ratios often reach a constant value. This decrease is caused by a loss of halogens during the burial of the sediments. The rate of decrease in iodine concentrations per unit length in the cores has provided a means of estimating the accumulation rates in the sediments.

Reynolds and Gloyna (1963) investigated factors involved in the transport of radioisotopes by suspended and bottom sediments in fresh-water streams, lakes, and estuaries in watersheds of Texas and San Antonio Bay. Uptake and release data for ^{103}Ru , ^{51}Cr , ^{137}Cs , ^{89}Sr , ^{59}Fe , and ^{131}I were collected. The bodies of water selected were the Guadalupe River, Lake Austin on the Colorado River, Lake Falcon on the Rio Grande River, and San Antonio Bay. These sampling areas provided a variety of geographical and environmental factors.

Tritremmel et al. (1966) studied the behavior of various radionuclides in surface water by field experiments in the Leitha-Muhl Canal and by complementary experiments in the laboratory. The boundary and profile characteristics of the stream were ascertained and flow rates calculated. Suspensions were examined for size and mineral or organic content in relation to current velocities, and core samples were collected from the bed at selected regions of deposition. Experiments were carried out on dispersion and transport of wastes under varying outlet conditions and the diffusion constant was measured. In the laboratory, sedimentation and uptake experiments were conducted on mineral and organic suspensions in conjunction with nuclides such as ^{90}Sr , ^{131}I , ^{140}La , ^{24}Na and mixed fission products. Uptake was found to be dependent on mineral species and varied inversely with particle size. Elution experiments were also carried out on accumulated sediments. From these results it is possible to assess the radioactive content and frequency of batch discharges of effluents that may be released to a river without causing unacceptably high concentrations.

A plot of iodine sorption versus grain size is shown in Figure 8.21.

FIGURE 8.21. Sorption of ^{131}I onto Leitha Sediment as a Function of Grain Size

Summary

Because the anion exchange capacities of most sediments are minimal over a normal pH range of 6 to 8, the adsorption of iodide (I^-), iodate (IO_3^-) and organic-iodine molecules is normally small. However, with soils of low pH (4 to 6) the iodide K_d value can rise to 50 ml/g. Wiedung et al. (1975) reported no statistical correlation between organic content and iodide K_d , as they did for methyl iodide. Others (Baker et al., 1964; Szabova, 1976; Pennington and Lishman, 1971) have shown a positive correlation between iodine content and organic material in sediments where the iodine is apparently covalently bonded to carbon (Walters and Winchester, 1971). It should be kept in mind that iodine, especially when present as an organic-iodine molecule, can change to a vapor phase and migrate much more rapidly than in an aqueous phase.

IRON

Natural Sediment and Rock Distributions

Iron is one of the major constituents of geologic materials and is found in both the Fe^{2+} and Fe^{3+} state typically described as FeO and Fe_2O_3 . Average values or typical ranges for sediments are shown in Table 8.39.

TABLE 8.39. Iron Contents of Sediments (%)

<u>Sediment Type</u>	<u>FeO</u>	<u>Fe₂O₃</u>	<u>Total Fe</u>	<u>Reference</u>
Pelagic Carbonates			0.9	Turekian and Wedepohl, 1961
Pelagic Clays		9.3	6.5	Turekian and Wedepohl, 1961
Mississippi Delta Mud		3.47		Niggli, 1952
Deep Sea Clay	1.13	7.04		El Wakeel and Riley, 1961
Deep Sea Sediments	0.94	4.89	3.5-5.2	El Wakeel and Riley, 1961
Manganese Nodules			22.44	Riley and Sinkaseni, 1958
Soils			3.8	Vinogradov, 1959

Brief Chemistry

There are 8 known isotopes of iron; stable isotopes include ^{54}Fe (5.9%), ^{56}Fe (91.52%), ^{57}Fe (2.24%) and ^{58}Fe (0.33%). The radioactive isotopes present in reactor effluents are ^{55}Fe (2.94 years) and ^{59}Fe (46 days).

Solution Equilibria

Iron can exist in Fe(II) and Fe(III) oxidation states in solution. In the oxidizing environment, the Fe(III) species will predominate. The nature of the species will be dependent upon the solution pH. Predominant iron species in oxidizing environment in <3 pH solutions is Fe^{3+} , Fe(OH)_2^+ in pH 3 to 6, Fe(OH)_3^0 in pH 6 to 9.5, and Fe(OH)_4^- in pH >9.5 (Baes and Mesmer, 1976). In reducing conditions, the predominant iron species in solutions of pH <10 will be Fe^{2+} (Baes and Mesmer, 1976).

Laboratory Adsorption Studies

The sorption of radiotracer iron onto marine and river sediments was investigated by Dawson and Duursma (1974), Duursma and Eisma (1973), Duursma and Gross (1971) and Duursma and Bosch (1970). Iron-59 added to sea water appears to precipitate from solution onto sedimentary particles. The half period of sorption is 18 ± 6 days. Because there is no observable correlation with sediment exchange properties precipitation probably is the controlling mechanism. Depending upon the experimental method used, the Kd_{Fe} observed for Mediterranean sediments in sea water for >2 to 45×10^4 ml/g. Two sediments, Wadden Sea (Holland) and Mediterranean Sea, were fractionated and Kd_{Fe} determined on the various size fractions. The Wadden Sea sediment shows an increasing Kd_{Fe} as particle size decreases. Average sorption values determined by Duursma and coworkers is found in Table 8.40.

TABLE 8.40. Kd_{Fe} Observed in Marine Sediments

<u>Sediment</u>	<u>log K</u>	<u>Estimated Kd_{Fe}, ml/g</u>	<u>$t_{1/2}$, days</u>
Atlantic Ocean	4.4 ± 0.8	4.2×10^4	16 ± 11
Pacific Ocean	4.4 ± 0.5	4.0×10^4	21 ± 13
Indian Ocean	4.2 ± 0.6	2.6×10^4	15 ± 8
Baltic Sea	4.5 ± 0.4	4.9×10^4	18
North Sea	4.6 ± 0.3	5.6×10^4	18
Mediterranean Sea	4.2 ± 0.7	2.3×10^4	14 ± 6
Black Sea	3.8 ± 0.3	1.0×10^4	18
Red Sea	3.9	1.2×10^4	14

Kawabata (1967) studied the sorption and release of radionuclides including ^{59}Fe by Sagami River sediments.

Salo and Saxen (1974) attempted to elucidate the role of humic substances in the transport of radionuclides in water. The surface waters of Bolnisan Bay, Finland, were studied by gel chromatography. The effect of salinity on organic-iron complexes was addressed. Part of the organic bound iron is readily destroyed by increases in salinity.

Schell et al. (1979) studied the fate of ^{59}Fe added to sea water in contact with montmorillonite clay, plankton and organic detritus separated from the sea water by dialysis bags. Of the six elements studied, iron showed the greatest tendency to become associated with particulate matter (see Table 8.10 in the americium section).

Field Studies

Robertson et al. (1973) and Robertson and Perkins (1975) studied the physicochemical state of iron in cooling water, Columbia River water and bed sediments. Iron bound to river sediments was not leached by sea water. Thirty grams of sediment were placed in a column and leached with 8 liters of sea water but less than 1% of the iron was removed from the sediment, which confirms iron is not controlled by ion-exchange reactions. Iron present in cooling waters emanating from N-Reactor is 98% particulate ($<0.3\ \mu\text{m}$). No quantifiable iron is reaching the springs on the banks of the Columbia River which are fed by the cooling water.

Labeyrie et al. (1975) present data showing the distribution of ^{55}Fe radioactivity in marine sediment cores and water. Iron appears to move different than fallout plutonium. The iron is present in particles sinking at a mean rate of 350 m/yr. Part of the iron in coastal sediments is redissolved probably by reduction associated with decaying organic matter, but the solubilized iron should reprecipitate after return to overlying water. Oxidation would form microparticulates which could be dispersed and translocated to the open sea. Reynolds and Gloyna (1963) studied the uptake and release of iron in model river flumes.

Summary

The fate of radioiron in marine and fresh-water environments is probably controlled by the stable iron cycle in the system. Under oxidizing conditions iron is rather insoluble and readily forms microparticulates or amorphous coatings on sediment. Under mildly reducing conditions Fe^{+2} might be solubilized with the potential of being precipitated in sulfide-bearing sediments. The observed K_d_{Fe} in the marine environment is quite large for either oxidizing or reducing conditions, 10^3 to 10^4 ml/g.

MANGANESE

Natural Sediment and Rock Distributions

Average concentrations of manganese in sediments consist of structural manganese and amorphous hydrous manganese oxides and are listed in Table 8.41.

TABLE 8.41. Manganese Content of Various Sediments (%)

Type	MnO	Total Mn	Reference
Pelagic Carbonates		0.10	Turekian and Wedepohl, 1961
Pelagic Clays		0.67	Turekian and Wedepohl, 1961
Mississippi Delta Mud	0.06		Niggli, 1952
Deep Sea Red Clay	0.48		El Wakeel and Riley, 1961
Deep Sea Sediments	0.41		El Wakeel and Riley, 1961
Manganese Nodules		32.04	Riley and Sinhaseni, 1958
Atlantic Sediments		0.006-0.08	Duursma, 1974
Pacific Sediments		0.04 -1.08	Duursma, 1974
Indian Ocean Sediments		0.42	Duursma, 1974
Soils		0.085	Vinogradov, 1959

Brief Chemistry

There are five known isotopes of manganese including only one stable one, ^{55}Mn . Manganese-54 ($t_{1/2}$ 310 days) and ^{52}Mn ($t_{1/2}$ 6.2 days) are the only radioactive isotopes of interest in reactor liquid effluents.

Solution Equilibria

Manganese can occur in solution in +2, +3, and +7 oxidation state (Baes and Mesmer, 1976). However, the +2 is the most stable. Lindsay (1972) reported that none of the manganese complexes with common inorganic ligands, present in soils (OH^- , CO_3^{2-} , SO_4^{2-}), are important. The manganese in solution below pH 9.5 will be expected to be present as Mn^{+2} (Lindsay, 1972).

Laboratory Adsorption Studies

The sorption of trace manganese onto marine sediments was investigated by Dawson and Duursma (1974), Duursma and Eisma (1973), Duursma and Gross (1971) and Duursma and Bosch (1970). It appears that trace ^{54}Mn added to sea water forms insoluble compounds on the surfaces of sediments with a half-time period of reaction equivalent to 6 days but observations were quite irregular. The distribution coefficient $K_{d_{\text{Mn}}}$ versus particle size of two marine sediments (Table 8.42) shows a somewhat irregular trend of higher sorption on smaller particle sizes.

TABLE 8.42. $K_{d_{\text{Mn}}}$ Versus Particle Size

<u>Sediment</u>	<u>Size Fraction, μ</u>	<u>$K_{d_{\text{Mn}}}$, ml/g</u>
Wadden Sea	>64	0
	32-64	2.1×10^2
	16-32	5.2×10^3
	8-16	1.2×10^3
	4-8	7.2×10^4
	<4	1.5×10^4
Mediterranean Sea	>64	0
	32-64	2.9×10^3
	16-32	6.2×10^3
	8-16	9.2×10^3
	4-8	1.1×10^4
	<4	3.5×10^3

There was also an order of magnitude larger K_d observed for manganese in oxidizing conditions versus reducing conditions for a Black Sea sediment/seawater system (6.9×10^4 versus 6.45×10^3).

The type of experimental method used to obtain the $K_{d_{\text{Mn}}}$ also affected the value somewhat (Duursma and Bosch, 1970). A value of 1.2 and 4.5×10^4 ml/g was obtained on the same sediment using two different techniques. A list of average $K_{d_{\text{Mn}}}$ for marine sediments is found in Table 8.43.

TABLE 8.43. K_d and $t_{1/2}$ for Various Sediments

<u>Sediment</u>	<u>log K, Unitless</u>	<u>K_d (estimated), ml/g</u>	<u>$t_{1/2}$, days</u>
Atlantic Ocean	3.8 ± 0.8	1.0×10^4	6 ± 6
Pacific Ocean	4.2 ± 0.9	2.5×10^4	4 ± 3
Indian Ocean	4.1 ± 0.4	1.8×10^4	8 ± 10
Baltic Sea	4.6 ± 0.3	6.0×10^4	7
North Sea	4.6 ± 1.0	6.4×10^4	17
Mediterranean Sea	3.8 ± 1.0	9.5×10^3	2 ± 2
Black Sea	4.2 ± 0.7	2.1×10^4	8
Red Sea	3.6	8.6×10^3	0.5

Gromov (1975) studied the adsorption/desorption of ^{54}Mn by various sorbents in sea water. Samples of ocean sediments were contaminated with radioisotopes and desorption carried out in fresh water.

Kawabata (1967) studied factors affecting the sorption of ^{54}Mn by river sediment in fresh and saline water. Release of ^{54}Mn adsorbed on river sediments upon exposure to sea water was slow, and with time readsorption was observed.

Salo and Saxen (1974) studied the relationship of humic acids and soluble manganese in Bothnian Bay, Finland. The greatest percentage of manganese in the water was uncomplexed and would be expected to sorb on suspended particles both mineral and high molecular weight humics.

Field Studies

Evans (1973) and Evans and Cutshall (1973) mixed unfiltered Columbia River water with filtered sea water. After 4 hr the samples were filtered and soluble and particulate manganese measured. Some of the manganese bound to suspended sediment in the river water was desorbed by sea water (particulate manganese dropped from 71 to 53%). When suspended river sediments were put in sea water the manganese showed desorption from 5% in the first hour to 55% within 1 week. For river bottom sediments suspended in sea water after

11 weeks, 50% of the manganese was released to the water. These results can be explained by ion exchange-like adsorption of manganese on fresh-water sediments. Robertson et al. (1973) confirmed a large release of manganese (40%) from river bed sediment upon leaching with sea water.

Nelson et al. (1966) and Perkins et al. (1966) determined the physico-chemical state of manganese in the cooling water and at various stations along the Columbia River. The manganese present in reactor cooling water is 3% particulate, and the percentage particulate increases downstream to 20 to 50% at Pasco and 70 to 88% at Vancouver, Washington. The soluble manganese in the cooling and river water is over 90% cationic. Upon reaching the saline estuary portion of the river the soluble manganese is significantly different (48% cationic, 43% anionic and 10% uncharged).

Robertson and Perkins (1975) found the ^{54}Mn present in M-Reactor cooling water was 10% particulate and 89% cationic. Quantifiable manganese is not observed in spring water on the banks of the Columbia River which is fed by the cooling water.

Bonatti et al. (1971) observed that manganese is enriched in the upper oxidized zone of deep sea cores versus reduced layers.

Summary

The fate of manganese in the marine environment appears to be controlled by oxidation-reduction precipitation-dissolution of hydrous oxides. The observed K_d_{Mn} in sea water is large 10^3 - 10^4 ml/g. The fresh-water oxidizing environments, manganese appears to exhibit ion-exchange-like behavior. No K_d_{Mn} values are reported but studies on the Columbia River suggest manganese is found on particulates.

NEPTUNIUM

Natural Sediment and Rock Distributions

Very small quantities of ^{237}Np ($^{237}\text{Np}/^{238}\text{U} = 10^{-12}$) were reported by Keller (1971) but for practical purposes neptunium does not occur naturally in sediments or rocks.

Brief Chemistry

There are 16 known isotopes of neptunium from ^{228}Np to ^{241}Np (Keller, 1971). Only ^{237}Np , a neutron reaction product of ^{238}U ($n, 2n$) and ^{235}U (n, γ)², with a half-life of 2.14×10^6 years is of interest here. The 5000 year half-life ^{236}Np is a cyclotron product only. Neptunium exists in aqueous solutions in five oxidation states, Np(III) , Np(IV) , Np(V) , Np(VI) and Np(VII) . In the absence of complexing agents, the first four oxidation states exist as hydrated ions $\text{Np}^{+3} \cdot \text{aq}$, $\text{Np}^{+4} \cdot \text{aq}$, $\text{NpO}_2^+ \cdot \text{aq}$ and $\text{NpO}_2^{+2} \cdot \text{aq}$ (Keller, 1971). Np(VII) is a strong oxidizing agent that is stable in strong alkaline solutions as NpO_5^{-3} . The most stable oxidation state in solution is the pentavalent one where neptunium exists as a single charged neptunyl ion, $\text{NpO}_2^+ \cdot \text{aq}$, with symmetrical linear bonding ($\text{O}-\text{Np}-\text{O}$)⁺. It hydrolyzes only at a pH of greater than 7, disproportionates only at high acid concentrations and forms no polynuclear complexes (Keller, 1971). The NpO_2^+ ion is a poor complexing agent with inorganic ligands.

Solution Equilibria

The activity of various solution complexes of neptunium in equilibrium with $\text{NpO}_2(\text{s})$ in an oxidizing environment ($p\text{O}_2 = 0.68$) and assumed weathering environment is given in Figure 8.22. Thermodynamic data for $\text{NpO}_2 \cdot \text{HPO}_4^-$ were obtained from Sillen and Martell (1964). The remaining data were from Burney and Harbour (1974). The solution complexes of Np(IV) , Np(V) , and Np(VI) in order of increasing importance are Np(IV) , Np(VI) , and Np(V) . The activity of Np(IV) and Np(VI) complexes is so small that these complexes can be safely ignored since they would not contribute significantly to the total activity of Np in solution (Burney and Harbour, 1974). The lines of Np(V) and Np(VI) complexes will shift downward with the increase in reducing environment but still

be parallel to the present lines. Under the oxidizing conditions assumed in Figure 8.22, NpO_2^+ is the most dominant solution species in a pH range of 0 to approximately 9. Beyond pH 9, $\text{NpO}_2\text{HPO}_4^-$ and $\text{NpO}_2\text{HCO}_3^0$ would control the total concentration of neptunium in solution. In reducing environments, the expected predominant solution species are NpOH^{3+} and Np^{4+} .

FIGURE 8.22. The Activity of Various Neptunium Species in Equilibrium with $\text{NpO}_2(\text{s})$ in an Oxidizing Soil Environment [$\text{pO}_2(\text{g}) = 0.68 \text{ atm}$], $\text{pCl}^- = \text{pSO}_4^{2-} = 2.5$, $\text{pH}_3 = 3.0$, $\text{pF}^- = 4.5$ and $\text{pH}_2\text{FO}_4 = 5.0$

NpO_2 is the usual form of charged neptunium species up to pH 9. Above pH 9, an uncharged bicarbonate complex is formed. According to Keller (1971) neptunium (V) does not hydrolyze below a pH of 7. Consequently, a singly charged neptunyl ion is the usual form. Hence, NpO_2^+ would be expected to enter

into ion-exchange reactions. NpO_2^+ does not compete favorably with Ca^{+2} and other common divalent ions, and the distribution coefficients are usually relatively low on most soils (Routson et al., 1976b; Sheppard et al., 1976).

Laboratory Adsorption Studies

Bensen (1961) examined the adsorption on minerals of radionuclides in reactor effluent cooling water. One of the radionuclides studied was ^{237}Np , which was adsorbed on 25 different common sulfide, silicate and carbonate minerals, 0.05 to 0.25 mm, in equilibrium tests with trace amounts in Columbia River water at 80°C. According to Bensen, neptunium was adsorbed poorly or not at all by the minerals tested.

Robertson (1974) determined the speciation of neptunium in the cooling water effluent from the Hanford N reactor. Through the use of filter membranes and cation and anion exchange resins, the following distribution was observed: 26% particulate, 70% cationic, <3% anionic and <1% nonionic.

Routson et al. (1975, 1976) determined neptunium Kd values for a Washington sand and a South Carolina sandy clay. The properties of these soils are given in Table 8.44. The neptunium Kd values are given in Table 8.45. Pre-equilibrations of the soils with nonradioactive solutions prior to contact with the traced solution containing ^{237}Np were carried out. Calcium nitrate and sodium nitrate salts were used as calcium and sodium ion sources. Cation exchange of NpO_2^+ cannot be the principal adsorption mechanism because Na^+ concentration essentially does not affect the neptunium Kd values from no sodium competition to 3.0M Na^+ competition. Calcium has some effect on the neptunium Kd, but much less than there would be if neptunium adsorption were due to ion exchange.

Sheppard et al. (1976) determined neptunium distributions on several Washington and North Carolina soils. The distilled water-trace ^{237}Np solutions and soils were equilibrated over long periods of time to obtain a rate of change per month in the distribution values. The 50-day values are given in Table 8.46. A positive value for the monthly change in the distribution

**TABLE 8.44. Properties of Soil Samples
(Routson et al., 1976)**

<u>Soil</u>	<u>CaCO₃ mg/g</u>	<u>Silt, wt%</u>	<u>Clay, wt%</u>	<u>CEC, meq/100 g</u>	<u>pH</u>
Washington Soil (Burbank sandy loam)	0.8	10.1	0.5	4.9	7.0
South Carolina Subsoil	0.2	3.6	37.2	2.5	5.1

**TABLE 8.45. Neptunium Kd (ml/g) as a Function of Soil
and Solution (Routson et al., 1976)**

<u>Soil</u>	<u>Ca</u>		<u>Na</u>	
	<u>0.002 M</u>	<u>0.2 M</u>	<u>0.015 M</u>	<u>3.00 M</u>
Washington	2.37	0.36	3.9	3.2
South Carolina	0.25	0.16	0.7	0.4

**TABLE 8.46. Neptunium 50-day Distribution Values Computed
from Sheppard et al. (1976)**

<u>Soil Identity</u>	<u>Kp Distribution, ml/g</u>	<u>Monthly Change in Distribution, %</u>
Muscatine silt loam	127	+10
Burbank loamy sand	15.4	+48
Ritzville silt loam	20.2	+28
Fuquay sand 0 to 5 cm depth	33.7	+25
Fuquay sand 5 to 15 cm depth	37.2	+25
Fuquay sand 15 to 50 cm depth	32.4	+19

means an increase in the size of the distribution value. The distribution was determined in the same way that a K_d value is determined, but does not have the connotation that equilibrium has been attained.

The neptunium K_d value of about 3.9 ml/g was given by Routson et al. (1975, 1976) for the Burbank sandy loam without sodium in the solution. Sheppard et al. (1976), apparently for the same conditions, gives a neptunium 50-day distribution value of 15.4 ml/g for Burbank and states that this value is increasing at the rate of +48%/month. At 100 days, the distribution was approximately 50 ml/g on the Burbank loamy sand. The differences in neptunium distribution between soil and solution probably resulted from the experimental differences because the Burbank sandy loam of Sheppard was obtained from Routson. However, Sheppard showed the Burbank sample to contain 21.2% silt and 2.8% clay with a pH of 8.1 and a cation-exchange capacity of 5.94 meq/100 g compared to Routson's Burbank soil sample (Table 8.44). Sheppard's Burbank must have contained calcite (CaCO_3) to attain a pH of 8.1. There is no evidence in Sheppard et al. (1976) that the soil samples were pre-equilibrated in any way with the nonradioactive solution before the neptunium tracer was added, or that a blank solution without the soil was run with the soil equilibrations for reference and to observe container adsorption. In addition, Sheppard reported that his $^{237}\text{Np(V)}$ in the aqueous phase equilibrating with Ritzville soil was partially filterable on Whatman number 50 filter paper. Routson, on the other hand, reported that upon filtering previously centrifuged samples of solution containing neptunium and in contact with Burbank or South Carolina subsoil through 0.01 and 0.45 μm filters, no evidence of colloidal ^{237}Np was found. This is further evidence that Sheppard's high neptunium distribution values require further elucidation in light of Routson's results.

Field Studies

Sedlet and Colchert (1977) measured the ^{237}Np content of Sawmill Creek which receives waste water from Argonne National Lab. They found detectable Np (10^{-14} Ci/l). Ninety percent of the neptunium appeared to pass through an unspecified filter size after acidification to pH 1.

Summary

The existing thermodynamic data (Figure 8.22) show that neptunium should exist in an oxidizing soil environment as Np(V) in the form of NpO_2^+ . However, existing adsorption results, a study by Routson et al. (1975, 1976) and Sheppard et al. (1976), inferred that there is little evidence of NpO_2^+ ion exchange as a neptunium adsorption mechanism. Sheppard et al. (1976) reported neptunium colloids present in the soil-solution environment, while Routson et al. (1975, 1976) specifically showed that they were absent from his solutions that had contacted soils. Little more can be said based on the adsorption and migration studies now available in the literature. Additional research is required on neptunium/sediment reactions. Attention should be focused on whether NpO_2^+ can be reduced to much less soluble Np(IV) forms by reducing sediments.

PHOSPHORUS

Natural Sediment and Rock Distribution

Phosphate minerals, in addition to schreibersite and perryite, are the only phosphorus compounds known to occur in nature. Average values for phosphorus often reported as P_2O_5 are found in Table 8.47.

TABLE 8.47. Phosphorus Content of Rocks and Sediments

<u>Type</u>	<u>P, %</u>	<u>P_2O_5 %</u>	<u>Reference</u>
Sandstone		0.08	Wedepohl, 1969
Shale		0.16	Wedepohl, 1969
Carbonates		0.07 to 0.16	Wedepohl, 1969
Pelagic Clays		0.72	Wedepohl, 1969
Igneous Rocks	0.11		Hem, 1970
Sandstone	0.05		Hem, 1970
Shale	0.07		Hem, 1970
Carbonates	0.028		Hem, 1970

Brief Chemistry

There is only one stable isotope of phosphorus, ^{31}P . There are two radioactive isotopes with half-lives larger than a few minutes P^{32} (14.3 days) and P^{33} (25 days). Phosphorus in the environment is typically found in the +5 valence state as a phosphate PO_4^{3-} , HPO_4^{2-} , $H_2PO_4^-$ anions both in the water column and sediments. Phosphorus along with carbon and nitrogen form the building blocks of most organic matter. Thus organic bound phosphorus can contribute to the overall distribution. The average concentrations of phosphorus in oceans and North American streams are 0.088 and 0.019 ppm, respectively (Wedepohl, 1969). In sea water phosphorus is found as $H_2PO_4^-$ and ion pairs with cations (Kester and Pytkowicz, 1967). In fresh waters phosphorus is likely to be present as phosphate anions, complexes with metal ions and colloidal particulate matter (Hem 1970).

Laboratory Adsorption Studies

Numerous investigators have observed that under oxidizing conditions phosphorus (phosphates) is readily adsorbed by sediments and under reducing conditions phosphates are resolubilized (Berner, 1975, Khalid et al., 1978, Fitzgerald, 1970, Harter, 1968, Li et al., 1972, Mortimer, 1941, Shukla et al., 1971, Syers et al., 1973, and Williams et al., 1971). The key to this redox sensitive reaction is the very high affinity for hydrous oxides of aluminum, manganese and iron for phosphate anions. Under oxidizing conditions these hydrous oxides lower the phosphate concentrations to less than 0.1 ppm typically. Other sorbates include the precipitation of apatites $\text{Ca}_3(\text{PO}_4)_2$ and organic matter. Under reducing conditions the reduction of hydrous oxides, degradation of organic material releases phosphates.

Green et al. (1978) studied the adsorption-desorption characteristics of Ohio river sediments and suspended sediments. Suspended sediment contained more total phosphorus than bottom sediments 1350 ppm versus 900 ppm. The suspended sediments and bottom sediments adsorption followed Langmuir isotherms. The higher phosphorus suspended solids may be caused by the increased contact with soluble phosphorus, more oxidizing conditions, algae measured as suspended solids or smaller particle size (larger surface area) distribution than bottom sediments. The energy of adsorption (resistance to desorption) was larger for bottom sediments than suspended solids.

Kuo and Lotse (1974) studied the rate and extent of phosphate adsorption and desorption and the energy of phosphate adsorption by lake sediments. They found that phosphate adsorption could be described by the Freundlich equation over a large phosphorus concentration range (0 to 200 ppm phosphorus) while Langmuir adsorption isotherms provided a good data fit only at low phosphorus concentrations 0 to 75 ppm phosphorus. The rate of phosphorus adsorption by the sediments could be described by the equation $X = K C_0^{1/n} t^{1/m}$ where

X = phosphorus adsorbed ($\mu\text{g/g}$)

C_0 = initial phosphorus concentration (ppm)

t = time

$K, 1/n = \text{empirical constants}$

The activation energy of sorption and desorption were found to be quite low suggesting phosphate adsorption desorption are diffusion controlled processes. They also noted that freshly adsorbed phosphorus exhibited a much higher degree of "exchangeability". Desorption of native phosphorus from sediments using $2.5 \times 10^{-3} \text{ M EDTA}^{2-}$, F^- , HC_2O_4^- or OH^- showed that only EDTA^{2-} significantly increased desorption. As EDTA is a strong complexer of iron it probably induced decomposition of amorphous hydrous iron oxides. At a sediment to solution ratio of 0.01 g/ml adsorption and desorption reached steady-state after 48 hours.

Enfield and Bledsoe (1975) measured the kinetics of orthophosphate sorption with 25 soil minerals. They found the reaction of phosphorus with soil minerals is not instantaneous. Thus, using equilibrium isotherms will yield erroneous conclusions as to the ability of soil to adsorb phosphorus. A diffusion-limited process paralleling heat flow theory for the storage of heat in spheres best describes the experimental data.

Collet et al. (1968) determined the fixation capacities of the Rhine river silt for radioactive material in order to draw conclusions on the deposition of fission products and other radioisotopes in the river bed. Therefore, the distribution coefficient C_p between river silt and river water (the ratio of the absorbed mass of the element studied per gram silt to the concentration of the same element in the water in equilibrium with the silt) was determined in the laboratory for the elements Ce, Cs, I, P, Ru, and Sr. Cerium-141, ^{37}Cs , ^{131}I , ^{32}P , ^{103}Ru , and ^{88}Sr were used as the labeling isotopes. Altogether 756 individual samples were processed. These samples were separated by a centrifuge method into the three fractions sand, clay, and organic material, in order to obtain conclusions on the effect of the individual constituents of the silt. The methods were outlined, the results were reported, and the fixation capacities found were related to the activity of the individual fallout nuclides present in the silt.

Schneider (1970) investigated the sorptive properties of artificial monomineralic fine sands of uniform grain size. Montmorillonite, kaolinite, muscovite, and biotite have a higher sorptive power. The sorptive power of quartz

oxides and magnetite and of microcline and albite is low. Hornblende and augite occupy a medium position. The highest affinity for the minerals show the cations ^{137}Cs , ^{90}Sr , and ^{65}Zn . Phosphorus-32, as complex phosphate anion, is less highly adsorbed. The sorption of ^{131}I is negligible.

Carritt and Goodgal (1954) studied the sorption of dissolved substances on suspended solids in natural waters using Chesapeake Bay materials in the laboratory and field. The field results did not conclusively fit a Freundlich isotherm. Laboratory studies of phosphate uptake showed a rapid adsorption process and a much slower diffusion controlled reaction. In the laboratory a log-log plot of percent phosphorus sorbed versus time remained linear up to 70 hours. In other words adsorption continued throughout the experimental period without reaching equilibrium. Phosphorus adsorption versus pH is shown in Figure 8.23.

FIGURE 8.23. Removal of Phosphate by Roanoke River Solids as a Function of pH. Initial conditions; temperature 21°C, solids 310 ppm, total phosphorus 0.5 μg at P/l.

A comparison of these curves with phosphoric acid dissociation curves indicates that maximum uptake occurs in the pH range in which H_2PO_4^- is the predominant species. Temperature also affects phosphorus sorption. For a given initial phosphorus concentration in solution more phosphorus is adsorbed by sediments at higher temperatures. Time dependent studies show a rapid <1 min portion and a slow diffusion controlled portion. The driving force for the slow reaction was identified as the phosphorus gradient in and near the adsorbed layer on the solid surface. During desorption the amount of phosphorus and rate of removal will depend upon the length of time the complex has had to form. With long contact time a greater fraction of the phosphorus will have diffused into the solid and so will be slower to desorb. For example, Figure 8.24 contains results of successive 2-min desorption experiments on sediments on two samples, which have been in contact with phosphorus for 4 days and 30 min.

FIGURE 8.24. The Effect of Prior Contact Time on the Desorption of Phosphorus from Solids (pH of wash 3-4)
 A. 4 days contact.
 B. 30 min contact.

The effect of salinity on phosphorus adsorption are shown in Figure 8.25. The reduction in adsorption of phosphorus at higher salinities was hypothesized to be due to agglomeration or clumping of the finely dispersed solids, which reduces surface area for adsorption. Competition of other anions such as sulfates also cannot be ruled out.

Lean and Charlton (1976) measured the biological (algae) interaction of phosphorus in a leak ecosystem but found the interpretation difficult.

FIGURE 8.25. The Effect of Variations in Salinity on the Uptake of Phosphorus. Initial conditions; pH 3.4, solids 310, phosphorus 0.9 μg at P/l, salinity as noted.

Field Studies

Plutonium-32 is an activation product formed in nuclear reactors. At Hanford through the mid-1960s an average of about 40 curies/day were released to the Columbia River from Hanford plutonium producing reactors (Foster 1963a, 1963b, 1964) and Wilson and Eggers (1970). The average Columbia River ^{32}P concentration varied seasonally with river flow rate between 80 and 500 pCi/l. Whitefish caught in the vicinity of the chronic release were found to contain 10^{-4} $\mu\text{g/g}$ of ^{32}P . After the reactors were shut down the ^{32}P rapidly decayed away. In 1970, the year that the last plutonium reactor was shut down, the estimated total Columbia River-North Pacific Ocean inventory of ^{32}P was 600 curies. Within 1/2 year this inventory had decayed to 0.15 curies.

In a draft document on reactor coolant water Dames and Moore (1978) showed a typical range of 4 to 110 pCi/ml of ^{32}P .

Simpson et al. (1975) studied the phosphorus budget in the Hudson River estuary. Sewage pollutants rich in phosphorus were found. Once mixed in the estuary the organic phosphorus content was quite low while particulate phosphorus reached levels of 30 to 50% of the total phosphorus.

Taft and Taylor (1975) described the annual cycle of phosphorus in Chesapeake Bay and not for the dissolved component, organic nitrogen is often abundant as orthophosphate species.

Summary

Phosphorus is found to adsorb readily to suspended sediments and bottom deposits under oxidizing conditions. The main adsorbate mechanism is hydrous aluminum iron and manganese oxides. Under reducing conditions these amorphous precipitates readily dissolve releasing bound phosphorus. Phosphorus also enters biological processes and can be found in living and decaying biomass. A K_d ^{32}P is dependent upon the specific activity (amount of radioactive ^{32}P /amount of stable phosphorus). The more stable phosphorus present the smaller will be the K_d ^{32}P caused by isotope dilution.

The half-life of ^{32}P (14.3 days) would require chronic releases to continually supply a renewed source before serious environmental consequences would be expected.

PLUTONIUM

Natural Soil and Rock Distributions

Except for extremely small quantities of plutonium in the natural environments, plutonium does not occur in any significant amount in sediments or rocks. Cherdyntsev et al. (1968), for example, lists ^{239}Pu values in natural rocks and minerals varying from $7 \times 10^{-12} \text{ g } ^{239}\text{Pu/g}$ to $1 \times 10^{-15} \text{ g } ^{239}\text{Pu/g}$.

Brief Chemistry

Fifteen isotopes of plutonium are known, including 10 isomers with different decay modes (Keller, 1971). Most of the isotopes are formed by multiple neutron capture and, therefore, are not ordinarily encountered in natural environments. An exception is the natural reactor at Oklo, Gabon (IAEA, 1975) and very small amounts ($\text{Pu/U} = 10^{-11}$) found in the uranium mineral pitchblende (Cleveland, 1970).

The plutonium isotopes of concern to waste disposal, either because they are contained in the fission product wastes or are a part of an important decay chain for waste constituents, are listed in Table 8.48. In the short term, almost any plutonium radionuclide would be of concern in waste-radionuclide reactions although, on a weight basis, longer-lived ^{242}Pu is not nearly as hazardous as ^{239}Pu . Long irradiation times and high neutron fluxes are required to produce significant amounts of ^{242}Pu , so that a prevalence of the higher mass Pu isotopes usually will not occur in waste solutions from commercial fuel treatment facilities.

TABLE 8.48. Plutonium Radionuclide Data (Keller 1971)

<u>Isotope</u>	<u>Half-Life, yr</u>	<u>Decay Mode</u>
^{238}Pu	86.4	α
^{239}Pu	24,400	α
^{240}Pu	6,600	α
^{241}Pu	14.1	β
^{242}Pu	387,000	α

Plutonium exists in five oxidation states in aqueous solutions: Pu(III), Pu(IV), Pu(V), Pu(VI), and Pu(VII). These states can occur as the hydrated ions $\text{Pu}^{+3} \cdot \text{aq}$, $\text{Pu}^{+4} \cdot \text{aq}$, $\text{PuO}_2^+ \cdot \text{aq}$, $\text{PuO}_2^{2+} \cdot \text{aq}$ and $\text{PuO}_2^{-3} \cdot \text{aq}$ (Keller, 1971). The most stable state of plutonium in aqueous solution is Pu(IV). However, disproportionation, in which Pu(III), Pu(IV), Pu(V) and Pu(VI) states can coexist in unequal quantities, tends to further complicate plutonium chemistry in its reactions with soils and sediments. According to Cleveland (1970), plutonium in near-neutral solutions occurs in the order: $\text{Pu}^{+4} > \text{PuO}_2^+ > \text{Pu}^{+3} > \text{PuO}_2^{2+}$. Hydrolysis reactions lead to the formation of positively charged to neutral colloidal polymers in a stepwise manner. For example, $\text{Pu}^{+4} + \text{OH}^- \rightarrow \text{PuOH}^{+3} + \text{OH}^- \rightarrow \text{Pu(OH)}_2^{+2}$, etc., leads finally to Pu(OH)_4 which loses water to produce thermodynamically stable PuO_2 (Keller, 1971). Complexing agents such as fluoride or sulfate ions can accelerate the process. Plutonium can form complexes with most of the ions commonly encountered in natural solutions. Thus disproportionation, complex formation and hydrolysis reactions, all relatively pronounced with aqueous plutonium solutions, combine to add to plutonium chemistry complexity.

Figure 8.26 demonstrates the activity of various plutonium species expected in equilibrium with $\text{PuO}_2(\text{s})$ and in an oxidizing environment ($p\text{O}_2$, 16 atm). Plutonium in solution exists in four oxidation states (Pu^{3+} , Pu^{4+} , PuO_2^+ , PuO_2^{2+}) and forms complexes with OH^- , Cl^- , F^- , SO_4^{2-} , H_2PO_4^- and CO_3^{2-} ions. In general, the activity of all positively charged ions and ion-complexes and a few neutral ion-pairs decreases with the increase in pH, while the activity of all negatively charged ion-complexes increases with the increase in pH. In an oxidizing environment, Pu^{3+} and Pu^{4+} and their ion-pairs have an insignificant effect on the total activity of plutonium in solution. At any given pH, the total activity of plutonium in solution can be obtained by adding the appropriate activities of various plutonium species. Since the lines for some plutonium species are based on concentration constants, the position of the lines may change when converted to thermodynamic equilibrium constants. Figures 8.26 and 8.27 were constructed by assuming a weathering environment ($p\text{CO}_2 = 3.53$; $p\text{Cl}^- = p\text{SO}_4^{2-} - 2.5$; $p\text{F}^- = 3.5$) and $\text{PuO}_2(\text{s})$ as the compound that may be present in the environment at equilibrium.

FIGURE 8.26. The Activity of Various Plutonium Species in Soil Solution in Equilibrium with $\text{PuO}_2(\text{s})$ at pH 8, $p\text{CO}_2 = 3.52 \text{ atm}$, $p\text{Cl}^- = p\text{SO}_4^{2-} = 2.5$ and $p\text{H}_2\text{PO}_4^- = 5.0$ (Rai and Serne, 1977)

FIGURE 8.27. The Activity of Various Plutonium Species in Soil Solution in with $\text{PuO}_2(\text{s})$ in a Mildly Oxidizing Soil Environment [$p\text{O}_2 = 16 \text{ atm}$], $p\text{CO}_2 = 3.52 \text{ atm}$, $p\text{Cl}^- = 2.5$, $p\text{F}^- = 3.5$, and $p\text{H}_2\text{PO}_4^- = 5.0$ (Rai and Serne, 1977)

Figure 8.26 relates the activities of (a_i , moles/l) of various solution species at pH 8 to the oxidation potential as represented by the various oxygen pressures. In general, with a decrease in oxygen pressure (increases in reducing conditions), the kind of activity of the solution species changes: 1) Pu^{3+} species increase in activity, 2) Pu^{4+} species are unaffected, and 3) PuO_2^{2+} and PuO^{2+} species decrease in activity.

A few of the reactions are not plotted in the figures because either the activities of the species fall beyond the graph boundaries or the equilibrium constant data are not reliable. Cleveland (1970) suggested that the values for the formation constants of PuCO_3^{2+} and $\text{Pu}(\text{OH})_4^0$ were suspect; the values for $\text{PuO}_2(\text{OH})_3^-$, $\text{PuO}_2(\text{OH})_2^0$, and PuO_2OH^+ should be viewed with skepticism; and the value for PuO_2OH^0 should be considered only approximate. Under the assumptions of Figure 8.27, the lines for $\text{Pu}(\text{OH})_4^0$ and $\text{PuO}_2(\text{OH})_2^0$ would be parallel to the X-axis with $10^{-12.51}$ and $10^{-16.16}$ moles/l activity, respectively. Many researchers (Andelman and Rozzell, 1970; Fukai and Murray, 1974; Grebenshchikova and Davydov, 1961, 1965; Sheidina and Kovarskaya, 1970) have reported that plutonium in solution also exists as colloidal species over a wide pH range. Colloidal species and neutral ion-complexes [$\text{Pu}(\text{OH})_4^0$, $\text{PuO}_2(\text{OH})_2^0$] are not reported in Figures 8.26 and 8.27. If present in large quantities, these species would significantly influence the nature of the species and the total concentration of plutonium in solutions.

In an oxidizing environment, Pu^{3+} and Pu^{4+} and their ion-pairs have an insignificant effect on the total activity of plutonium in solution and the dominant plutonium species in low and high pH ranges are PuO_2^+ and $\text{PuO}_2\text{CO}_3\text{OH}^-$, respectively. In general, with a decrease in oxygen pressure (increase in reducing conditions), the kind of activity of the solution species changes: Pu^{3+} and its complexes will increase in activity while PuO_2^+ and PuO_2^{2+} and their complexes will decrease in activity. In moderately to well reduced conditions, the predominant solution species would be PuOH^{2+} , with Pu^{3+} of lesser importance. In reducing seawater solutions high in Cl^- ($\text{pCl}^- = 0.45$), PuCl^{2+} would be the most dominant solution species.

Laboratory Adsorption Studies

Davydov (1972) investigated the hydrolysis of Pu(IV) and sorption under acidic conditions.

- The sorption of Pu(IV) by silica gel was investigated in the range 0.5M HNO_3 to pH = 2.5.
- It was shown that in the region of hydrolysis of Pu(IV), hydrolyzed ions $\text{Pu}(\text{OH})_n^{4-n}$ are sorbed, and their sorption capacity is either equal to or greater than the sorption capacity of Pu^{4+} ions.
- It was shown that the sorption of hydrolyzed Pu(IV) ions does not depend on the concentration of the extraneous electrolyte in the range 0.1M to 3.0M NaNO_3 .

Duursma and Eisma (1973) and Duursma and Parsi (1974) have determined the proclivity of plutonium to sorb in the marine environment. The adsorption of plutonium is intermediate; less than Cs, Rb, Zn, Fe, Zr-Nb, Ru and Pm and greater than Ca and Sr. Plutonium has been observed to penetrate sediments at least to 8-14 cm and in the early 1970's, inventories in the sediment appear to show losses. Biological processes or upward migration in interstitial waters as a reduced species are two possible explanations although Mo and Lowman (1975) show data which find reducing conditions tend to lower Pu mobility. Changes in the Am/Pu ratio from waters to sediments in the ocean led Duursma to conclude americium is preferentially sorbing or not being remobilized as fast as plutonium. In sea water $\text{PuO}_2(\text{CO}_3)_3^{-4}$ may predominate and cause the lower plutonium sorption. Using a ^{237}Pu tracer in valence states +3, +4, and +6 in both oxic and anoxic sea waters at pH 7.8 to 8.0, the K_d_{Pu} for marine sediments was found to be about 10^4 . Valence states and solution Eh states did not cause marked differences.

The $t_{1/2}$ sorption times for Pu(III) were about 3 days, Pu(IV) about 1.4 days and Pu(VI) about 4 days. The spiked sea water when allowed to sit in blank reaction vessels (no sediment) showed significant losses of Pu. The Pu(III) and Pu(IV) loss was 30 to 50% while the Pu(VI) loss was 9% over a

three week period suggesting Pu(VI) is more prone to remain soluble in water. The fact that the $K_{d_{Pu}}$ for all three valence states were similar probably reflect the reduction of Pu(VI) to Pu(IV) or Pu(III).

Fukai and Murray (1974) performed plutonium sorption-desorption experiments for both freshwater and saline conditions. Plutonium (III) sorption experiments from river water to river sediments (100 ml traced solution/g sediments) were performed. The initial stage of adsorption was rapid; 50% within 10 hr. For pHs 3 to 11 over 90% of the Pu(III) was adsorbed by the river sediment. Desorption experiments were performed wherein the sediments used in the adsorption experiments were suspended in sea water. Over the pH range 4 to 10 about 10% of the adsorbed plutonium was released without apparent pH differences. Similar adsorption-desorption experiments were performed with river sediments contacted with various dilutions of fresh water sewage effluent at pH 8.1. The Pu(III) adsorption increased from 85% in river water to over 95% at 100% sewage effluent. These sediments were next contacted with sea water and desorption monitored. At equilibrium, river sediments which had not been contacted with sewage effluent released only 5% of its plutonium whereas sediments contacted with 5 to 100% by volume sewage effluent released 12% of their plutonium burden.

In blank experiments Pu added to filtered river water and sea water (0.45 μ m), particulate formation is shown to be dependent upon the nature of solution and the pH. The particulate fractions of all species increased with the increase in pH. For river water at pH 4, some 25, 20, and 30% of the added Pu-237 were associated with particulate (>0.45 μ) for the III, IV, and VI valence states, respectively. The percentage of particulate formation was >60 at pH 8 for all species, except Pu(VI). These results for Pu stability in river water and sea water are shown in Figures 8.28 and 8.29. Figure 8.28 shows the adsorption of Pu(III) versus Am(III) onto Var River sediments from river water. The Pu(III) readily adsorbs at all pHs studied (3 to 11). Figure 8.30 shows the adsorption of Pu(IV) onto the same sediment at pH 8 versus time as well as the desorption of Pu when the river sediments contact sea water. Figure 8.31 shows the desorption of Pu(III) and Am(III) from river sediments versus pH of sea water. For both adsorption and desorption Pu shows a greater affinity for sediments at lower pHs.

FIGURE 8.28. Particulate Formation of Pu(III, IV, VI) in Var River Water as a Function of Changes in pH

FIGURE 8.29. Particulate Formation of Pu(III, IV, VI) in Sea Water as a Function of Changes in pH

FIGURE 8.30. Equilibrium Time for Adsorption on Sediments of Pu(IV) in Var River Water ($\text{pH} \approx 8$) and Its Desorption from Sediments in the Seawater Medium

FIGURE 8.31. Desorption of Pu(III) and Am(III) from Sediments in the Seawater Medium at Different pH Levels

Kd_{Pu_3} calculated from data in the figures for neutral pHs were typically around 10^3 ml/g whether measured in the adsorption or desorption direction.

Gromov and Spitsyn (1974a,b) and Gromov (1975) investigated the change in the physiochemical state of Pu due to its interaction with phytoplankton and the adsorption-desorption of ^{239}Pu onto Pacific Ocean red clays, carbonates, diatomaceous ooze. Red clay and carbonaceous sediments adsorb more Pu. The phytoplankton interactions change the Pu form and thus alter the entrapment of Pu in bottom and suspended sediments.

Mo and Lowman (1975) placed plutonium contaminated calcareous sediment in aerated sea water and anoxic sea water and stirred the system until solution activities were at equilibrium. The resultant Kd_{Pu} desorption distributions were 1.64×10^4 and 3.85×10^5 .

Pillai and Mathew (1975) quantitatively leached the plutonium present in Bombay sediments with 8M HNO_3 . Hydrogen peroxide treatment at $80^\circ C$ and pH 5.8 did not appear to release plutonium but under these conditions it is likely released Pu would precipitate or quickly resorb. Alkali treatment to extract organics removed 0.4 to 7.5% of the total plutonium. Contaminated sediments stirred with uncontaminated sea water for 8 hr before filtration did not release any plutonium into the sea water. Kd values for suspended silt and bottom sediments were observed to average 9×10^4 ml/g with a range of 4.8×10^4 to 1.3×10^5 .

In laboratory experiments to study the speciation of Pu in sea water and soluble organic effects, Pillai and Mathew found at pH 7.4 to 7.8 that the soluble Pu concentration in sea water calculates to $10^{-11}M$. Both cationic and anionic species decreased with time while nonionic species increased.

In the case of sea water to which soluble organic matter had been added more Pu was retained in solution for the first 30 days, then there was a tendency for more Pu precipitation along with organic matter. The remaining soluble Pu in the organic rich water had a larger anionic distribution. The implication is that organic matter reduces the tendency of Pu to hydrolyze and form colloids.

Rozzell and Andelman (1971) studied the sorption-desorption of aqueous Pu (10^{-8} to 10^{-7} M) on quartz and other silica surfaces. Sorption continued typically for 12 to 15 days before apparent equilibrium was reached. At pH 7, sorption increased with increasing ionic strength, but decreased when HCO_3^- was added. The amount of sorption varied at pH 5 and 7, but differently at high and low ionic strengths, as well as with age of the solution. Plutonium desorption indicated that there were two basically different sorbed species. There was a greater net desorption at pH 5 versus pH 7 to 9.

Many investigations have been performed on plutonium adsorption by sediments, both fresh water and marine. Schneider and Block (1968) found plutonium to sorb more than I^- and Sr^{+2} but less than Zn^{+2} or Cs^{+1} on Rhine River sediments. Equilibrium was reached within 24 hr.

Seymour (1977), Sanchez (1977), Sanchez and Schell (1977), and Schell et al. (1979, 1980) studied the distribution of plutonium in both fresh and marine environments. The experimental design used was to place a known amount of sediment in a known volume of water and add Pu tracer. After pH adjustment the system is shaken for a set time and an aliquot of the suspension removed. This aliquot is filtered to separate solution from solids. Both the solution and solids are counted to obtain a $K_{d_{\text{Pu}}}$. The contaminated sediments after centrifugation to remove tracer solution were contacted with "clean" water in a similar fashion to allow determination of $K_{d_{\text{Pu}}}$ desorption. Three sediments were investigated: a fresh-water lake (Lake Washington), an oxic marine sediment (Columbia River Mouth) and an anoxic marine sediment (Lake Nitinat). The sediments were contacted with fresh and marine waters obtained during the sediment sampling. The sediment particle size distribution, total carbon and nitrogen contents are shown in Table 8.49.

The time needed to reach steady-state solution concentrations for the fresh water system was less than 30 hr. The average $K_{d_{\text{Pu}}}$ for the three systems under study observed both in the adsorption and desorption direction after 48 to 60 hr of contact are presented in Table 8.50.

TABLE 8.49. Sediment Characterization

	<u>% Sand</u>	<u>% Silt</u>	<u>% Clay</u>	<u>% Carbon</u>	<u>% Nitrogen</u>
Lake Washington	2.5	16.0	81.5	5.2	0.41
Columbia River Mouth	40.2	20.8	39.0	1.8	0.08
Lake Nitinat	3.7	21.4	74.9	2.8	0.26

TABLE 8.50. K_v Pu Results (Unitless Kd)

<u>Sediment</u>	<u>K_v Adsorption</u>	<u>K_v Desorption</u>
Lake Washington	$2.8 \pm 0.3 \times 10^5$	$7.1 \pm 0.3 \times 10^5$
Columbia River Mouth	$3.9 \text{ to } 11.1 \times 10^4$	$5.4 \text{ to } 11.3 \times 10^4$
Lake Nitinat	$1.4 \pm 0.2 \times 10^5$	$4.4 \pm 0.4 \times 10^5$

In general, the coarse grained oxic marine sediment shows the lowest Kd_{Pu} and the finer grained fresh water sediment the largest Kd_{Pu} . The anoxic marine sediment Kd_{Pu} is intermediate. In all cases the Kd_{Pu} desorption is larger suggesting plutonium is harder to remove from the sediment than would be expected if one assumed ideal reversibility between adsorption-desorption. The K_v values can be changed to Kd values by roughly multiplying by 1.5.

Schell et al. (1980) report on laboratory determinations of Kd_{Pu} in numerous fresh and marine water environments (see Table 8.11). The Kd_{Pu} is quite high for either fresh and marine environments. There is no clear trend in the observed Kd with increasing salinity. Kds determined by desorption methods were consistently much greater than those determined by adsorption. As seen for most elements Pu would not become soluble to the extent predicted by current models which assume reversibility if Kd_{ads} values were used.

In a separate experiment, Seymour (1977) placed Lake Nitinat sediments and "clean" sea water in a dialysis bag and suspended them in traced sea water for 10 days. The sediment contained $20.2 \text{ dpm/g } ^{238}\text{Pu}$ while the intimate sea

water contained 0.32 dpm/ml. The resultant K_d ml/g was 63 which is much lower than observed in the batch experiments. The dialysis experiment may reflect a true Pu ion exchange-like K_d while the other results include hydrolysis, precipitation and colloid scavenging. The experimental procedure of adding acid spike to the sediment slurry can artificially inflate the K_d if much of the Pu would automatically precipitate upon neutralization. This author prefers to add tracer to the solution, let it equilibrate several days and filter before contact with sediments.

Schell et al. (1979) studied the distribution of ^{238}Pu in a laboratory dialysis experiment between sediment, plankton and seawater. For some unknown reason 80% of the Pu remained outside the dialysis bags with most of this Pu in a soluble form. The Pu which did pass through the dialysis sac and contact the sediment became predominantly sorbed. The distribution of Pu in this dialysis experiment is shown in Table 8.9 in the americium section.

In continuing dialysis experiments Schell et al. (1980) found that Pu in a Lake Michigan freshwater environment rapidly became associated with sediment and particulate organic detritus and possibly colloids. Plutonium in the soluble form seemed to be stabilized in dialysis sacs which contained phytoplankton and organic detritus suggesting that soluble organic complexes might have been formed.

VanDalen et al. (1975) determined the distribution coefficient, $K_{d_{\text{Pu}}}$, for several Dutch subsoils from 90% saturated NaCl solutions between pH 7 and 8. Clay samples of mainly illite and kaolinite had a $K_{d_{\text{Pu}}}$ of $\sim 10^4$ and for a river sand a $K_{d_{\text{Pu}}}$ of 200 ml/g. Gypsum bearing and clay bearing sandstones were intermediate. The pH dependence on sorption of plutonium was minor between pH 5 and 8.

The dissolution rate of plutonium oxide particles by sea water and tap water have been reported by Adams (1971), Kubose et al. (1968) and Patterson et al. (1974a,b). The dissolution rate is quite complex and dependent on such properties as pH, T° , Eh, complexing agents, oxide surface area, and radiation

field intensity. Environmental chamber work showed that rain on large chunks of $^{238}\text{PuO}_2$ radioactively heated to 200°C led to increases in release of Pu of three orders of magnitude due to spallation.

Desai and Ganguly (1970) determined the ability of humic and fulvic acid in ammoniacal solutions to solubilize plutonium. In this basic solution without humic or fulvic extract, only 13% of added plutonium remained in solution, with humic extract present 54% of the added plutonium remained in solution and further testing showed that the soluble plutonium was noncationic. The fulvic acid extract solubilized 58% of the plutonium and again the complex was noncationic.

Bondietti (1974, 1975) found purified soil humates to absorb plutonium strongly (99.99+%) while reference clays (montmorillonite and kaolinite) adsorbed about 98% and 96% of plutonium added to a water solution at $163\text{ }\mu\text{g Pu/g}$ of solid. If clay materials had their organic matter and iron oxide coating removed, plutonium adsorption was 95% versus 99.9% while intact. Leaching solutions, citrate, DTPA, and fulvate removed small amounts of adsorbed plutonium as shown in Table 8.51.

Thus, it appears that natural soil organic matter can very strongly adsorb plutonium. The ability of soil organic matter to alter the valence state of plutonium in soil water solutions was also verified. Pu(VI) and by inference Pu(V) were unstable in the presence of fulvic acid, polygalacturonic acid and alginic acid. Positive proof of reduction to Pu(IV) was shown at environmental pHs 6.5 to 3. Plutonium (IV) was the most stable valence upon interaction with these organics. Further reduction of Pu(IV) to Pu(III) occurred in the presence of humic or fulvic acids, but was not observed above pH 3.1 under aerobic conditions. Bondietti also demonstrated that plutonium is at least partially associated with humic materials in ORNL soil contaminated 30 years ago.

The removal of plutonium in wastes and drinking waters by precipitation and/or sorption techniques has been studied by Lauderdale (1951), Christenson et al. (1951), Grebenshahikova et al. (1971), Blaine et al. (1974) and Corey and Boni (1975). Calcium phosphate, alum, ferric hydroxide, and barium

TABLE 8.51. Percent Pu Removed by Extractants

<u>Extractant</u>	<u>Humate</u>	<u>Mont.</u>	<u>Koal.</u>
10^{-3} M Citrate	0.3	8	11
10^{-3} M DTPA	30	15	20
10^{-2} M Fulvate	5	0.9	3

phosphate flocculations all are effective in removing most of the plutonium in waste streams at basic pHs. Adsorption on kaolin, pumice, tuff, celite and activated carbon has also been used to remove plutonium. In all methods a variable percentage of plutonium remains in solution, probably as a polymeric or colloidal form. Ultracentrifugation results tend to corroborate that colloidal species are less readily adsorbed or likely to precipitate.

Thorburn (1950) reported a sorption experiment in which plutonium in water was percolated through a soil column. The soil was then wet sieved and the activity of each particle size fraction counted. In general the decrease in particle size increased the amount of plutonium adsorbed (Table 8.52). In other adsorption experiments, Thorburn placed small aliquots of actual plutonium waste on top of soil columns and eluted with distilled water or saturated magnesium-calcium carbonate. There were no significant differences in the elution curves. It is interesting to note that the elution curves had higher plutonium activity in the first volume out of the column and always showed a small leakage which might signify physical transport of fine particulates, neutral polymers or colloids. Thorburn took the effluent from the distilled water leached column and percolated it through a second soil column at various flow rates. The data show that plutonium concentration in effluents through the second column varied with flow rate. The faster the flow the more plutonium in the effluent. Filtration of the influent through a fine filter paper did not change the results. Explanations of these phenomena are obscure but would seem to indicate plutonium transport as polymer. Final adsorption studies of plutonium in water versus pH by soil columns showed 87% adsorption

TABLE 8.52. Plutonium Adsorption Versus Particle Size (Thorburn, 1950)

<u>Size, mm</u>	<u>Pu, d/min/g</u>
>1.19	39.3
1.19 to 0.25	---
0.25 to 0.15	1,171
0.25 to 0.10	929
<0.105	8,578
Uncentrifugible Silt and Clay	62,750

at pH 3.8, 77% at pH 7.2 and 24% at pH 10. Note that this falling of plutonium adsorption with increasing pH is supported by the thermodynamic data of Figure 8.27.

Evans (1956) reported on percentage of plutonium removed from a 0.001 N HNO_3 solution by various grain sizes of quartz. The plutonium Kd values may be computed from these data, and are listed in Table 8.53. Data also were given on plutonium adsorption on different minerals of coarse clay size (2 to 0.2 μm). Plutonium Kd values were computed from these data and are listed in Table 8.54. Evans suggested that the lower Kd for plutonium by montmorillonite is probably due to experimental difficulties and believed that Rhodes' (1952) data may represent preferred plutonium Kd results. Rhodes' data, as reported by Evans, are given in Table 8.55, assuming a 1 ml to 1 g solution to soil ratio. This ratio was not given, but the results are proportional in any case.

Rhodes (1952, 1957a,b) performed similar plutonium Kd determinations on a Hanford sand soil (92% sand) with 2% calcium carbonate content. Using a soil to solution ratio of 1:20 and neutral pH, Rhodes found rapid adsorption. Analysis versus time yielded an equation for the amount adsorbed versus contact time, $\% \text{Pu}_{\text{ADS}} = 81 + 5.2 \log \text{time}_{(\text{min})}$. For example, after 1 min, 20 min and 60 min, 81%, 88%, and 90%, respectively, of the solution plutonium concentration was adsorbed. Increases in the soil to solution ratio were also

TABLE 8.53. Plutonium Kd Values for Quartz of Various Particle Sizes from a 0.001 N HNO₃-Plutonium Solution (Evans, 1956)

<u>Quartz Particle Sizes</u>	<u>Kd, ml/g</u>
Coarse Sand	5.6
Fine Sand	10.0
Coarse Silt (50 to 20 μ m)	11.3
Medium Silt (20 to 5 μ m)	33.5
Fine Silt (5 to 2 μ m)	48.8
Coarse Clay (2 to 0.2 μ m)	80.9

TABLE 8.54. Plutonium Kd Values for Different Minerals of Coarse Clay Size (2 to 0.2 μ m) from 0.001 N HNO₃-Plutonium Solution (Evans, 1956)

<u>Mineral</u>	<u>Kd, ml/g</u>
Feldspar	170.4
Quartz	82.0
Glauconite	∞
Montmorillonite	157.0
Kaolinite	1091.0

TABLE 8.55. Rhodes' Plutonium Kd Data as Reported by Evans (1956)

<u>Material</u>	<u>Kd, ml/g</u>
Montmorillonite	4990
Fine Micaceous Sand	49
Kaolinite	42.5
Soil	36
Coarse Sand	0.87

observed to increase the percent adsorbed. Rhodes also obtained adsorption versus pH data (see Figure 8.32) and found a rapid decrease in adsorption below pH 2 but almost total adsorption ($K_d > 2000$) between pH 3 and 8.5.

FIGURE 8.32. Adsorption of Plutonium by Soil as a Function of pH (Rhodes, 1957a)

Decreases at pH 10 to 12 were believed to indicate changes in plutonium speciation. In other experiments, coarse sand was observed to adsorb only 47% of the plutonium present compared to 97 to 99.8% for soils and clay minerals. Rhodes felt all these data indicated ion exchange adsorption mechanisms. Yet plutonium adsorption from distilled water, a synthetic high salt waste and an actual high salt waste all showed greater than 98% removal. Plutonium solution loading experiments onto soil columns at various pH's (1, 4, 10) showed good removal at the first two pH's until the high acid case had destroyed the CaCO_3 buffering capacity. As the effluent pH dropped to pH 1, increasing plutonium breakthrough was observed. Plutonium breakthrough at pH 10 was highly variable and rapid, possibly caused by fine plutonium particulate dispersion or polymer formation. Plutonium adsorption from distilled water, 4M NaNO_3 and 2M $(\text{NH}_4)_2\text{HPO}_4$ solutions was above 96%, but a 4M ammonium acetate solution showed only 59% adsorption. Acetate complexing of plutonium was probably responsible for the diminished adsorption rather than any effects from competing ions.

Further studies showed increasing the acetate concentration from 0.01M to 8M dropped plutonium adsorption from 74 to 21%. Acetate solutions were also observed to have the capability of extracting plutonium adsorbed on soils. Benson (1960) presented data showing that oxalate salts also inhibit plutonium adsorption by soluble Pu-oxalate complex formation. Benson also reinterpreted Rhodes' data and concluded precipitation reactions, not ion exchange, probably control plutonium adsorption on soils.

Other investigations on plutonium were performed at Savannah River by Prout (1958, 1959). Plutonium adsorption by a soil (80% sand to 20% clay) with the clay mineral kaolinite dominant was determined versus pH for distilled water traced with plutonium ($\sim 10^{-6}$ M). The soil/solution ratio was 1:10 and the mixtures shaken for 2 hr before phase separation by centrifugation. Adsorption of plutonium depended on pH and the valence state of the plutonium added to solution. Adsorption was more than 90% complete from solutions of Pu(III) and Pu(IV) between pH 2.5 and 12 and from solutions of Pu(VI) at pHs greater than 6. Strong adsorption at mildly acidic to mildly basic pHs is probably due to a combination of cation exchange and precipitation of hydrolysis products. Decreased adsorption above pH 9 possibly represents the formation of soluble negatively charged plutonium polymers which do not readily exchange with the soil (see Figure 8.33).

Tamura (1972) discussed the adsorption of plutonium on several materials including the soil constituents listed in Table 8.56. The suspension pH represents the final system pH.

Miner et al. (1973, 1974), Polzer and Miner (1974, 1977) and Glover et al. (1977) described experiments in progress to measure the adsorption of both "soluble" plutonium and particulate plutonium (PuO_2) in numerous soils at three plutonium levels between 10^{-6} and 10^{-8} M. The plutonium adsorption was rapid and quite high: 59% of the time, adsorption was greater than 99% ($K_d > 430$) and only 5% of the time was it below 90% adsorption ($K_d < 39$). Correlations were found between soil characteristics associated with soil ion

FIGURE 8.33. Effect of pH and Plutonium Oxidation State on the Adsorption of Plutonium by Soil (Prout, 1959)

TABLE 8.56. Removal of Plutonium from pH 7 Water by Several Soil Minerals (Tamura, 1972)

Constituents	Kd, ml/g	Suspension pH
Attapulgite	4,370	9.60
Montmorillonite	630	9.20
Alumina, activated	755	8.35
Kaolinite	352	6.25
Illite	129	5.90
Quartz	0	6.35

exchange or acidity. The adsorption also depends on the initial plutonium concentrations for which several possible causes are discussed including precipitation with increasing plutonium concentration and the formation of carbonate complexes.

Lindenbaum and Westfall (1965) prepared several dilute solutions of colloidal plutonium with citrate to plutonium ratios of 1800 ($3.4 \times 10^{-2}M$ citrate) to 1. The colloid was about 80% ultrafilterable at pH 4.0 and a citrate to plutonium ratio of 1. The cellophane used in the ultrafiltration had a pore size that corresponded to a plutonium hydroxide molecular weight of about 200,000. At pH 10 and a citrate to plutonium ratio of 1 colloid, 65% of the Pu was ultrafilterable and only 5% was filterable at pH 11. At citrate to plutonium ratio of 1800, the colloid behaved in a similar fashion decreasing from 92% ultrafilterable at pH 4 to 72% at pH 11. With no citrate present, the plutonium was about 13% ultrafilterable at pH 4 and fell to near 0% at pH 11. Qualitatively, Zr(IV), Th(IV) and the rare earths may behave in a similar manner, peptizing at higher pH, as suggested by the works of Rhodes (1957b). The dispersed polymers are less soil-reactive and should migrate farther through the soil.

Bondietti (1974) determined the plutonium Kd for clays separated from a soil (Miami silt loam) and montmorillonite using $5 \times 10^{-3}M$ calcium solutions at pH 6.5 for two plutonium valence states. The results are shown in Table 8.57. The high adsorption of Pu(VI) on the soil clay, in contrast to or as compared with montmorillonite, indicated that plutonium reduction by clay components must have occurred, since adsorption values similar to the Pu(IV) were obtained. Pu(VI) appeared to adsorb less than Pu(IV).

Nishita et al. (1976) determined the extractability of plutonium from a contaminated soil as a function of pH. The pH influences hydrolysis and precipitation of the plutonium. In the study, 2 g of contaminated soil was agitated in 25 ml of solution, in duplicate, and the pH adjusted with NaOH or HNO_3 . The Kd values are given in Table 8.58 for the Aiken clay loam, a kaolinitic soil, at several pH values. It is not clear from the report whether these values are initial or final system pH measurements. The pH values at the high and low ends of the range especially, usually drift considerably during equilibrations with soils so a final pH measurement is most meaningful.

TABLE 8.57. Plutonium Kd as a Function of Oxidation State (Bondietti, 1974)

<u>Material</u>	<u>Initial Oxidation</u>	<u>Kd, ml/g</u>
Soil Clay Fraction	Pu(IV)	1.0 to 1.7×10^5
	Pu(VI)	7.5×10^4
Montmorillonite	Pu(IV)	2.1×10^4
	Pu(VI)	2.5×10^2

TABLE 8.58. Kd Values of ^{238}Pu in Untreated Aiken Clay Loam (Mishita et al., 1976)

<u>pH</u>	<u>^{238}Pu Kd, mg/l</u>	<u>pH</u>	<u>^{238}Pu Kd, mg/l</u>
1.21	430 ± 44	8.54	963 ± 130
2.12	862 ± 33	9.43	512 ± 14
2.56	796 ± 59	10.31	302 ± 1.6
4.69	2591 ± 591	11.25	213 ± 5.8
5.55	2347 ± 220	12.22	138 ± 4.8
7.08	3086 ± 19	13.25	207 ± 14

Field Studies

In investigations at the Thule Greenland air crash site, Aarkrog (1971, 1972), two years after the incident, shows plutonium levels above background as far as 15 km from the point of impact. Samples of bottom sediments yield a vertical movement of plutonium to a depth of at least 10 cm. Close to the crash site sediment plutonium values were 16 pCi/g while overlying waters were 6.5×10^{-3} pCi/l, further from site sediments contained 1.3 pCi/g while the overlying water was 4.5×10^{-3} pCi/l. These results yield field Kd's of 2.5×10^6 ml/g and 2.9×10^5 ml/g, respectively.

Articles which describe the distribution of Pu fallout in the marine environment include Bowen (1971, 1974b, 1975, 1977), Bowen et al. (1971, 1975), Goldberg (1975), Labeyrie et al. (1975), Miyake and Sugimura (1975), Wong et al. (1970), and Noshkin and Bowen (1973). In the marine water column these

investigators find plutonium to become geochemically separated from ^{90}Sr and ^{137}Cs and removed more quickly, possibly because of biological processes as well as particulate sedimentation.

Bowen et al. (1975) described in detail the role of biological processes in the vertical migration of plutonium and present some core data to substantiate their hypothesis. They believe biota are responsible for both the downward migration and upward migration with possible water remobilization, especially in shallow water marine environments. Buzzard Bay, Massachusetts, sediments showed no concentration of plutonium in the fine fraction of the sediments. Contradictory evidence showing plutonium concentrations in the ocean sediments to increase with decreasing particle size is presented by Fukai et al. (1974). Typical fallout values for $^{239,240}\text{Pu}$ in ocean waters are: Atlantic Ocean 0.22×10^{-3} to 1.2×10^{-1} pCi/l, Pacific Ocean 0.1 to 17×10^{-3} pCi/l. The overlying sediments were found to contain 5 to 73×10^{-3} pCi/l. A range of K_d_{Pu} based on fallout in the Atlantic would be 40 to 3300 ml/g. Much of the observed plutonium in solution is really already bound to filterable suspended solids such that the observed K_d_{Pu} would be higher. Fallout plutonium seems to be settling at a rate of 70 to 392 m/yr in the open ocean.

Fukai et al. (1974) reported $^{239,240}\text{Pu}$ values for Ligurian Sea surface water (5 m depth) of 0.5 to 2.8×10^{-15} Ci/kg, which are similar to values reported for Pacific and Atlantic Ocean waters. The $^{239,240}\text{Pu}$ content of the sediments ranged from 0.3 to 4.2×10^{-12} Ci/kg. In general, the plutonium concentration decreased with the increase in particle size. The field K_d can be calculated 0.2 to 2.2×10^3 ml/g.

Nevissi and Schell (1975), Noshkin et al. (1971, 1975) and Schell and Walters (1975) investigated the distribution of plutonium in Bikini and Enewetak lagoons and ground-water environments in the Pacific at which nuclear weapons tests were performed. Plutonium released to the lagoon system became insoluble and rapidly settled. Up to 90% of the plutonium in the lagoons is associated with particulates but heterogeneity abounds. Resuspension of fine material and wave driven water transport actively cause redistribution. Detailed studies show plutonium to exist in particulate, soluble and colloidal

states in the lagoon waters. Studies of the ground waters at several islands in Enewetak Atoll show that small quantities of plutonium radionuclides have migrated through the soil columns (80 m in one instance) and are redistributed throughout the ground-water reservoirs. Distribution of plutonium is spatially heterogeneous and independent of processes controlling the cycling of ^{137}Cs and fresh water. A linear correlation was found between the average surface water concentrations and soil plutonium concentrations independent of the physical, chemical and biological characteristics of the islands. Whatever the transport mechanism, plutonium has proven to be very mobile in the water-saturated coral-soil environment.

The plutonium distribution of surface soils on Bikini Atoll followed the same pattern as fission products. Horizontal movement of plutonium due to soil erosion and transport was localized and restricted to areas without vegetation and organic detritus. Air resuspension appeared to be minor. A vertical soil profile showed 70% of the plutonium retained in the top 5 cm, 28% retained in the 5 to 25 cm layer and the remaining 2% as deep as 100 cm. Of the possible transport mechanisms: solution, biological and suspension and resuspension of particles, the latter probably dominates.

Noshkin et al. (1975) took seven plutonium contaminated soil samples from Enewetak and equilibrated them with uncontaminated sea water. At equilibrium water filtered through 0.4 μm filters and soils were analyzed for plutonium contents. The K_d_{Pu} calculated from these samples was 8×10^4 ml/g. Particulates in the ground water versus the ground waters themselves gave an average K_d_{Pu} equal to 2.5×10^5 ml/g. The observed concentrations of $^{239,240}\text{Pu}$ and ^{238}Pu from bomb testing for Bikini Atoll and environs are shown in Table 8.59.

The suspended sediments contained 4 to 75% of the total $^{239,240}\text{Pu}$ found in the total water sample. K_d_{Pu} for the bottom sediments range as follows: Bikini lagoon, 0.01 to 120×10^3 ml/g; Bikini crater, 0.6 to 71×10^3 ml/g; and neighboring Pacific Ocean, 0.1 to 51×10^3 ml/g.

TABLE 8.59. Bikini Atoll Data

<u>Location</u>	<u>Material</u>	<u>$^{239,240}\text{Pu}$</u>	<u>^{238}Pu</u>
Bikini Lagoon	Bottom Sediments	0.4 to 120 pCi/g	0.02 to 3 pCi/g
Bikini Craters	Bottom Sediments	29 to 71 pCi/g	0.3 to 17 pCi/g
Pacific Ocean	Bottom Sediments	2 to 31 pCi/g	0.2 to 0.5 pCi/g
Bikini Lagoon	Waters (Filtered)	1 to 31×10^{-3} pCi/l	3.9×10^{-3} pCi/l
Bikini Craters	Waters (Filtered)	1 to 45×10^{-3} pCi/l	
Pacific Ocean	Waters (Filtered)	0.6 to 17×10^{-3} pCi/l	
Bikini Lagoon	Suspended Solids ($>1 \mu\text{m}$)	0.3 to 97×10^{-3} pCi/l	
Bikini Craters	Suspended Solids ($>1 \mu\text{m}$)	6 to 35×10^{-3} pCi/l	
Pacific Ocean	Suspended Solids ($>1 \mu\text{m}$)	0.1 to 8×10^{-3} pCi/l	

Alberts et al. (1974a, 1974b), Bowen (1974), Bowen and Noshkin (1973), Edgington et al. (1975), Karttunen and Edgington (1974), Marshall et al. (1973), Wahlgren and Nelson (1972, 1973a, 1973b, 1973c, 1974), and Wahlgren et al. (1976) measured the distribution of fallout plutonium in the Great Lakes. Plutonium impinging on the lake's surface rapidly falls to the bottom sediments with a removal half-life of about one year. Some evidence points to a biological mechanism such as incorporation in plankton followed by rapid settling of fecal pellets and dead plankton. The particle size of the plutonium reaching the water is greater than 75% colloidal or subcolloidal, i.e., passes through $0.45 \mu\text{m}$ filters. In all cores studied, plutonium activity was confined to the top six centimeters and in many to the top three centimeters which agrees with known deposition rates. Cesium and plutonium from fallout appear to be depositing with equal efficiency and mobility is reduced to only a periodic resuspension by physical or biological means. Plutonium to americium ratios in the sediments show no elemental differences in mobility. Chemical leaching experiments to be described later show plutonium to be

chemically immobile as long as oxidizing conditions are present. A field K_d_{Pu} of 2 to 7×10^5 is observed from surficial sediments and filtered lake water.

Edgington et al. (1975) treated fallout contaminated Lake Michigan sediments with various extractants to investigate plutonium speciation. A sequential treatment with $0.1M$ $MgCl_2$, sodium dithionite - $0.3M$ sodium citrate, $0.1N$ $NaOH$ and finally total fusion was tried. In general the results showed none or small amounts of plutonium in the $MgCl_2$, $NaOH$ and fusion extracts. Almost all of the plutonium was found in the citrate-dithionite extract. Changing the sequence of the chemical extractions did not significantly change the results. It was, therefore, concluded that plutonium in the sediments was present in a reductant soluble form such as hydrous iron and manganese oxides and not as ion exchangeable, humic bound or refractory particles.

Edgington et al. (1977) and Sprugel et al. (1975) have observed the transport of Pu disposed into the Great Miami River (Ohio) from sporadic controlled releases of low level nuclear liquid wastes at Mound Laboratory. The field studies show Pu transport occurs essentially totally on suspended particulates. Mass balances necessitate a larger source of Pu than these sporadic releases. Two possible sources of the excess Pu are release/resuspension of plutonium from bed sediments or seepage from other land burial sites.

Wahlgren and Nelson (1976) have calculated the K_d for Pu on suspended particles within the Great Miami River to be $\geq 10^5$ ml/g.

Wahlgren et al. (1977a) have followed the seasonal cycling of Pu in Lake Michigan for several years. Pu in the upper water column (0 to 60 m) is removed each spring coincident with a diatom bloom. Presumably Pu retained on diatom carcasses settles out. Each fall (late November) turnover occurs and the lake water column becomes uniform again in regard to Pu concentration.

Wahlgren et al. (1977b, 1977c) have studied the distribution of total concentrations, and valence states of Pu in freshwater lakes. A simple plot of total Pu concentration versus pH over the observed range (4 to 8.5) shows no straightforward trend but at pH < 7 Pu concentrations on the average are ten times greater than Pu concentrations at pH > 7. Other variables such as alkalinity, redox potential (Eh), organic content need to be considered. Speciation tests show Pu dissolved in Lake Michigan is present predominantly (>80%) as Pu(V,VI) while less than 10% of Pu adsorbed to suspended particulate matter is in these oxidation states. These results strongly suggest that reduction of Pu from V/VI to Pu(IV) is a major factor in controlling its distribution between solution and solids in nature. Tracer additions of Pu(IV) and/or Pu(VI) showed that steady-state valence distributions would occur within a few months. Data for other lakes with pH > 7 are similar to Lake Michigan while lakes with acidic pHs show Pu(III/IV) predominate over Pu(V/VI).

Nelson and Lovett (1976) in a similar species study determined the oxidation state of Pu in the Irish Sea near the Windscale reprocessing plant. Seawater samples both unfiltered and filtered (<0.22 μ m) were analyzed. Plutonium which was filtered was predominantly Pu(III and IV) while Pu which remained in solution was Pu(V and VI). Kds for the total Pu based on dissolved Pu versus filtered Pu and for Pu(III and IV) and Pu(V and VI) show unmistakably that Pu in the lower valence states have a Kd up to 1000 times larger.

Emery and coworkers (1974a, 1974b, 1975 and 1977) have studied the ecological behavior of one Hanford liquid waste pond. Ninety-five percent of the incoming low level waste percolates through the desert sands. The sediments are the principal repository (>99%), with the top ten centimeters containing an average 390 pCi Pu/g. The overlying water contains 0.01 pCi Pu/l. Assuming that these values constitute equilibrium conditions, an estimate of the Kd_{Pu} can be made. The resultant Kd_{Pu} value is 3.7×10^7 ml/g. Plutonium in the interstitial waters appeared to be mainly cationic or nonionic forms. Plutonium in the pond water appeared to be mainly fine particulates, possibly signifying that the waste stream plutonium content is predominantly PuO_2 particles.

Sequential chemical extraction of Hanford Uranium Pond sediments with 0.1M NaCl, 0.1M oxalic acid - 2.0M $(\text{NH}_4)_2\text{C}_2\text{O}_4$, and 0.01M EDTA revealed releases of 1 to 3%, 3 to 5%, and 2 to 22%, respectively, of the total plutonium. The first extractant should have removed ion exchangeable plutonium, the second amorphous hydrous oxide bound, and the third complexible plutonium.

Hayes et al. (1975) surveyed the plutonium content in the Savannah, Neuse and Newport estuaries in the southeastern United States. The sediments contained $2 \text{ to } 20 \times 10^{-3} \text{ pCi/g}$ while filtered ($1 \mu\text{m}$) waters contained $0.24 \text{ to } 2.4 \times 10^{-6} \text{ pCi/ml}$ for a field $K_{d_{\text{Pu}}}$ range of $0.8 \text{ to } 80 \times 10^3 \text{ ml/g}$. A $5 \mu\text{m}$ filter would remove one-third the amount of plutonium that a $1 \mu\text{m}$ filter would. When the salinity increased above 10 parts per thousand in the estuaries, plutonium content of suspended solids was seen to decrease, suggesting some desorption from suspended particulates.

Hetherington (1975), Hetherington et al. (1975), and Templeton and Preston (1966) studied the migration of plutonium from the effluents pumped into the Irish Sea which are produced from the reprocessing plant at Windscale. Plutonium is removed rapidly to the sediments (95%). The highest concentration of plutonium is found in fine muck close to the outfall, the lowest in sand. The observed field $K_{d_{\text{Pu}}}$ is $1 \times 10^3 \text{ ml/g}$ for sand and 2×10^5 for fine muck. The residual fraction which apparently remains in solution in sea water appears to behave conservatively and in a fashion which is qualitatively similar to ^{137}Cs . An interesting similarity between the distributions of ^{239}Pu and ^{137}Cs with depth in core samples is confirmed and this is taken as evidence of the fact that sedimentation of material that has become contaminated while in suspension is the primary mechanism by which both these nuclides are being incorporated into the sediments of this area. Support for this belief is provided by the behavior of the ratio of $^{239}\text{Pu} : ^{238}\text{Pu}$ with depth in some core samples. This ratio in the cores has been related to that in the Windscale effluent during the past decade in order to estimate the sedimentation rates in the areas from which the cores were taken.

Murray and Kaursky (1975) feel the North Sea is probably a unique sea region in that the distribution of artificial radionuclides is influenced by the discharge of activity from three nuclear fuel reprocessing plants, those situated at La Hague in Northern France, Windscale in the northwest of England and Dounraey in Northern Scotland, as well as from fallout from nuclear weapon testing. Data is presented on the distribution of $^{239+240}\text{Pu}$, ^{238}Pu and ^{241}Am in seawater samples taken from the German Bight and German Baltic coastlines as well as from other parts of the North Sea up to latitude 60°N .

Results from the Pentland Firth in the north of Pentland and the English Channel show $^{239+240}\text{Pu}$ activities in sea water between 5 to 15 times higher than North Atlantic fallout levels. The ratio $^{238}\text{Pu}/^{239+240}\text{Pu}$ is significantly higher in the Pentland Firth area (0.21 ± 0.01) than in the Channel (0.15 ± 0.02) and this difference may well be a reflection of different input sources of plutonium in the water. German coastal sea water and sediment plutonium activities appear to be due only to fallout, the isotope ratio being about 0.06 ± 0.02 , a value in good agreement with accepted North Atlantic values. Field K_d_{Pu} for the Baltic Sea and North Sea were calculated from data presented in this paper and are about $3 \text{ to } 15 \times 10^3$ and $0.08 \text{ to } 30 \times 10^3 \text{ ml/g}$, respectively.

Pillai and Mathew (1975) studied the migration of plutonium from a fuel reprocessing plant in the marine environment off Trombay, India. Nearly 99% of the plutonium in the waste was rapidly removed by sediments. Sediments near the outfall contained 10 to 100 times the plutonium concentration of background sediment. Plutonium levels decreased with distance from the discharge site although resuspension, tidal transport and seasonal effects complicated the distribution. Resuspension of plutonium-laden sediments in sea water did not increase the filtered water concentration, therefore, plutonium transport is mainly with silt movement. A field K_d_{Pu} of $9 \times 10^4 \text{ ml/g}$ can be calculated from their data.

Sedlet and Golchert (1977) measured the $^{239,240}\text{Pu}$ in the creek and rivers nearby Argonne National Lab. Near a waste outfall the plutonium present in an acidified water sample was found to distribute 64% on an unspecified filter and 36% in the filtrate. The filtrate waters contained the following Pu

concentrations: Sawmill Creek $9.4 \pm 1.3 \times 10^{-3}$ pCi/l, Des Plaines River $0.7 \pm 0.2 \times 10^{-3}$ pCi/l, and Illinois River $0.3 \pm 0.1 \times 10^{-3}$ pCi/l. Respective stream sediments contained 19, 25 and 1×10^{-3} pCi/g. Field Kds are Sawmill Creek 2×10^3 , Des Plaines River 4×10^4 and Illinois River 3×10^3 ml/g, respectively.

Simpson et al. (1980) have measured the fallout $^{238,239,240}\text{Pu}$ in unfiltered Mono Lake (California) water and sediments. Mono Lake is a high pH (10) high carbonate (~ 0.3 M) saline (2 times seawater) lake. Results show an abnormally high amount of Pu in solution versus the sediments and yield a Kd of only 10^3 compared to usual field values of 10^5 ml/g. The authors feel that soluble carbonate complexes may be the cause.

Magno et al. (1970), in investigations of radionuclide migration from the Nuclear Fuel Services plant in West Valley, New York, estimated that more than 90% of the ^{238}Pu , ^{239}Pu , and ^{241}Pu contained in the plant effluent remained in the sediments of the lagoon system.

Water infiltration and plutonium migration at Maxey Flats burial grounds were studied by Meyer (1975). A hydrostatic head of 4 to 6 m was found in some trenches, causing lateral and downward migration of leachates. Surficial plutonium migration also had occurred from trench leakage. Above background plutonium concentrations have been detected in onsite and offsite surface soils and stream sediments, in soil cores to 90 cm and in wells 15 to 27 m deep. Other radionuclides accompanying the plutonium included tritium, ^{60}Co , $^{89,90}\text{Sr}$ and $^{134,137}\text{Cs}$.

Radiological measurements at the Maxey Flats burial site, Kentucky, also have indicated some radionuclides physically transport on particulate matter (Meyer, 1975; Montgomery et al., 1977). The authors mentioned that ^{54}Mn , ^{60}Co , ^{90}Sr , ^{137}Cs , ^{238}Pu and ^{239}Pu were detected in stream sediments, although the water levels were quite low. In E-Series test well measurements, all plutonium within the detection limit was associated with sediment. The authors suggest that this raises a question as to the mechanism of plutonium migration from the disposal trenches.

Bondietti and Reynolds (1977) investigated the species of plutonium found in Oak Ridge seepage water from a solid waste burial ground. Pu(VI) was identified as the main plutonium species in the seepage solutions. The implication is that Pu(VI) is more mobile than Pu(IV).

Christenson et al. (1958), Christenson and Thomas (1962), Purtymun (1971, 1974), Hakonson et al. (1973a,b, 1975) and Richmond and Sullivan (1974) conclude that the plutonium concentration of LASL canyon soils receiving low level wastes has moved slowly downstream. Sorption studies on the tuff material which lies below the alluvial soils show high plutonium retention. The tuff contains many cracks and fissures through which plutonium has penetrated to a depth of 28 ft in localized areas. High percentages of clays, deposited by local weathering, sorbed plutonium and result in local high alpha activity. Since 1963 nearly 2×10^5 l/day of low-level waste has been discharged. Comprehensive sampling of the stream bed from the outfall to a distance of 10 km downstream show 35 to 40% of the calculated inventory present in the first kilometer downstream, which happens to represent the region containing permanent surface water. Over 50% of the plutonium is present in the lower portion of the canyon where the stream channel is normally dry, indicating that considerable downstream transport had occurred. Rainstorm runoff has been shown to be the transport mechanism. During one runoff study 99% of the radionuclide inventory in the slurry was associated with suspended particulates. The faster stream velocities suspend more and larger particles and physically move plutonium down the canyon. To date plutonium migration down the canyon has been less than 5 km and held within the Los Alamos boundaries. Plutonium concentration patterns with depth are not consistent and show considerable vertical mixing has occurred.

Summary

In most oxidizing environments, ionic plutonium is expected to be present in solution predominantly as Pu(V) or Pu(VI). With high plutonium concentrations, PuO₂ could be expected as a stable solid phase. The plutonium adsorption data indicate that more than one mechanism is operating during reactions with rocks and sediments. There is a direct correlation of plutonium adsorption results with cation exchange capacities, indicating that part of the

adsorption is due to ion exchange. However, little effect on adsorption was obvious from competing cation concentrations that were very high (Rhodes, 1957a; Mo and Lowman, 1975). Perhaps the principal correlation of plutonium adsorption is with pH. A relatively rapid soil column breakthrough of plutonium was obtained with a low pH (<1) solution. Strong adsorption occurs over the pH range of from 4 to 8, but above pH 8 the formation of negative complexes or polymers with low charge densities can cause lowered adsorption. In addition, plutonium is easily complexed with humic acids, oxalate, acetate, and a large number of phosphorus-bearing organics used in the nuclear fuel reprocessing industry. Even the precipitated or absorbed plutonium can be readily moved through the aqueous environments in the form of particulates or suspended sediments. If the Eh environment allows it, Pu(IV) can be oxidized to Pu(V) or (VI), with much lower plutonium adsorption values resulting. The plutonium polymers usually are adsorbed readily, but can migrate more rapidly than soluble plutonium in some instances where the surface charge density is low. Much experimental work remains to be done to separate and understand the several reactions or mechanisms occurring in plutonium adsorption. A controlled Eh environment for the adsorption work is important as an experimental condition when an element disproportionates as readily as plutonium.

PROMETHIUM

Natural Sediment and Rock Distributions

Promethium has not been found to occur naturally in sediments and rocks.

Brief Chemistry

There are 16 known radioactive isotopes and isomers of promethium with mass numbers from 141 to 154 and half-lives ranging from 34 sec to 17.7 yr. Promethium-147 (half-life 2.5 yr) is the only promethium isotope obtained in large amounts from ^{235}U fissioning by thermal neutrons, and is present in fuel reprocessing fission products.

Promethium is a lanthanide and like most lanthanides exists in a trivalent state. Only the (III) oxidation state of promethium is stable in aqueous solutions. Starik and Lambert (1958) studied the state of micro-amounts of promethium in aqueous solutions at different pH values by ultrafiltration and centrifugation. The results showed that promethium was present as Pm^{3+} at $\text{pH} \leq 3$. With an increase in pH, hydrolysis products gradually accumulate as multiply-charged aggregates. After a maximum is reached at pH of about 7, the charged aggregates begin to flocculate. At higher pH values, the aggregates become neutral or negatively charged. Electrophoretic measurements showed that from pH 5.3 to 6.7, the bulk of the polynuclear particles was positively charged. At pH 9, no mobility is seen, indicating neutrally charged particles. At pH 5 to 8, no promethium can be centrifuged, indicating a colloid in solution. At pH 9, uncharged forms such as $[\text{Pm}(\text{OH})_x (\text{NO}_3)_{3-x}]^0$ predominate (Starik et al., 1959).

Promethium is a lanthanide and like most lanthanides exists in a trivalent state (Pm^{3+}). No data were found on solution species of promethium except for PmNO_3^{2+} ($\text{Pm}^{3+} + \text{NO}_3^- \rightleftharpoons \text{PmNO}_3^{2+}$ $\log K^\circ$ at $I = 1$ is 2.48). The solution species is probably predominantly Pm^{3+} , much like europium. If it is assumed that promethium does not form any other complexes, then the concentration of promethium in solution will be governed mainly by Pm^{3+} . Under these conditions, ion exchange can be an important promethium removal mechanism in acidic environments and at trace promethium concentrations.

Laboratory Adsorption Studies

Cerrai et al. (1969) contacted Ligurian Sea Sediments with sea water traced with ^{147}Pm . Up to 200 mg sediment in 400 ml of traced sea water (pH 8.1) was shaken in a batch experiment for 1 hr. The samples were then centrifuged 20 min at 5000 rpm and the supernatant removed. The supernatant and sediment were both counted. The $K_{d_{\text{Pm}}}$ was relatively independent of the amount of sediment in contact with the sea water aliquot. The sediment/volume ratio was varied between 750 mg/l to 5000 mg/l while the average K_d was 3.8×10^3 . Uptake onto the same sediment in contact with distilled water showed $K_{d_{\text{Pm}}}$ sensitivity to sediment-solution ratio. As the amount of sediment encountering 40 ml of traced distilled water increased from 5 to 100 mg the $K_{d_{\text{Pm}}}$ dropped from 9.4×10^3 to 2.9×10^3 . The addition of $0.02 \mu\text{g/l}$ Nd to the distilled water did not affect the sorption of ^{147}Pm . The leaching of previously sorbed Pm by "clean" sea water was between 6 to 13% after 1 hr contact and depended upon sediment weight present. The more sediment contacted with 40 ml sea water the more Pm released. The effect of increasing leaching time from 1 to 15 hr was small 9% + 12%. The $K_{d_{\text{Pm}}}$ desorption was 4.0×10^3 ml/g compared with 3.8×10^3 ml/g for the adsorption.

Dawson and Duursma (1974), Duursma and Gross (1971) and Duursma and Eisma (1973) report on Pm sorption for marine sediments. Promethium was found to hydrolyze in sea water and precipitate out without sediments present although some resolubilization appeared to occur with time. $K_{d_{\text{Pm}}}$ is usually lower than another rare earth, Cerium. The sorption versus particle size for two marine sediments shows Pm to be retained predominately by the $<8 \mu\text{m}$ fractions. Promethium sorption on a Black Sea sediment appears to be quite sensitive to redox conditions. Under oxidizing conditions a $K_{d_{\text{Pm}}} 7.2 \times 10^4$ ml/g occurs while under reducing conditions 7.7×10^3 is observed. The average $K_{d_{\text{Pm}}}$ and $t_{1/2}$ sorption rate observed on experiments on various marine sediments are shown in Table 8.60.

Essington and Nishita (1966) evaluated the removal of soil bound ^{147}Pm with distilled water, irrigation water and soluble chelating agents. Waters devoid of chelating agents would not leach Pm. The chelates CDTA and EDDHA were also ineffective but DTPA did remove significant amounts of Pm.

TABLE 8.60. K_d_{Pm} and $t_{1/2}$ Values on Selected Sediments

<u>Sediment</u>	<u>log K Unitless</u>	<u>K_d_{est} ml/g</u>	<u>$t_{1/2}$ Days</u>
Atlantic Ocean	4.8 ± 0.5	9.8×10^4	9 ± 6
Pacific Ocean	4.9 ± 0.6	1.1×10^5	9 ± 6
Indian Ocean	4.6 ± 0.7	5.7×10^4	10 ± 2
Baltic Sea	4.6 ± 0.2	5.6×10^4	7
North Sea	4.7 ± 0.6	7.0×10^4	13
Mediterranean Sea	4.9 ± 0.2	1.2×10^5	14.4
Black Sea	4.2 ± 0.7	2.4×10^4	12.6
Red Sea	4.4	3.8×10^4	5

Bensen (1960) reported the complete uptake of promethium and other trivalent rare earths at pH >6. Promethium behavior in soil systems was said to be identical to cerium behavior. The uptake of promethium is nearly complete and unaffected by 0.5M alkali metal and 0.25M alkaline earth metal cations at above pH 7. Below pH 3, the adsorption of all rare earths including promethium is depressed similarly by accompanying salts. The results indicate that promethium and other rare earths are ionic species below pH 3, and begin to precipitate as charged polymers above pH 3. Bensen (1960) also reported that the species and amount of accompanying anion affect promethium adsorption by soils. Citrate, acetate and carbonate ions were found to inhibit rare earth adsorption on soils. This was attributed to formation of complex ion species. Chloride and nitrate ions had no appreciable effect on adsorption, and sulfate had very little effects.

Ames (1960) reported the removal of promethium during a replacement reaction of calcite with phosphate in solution. The promethium was finally immobilized in apatite, $Ca_5(PO_4)_3OH$, where 2 Ca^{2+} are replaced by a Pm^{3+} and Na or some other univalent cation.

Schulz (1965) classified promethium with other rare earths as immobile in soils due to either very strong adsorption by clay particles or present as insoluble hydroxide.

Field Studies

Cerrai et al. (1967) measured the ^{147}Pm content of sediments from the Adriatic and Ligurian Seas. There was much more Pm in the fines (100 μm) of the Adriatic sediments compared to the coarser fractions 1.69 pCi/g versus 0.078 pCi/g. The total sediment concentrations reported were 0.98 pCi/g and 2.35 pCi/g for the Adriatic and Ligurian samples.

Magno et al. (1970) investigated migrating radionuclides from the Nuclear Fuel Services plant in western New York State. They estimated from analytical data that greater than 90% of the ^{147}Pm discharged from the plant was deposited by sedimentation in the lagoon system. These results imply that most of the promethium was a precipitate, probably $\text{Pm}(\text{OH})_3$, or adsorbed on other solids in the water that settled out in the lagoons.

Summary

Low concentrations of promethium are expected in equilibrium with $\text{Pm}(\text{OH})_3$ in slightly acidic to slightly alkaline conditions so that $\text{Pm}(\text{OH})_3$ precipitation may control promethium concentrations in soil and sediment solutions. Promethium, like europium, would be expected to be ion exchangeable below the concentration required for $\text{Pm}(\text{OH})_3$ precipitation. Only limited data are available on promethium adsorption on soils and sediments, but these data tend to support the above predictions.

The marine environments promethium is readily adsorbed K_d 10^3 to 10^5 ml/g apparently via precipitation. The removal of promethium is nearly complete on soils and rocks above pH 6 (Bensen, 1960). The effect of competing cation on promethium adsorption above pH 7 is minimal. Below pH 3, the adsorption of all rare earths including promethium are similarly depressed by competing salts. Charged polymers can form under the proper conditions during $\text{Pm}(\text{OH})_3$ precipitation (Starik et al., 1959; Bensen, 1960). Citrate, acetate and carbonate ions inhibited rare earth adsorption on soils, probably due to the formation of complex ion species. Over 90% of the promethium discharged to a lagoon system remained in the lagoon (Magno et al., 1970) as strongly adsorbed on clay particles or present as an insoluble hydroxide (Schulz, 1965). Promethium can be removed from solution during replacement reactions (Ames, 1960).

RADIUM

Natural Sediment and Rock Distributions

The radium content of various sediments and rocks is given in Table 8.61. Vinogradov (1959) reported that the radium content of soils ranged from 0.5×10^{-6} to 1.1×10^{-6} ppm. The small amount of radium present in soils has become separated from parent thorium and uranium during rock weathering processes, and most closely follows barium. The radium content of igneous rocks increases by 100 times from ultra-basic to granitic rocks. The radium content of most sedimentary rocks is about the same as that for granites.

TABLE 8.61. Average Radium Content of Various Geologic Media

Type	Ra, ppm	Reference
Ultrabasic Igneous	0.009×10^{-6}	Davis, 1947
Basic Igneous	0.6×10^{-6}	Evans et al., 1942
Intermediate, Igneous	0.917×10^{-6}	Senftle and Keevil, 1947
Granitic Igneous	1.395×10^{-6}	Senftle and Keevil, 1947
Sandstones	0.71×10^{-6}	Bell et al., 1940
Shales	1.08×10^{-6}	Bell et al., 1940
Limestones	0.42×10^{-6}	Evans and Goodman, 1941
Marine Sediment	$1 \text{ to } 50 \times 10^{-6}$	Turekian and Wedepohl, 1961
River Muds	1×10^{-6}	Shearer, 1962
Uranium-Polluted River Muds	374×10^{-6}	Shearer, 1962

Brief Chemistry

There are 16 isotopes of radium from ^{213}Ra to ^{230}Ra with no ^{218}Ra or ^{229}Ra . All of the isotopes of radium are unstable, and all of the naturally-occurring radium isotopes occur in the thorium decay series (^{228}Ra , ^{224}Ra), the ^{238}U -radium decay series (^{226}Ra), and the ^{235}U -Actinium decay series (^{223}Ra) (Vdovenko and Dubasov, 1973). The half-lives of ^{228}Ra , ^{224}Ra , ^{226}Ra and ^{223}Ra are 5.77 ± 0.02 years, 3.65 days, 1622 years and 11.43 days,

respectively. All are alpha emitters except ^{228}Ra which is a beta emitter. With the present uranium fuel cycle and the much longer half-life, only the ^{226}Ra isotope is of long-term concern in waste disposal. If future energy production includes thorium fuels, then ^{228}Ra also must be included in waste disposal management plans.

Radium is a homolog of the alkaline-earth elements, with a (II) oxidation state. The radius of the +2 radium ion is 1.52 Å compared to 1.43 Å for Ba^{+2} . The compounds formed by radium and their solubilities are similar to barium. For example, the solubility product of radium sulfate is 4.25×10^{-11} at 25°C (Vdovenko and Dubasov, 1973) and the solubility product of barium sulfate is 1.08×10^{-10} at 25°C (Weast, 1976). Metallic radium dissolves in water with the evolution of hydrogen and the formation of readily soluble $\text{Ra}(\text{OH})_2$. Of the alkaline-earth metal cations, Ra^{+2} shows the least tendency for complex formation, although 1:1 complexes with citric, tartaric, succinic and several other acids were detected at pH 7.2 to 7.4 by Schubert et al. (1950). It may be assumed that Ra^{+2} is not hydrolyzed in aqueous solutions, by analogy with Ba^{+2} , although there is no specific literature on the subject.

Solution Equilibria

No thermodynamic data were located for radium hydrolysis or complex ion species. It is expected that radium will behave in solution much like strontium does. The species Ra^{2+} is expected to be the most important over the pH range from 4 to 8.

Laboratory Adsorption Studies

Holland and Kulp (1954) studied the adsorption of radium onto deep sea red clay, globigerina ooze and green clay. The amount of radium left in solution at equilibrium was independent of the amount of tracer added to the sea water. Ion exchange appeared to be controlling the removal of radium.

Iskra et al. (1969) studied the distribution of ^{226}Ra in an experimental nonrunning fresh water basin. Radium appeared to be adsorbed by sediments and plants less than thorium but more than uranium.

Joshi and Ganguly (1970) showed radium could be leached from marine sediments and probably is in nature by sea water.

Titaeva (1967) found radium to adsorb readily by clay sediments and peat. Under oxidizing conditions the bonding was exchangeable for both clays and humics. If high concentrations of calcium carbonate are present radium adsorption loses its exchange properties, suggesting coprecipitation of radium into CaCO_3 .

Stead (1964) gave a radium Kd value of 6700 ml/g for NTS tuff. Arnold and Crouse (1965) ran batch adsorption tests on some exchange materials that included the natural zeolites, clinoptilolite and chabazite, as represented by a pelletized molecular sieve (AW-500) and barite (barytes), a natural BaSO_4 . The results of the adsorption tests were recomputed as distribution coefficients or Kd values. The solution was a lime-neutralized waste that contained 4100 pCi ^{226}Ra /l, 500 mg/l Ca^{+2} , 80 mg/l Mg^{+2} , 1000 mg/l Na^{+} , 2500 mg/l SO_4^{-2} and 900 mg/l Cl^{-} at pH 7.7. The radium Kd values are given in Table 8.62.

TABLE 8.62. Radium Kd Values from Lime-Neutralized Waste; 1.25 g Exchanger/l of Waste (Arnold and Crouse, 1965)

<u>Exchanger</u>	<u>Mesh Size</u>	<u>Exchanger Loading, pCi/g</u>	<u>Kd, ml/g</u>
Clinoptilolite	20 to 50	2650	646
Chabazite	20 to 50	2900	707
Barite	20 to 50	2000	490

R. J. Serne (1974) of PNL used soils from Utah and simulated river water to determine radium distribution coefficients. The soils were pre-equilibrated by four washings with the simulated river water composition shown in Table 8.63 minus the $^{226}\text{RaCl}_2$. The fifth solution contained the ^{226}Ra as well as the other constituents, and was used for the radium Kd determinations. The Kd values were determined in triplicate to allow measurement of

precision. The Utah soils contained 2 to 5% calcite, with quartz and feldspar constituting the bulk of these sandy, arid soils. Minor constituents included hydromica and a small amount of a smectite clay. The radium Kd results are listed in Table 8.64. The Kd correlated with the cation exchange capacities of the soils.

TABLE 8.63. Simulated River Water Composition (Serne, 1974)

<u>Constituent</u>	<u>Added as-</u>	<u>mg/l</u>
Ca	CaSO ₄ · 2H ₂ O, CaCl ₂	82
Mg	MgSO ₄	26
Na	NaCl	75
K	KCl	3.4
HCO ₃	NaHCO ₃	171
SO ₄	CaSO ₄ · 2H ₂ O, MgSO ₄	246
Cl	CaCl ₂ , NaCl, KCl	57
U	UO ₃	1
Ra	RaCl ₂ in HCL solution	7 µg/l

TABLE 8.64. Radium Distribution Coefficients with the Solution of Table 8.63 (Serne, 1974)

<u>Soil</u>	<u>Final pH</u>	<u>Kd, ml/g</u>
I	7.9	354 ± 15
	7.9	
	8.0	
II	7.6	289 ± 7
	7.7	
	7.6	
III	7.8	467 ± 15
	7.9	
	7.8	
IV	7.8	214 ± 15
	7.6	
	7.8	

Several reports have been concerned with the leaching of ^{226}Ra from uranium recovery process tailings and wastes (Whitman and Porter, 1958; Anonymous, 1960; Feldman, 1961), and other authors have shown that radium can be leached from stream sediments, minerals and uranium mill wastes (Starik and Plevaya, 1958; Starik and Lazerev, 1960). The factors that influence leachability of ^{226}Ra from uranium mill waste solids and river sediments were investigated by Shearer (1962) and Shearer and Lee (1964). Less than 1.5 wt% of the river sediments and mill waste solids were greater than plus 20 mesh size and less than 30 wt% were minus 140 mesh in particle size. The amounts of radium leached with distilled water versus time showed that essentially all radium was leached after 15 min. Diffusion of radium from the interior of the particles was relatively insignificant. By varying the liquid to solid ratio in distilled water-solid leaching equilibria, it was shown that the ratio affects the amount of radium leached. The largest ratio effect was shown with leaching of the acid leach process tailings, less with alkaline leach process tailings and the least from river sediments. It was demonstrated that sulfate was present in the waste solids and that the sulfate was easily solubilized. Trace amounts of barium present led to precipitation of BaSO_4 and the coprecipitation of RaSO_4 . If radium was added prior to the solids-distilled water equilibria, it too was removed from solution by coprecipitation with BaSO_4 . One-hundredth molar solutions were used in leaching equilibria (100 ml/g river sediment) to determine effects on radium leaching. MgCl_2 , KCl , NaCl , HCl and water solutions all leached less than 1 μg of radium while CaCl_2 leached 1.2 μg Ra , SrCl_2 6.3 μg Ra and BaCl_2 30 μg Ra . Apparently the radium on river sediments is in the form of Ra^{+2} and is exchangeable.

Havlik et al. (1968a) investigated the leaching of ^{226}Ra from uranium mill solids and uranium ores. The first report concerned the effects of pH on leaching rates. The authors found, like Shearer and Lee (1964), that equilibrium leaching was rapidly accomplished in 15 to 30 min. Homogenized uranium ores (540 pCi Ra/g and 85 pCi Ra/g) and milling tailings (14 pCi Ra/g) were shaken for varying lengths of time as a 3 g solid/30 ml solution ratio. The pH was modified from 1 to 14 with hydrochloric acid, boric acid and sodium

hydroxide. At pH 1, 22% of the ^{226}Ra was liberated. At pH 9, the amount leached had decreased to 2.8%. At pH 13, the amount of leached ^{226}Ra increased to 5%.

The second report by Havlik et al. (1968b) studied the leaching of radium from the same solids as affected by leaching solution composition in addition to acidity. Unlike the leaching results of Shearer and Lee (1964), Havlik et al. found that the largest concentrations of radium were leached by 1N KCl and 1N NaCl solutions. BaCl_2 , SrCl_2 and CaCl_2 also were used, but with much less radium liberated. The 1N KCl leached 100% of the radium in mill tailings and NaCl, 95%. Uranium ore leaching results were lower, showing 22 and 31 leached by KCl and 14 and 17% leached by NaCl. In all cases, the one normal salt solution removed more radium than ten normal salt solutions.

Field Studies

Baranov and Khristianova (1963) found in Pacific Ocean cores that clay fractions contained ten times more radium than sand fractions.

Bernat and Goldberg (1969) ascertained that radium in Pacific Ocean cores has diffused within the vertical profile.

Bhat and Krishnaswamy (1969) measured the dissolved radium content in several Indian Rivers. The range observed for ^{226}Ra was 0.02 to 0.09 pCi/l.

Cerrai et al. (1970) measured the ^{226}Ra content of Ligurian and Adriatic Sea sediments. There was little difference in the radium content in fine (<100 μm) and coarse (>100 μm) fractions. Total sediment radium concentrations were 0.578 pCi/g and 0.348 pCi/g, respectively.

Hamaguchi (1971) found the radium content of 13 deep sea sediments (Pacific Ocean) to be proportional to the iron and manganese content.

Havlik (1970) studied the content of ^{226}Ra in river water, sediments and plants in the vicinity of the Jachymov uranium mine.

Kurokawa (1971) measured the natural occurrence of ^{226}Ra in 40 Japanese soils and 10 rivers. He found 0.09 to 1.3 ppm in the soils and 8.2×10^{-10} ppm in the rivers which yield an apparent $K_d_{\text{Ra}} > 10^7$.

Starik et al. (1961, 1963) studied the geochemistry of radium in oceans. The leaching of radium from minerals suggests that the content of radium in ocean water should be higher than that of uranium, yet data show the opposite. The suggested reason is radium sorption by suspended and colloidal particles with precipitation into bottom sediments. Ocean deposits had a radium content of 4 to 50×10^{-6} ppm, Black Sea deposits had 5 to 9×10^{-7} ppm radium, and Azov Sea sediments 7.2×10^{-7} ppm radium.

Somayajulu and Church (1973) found the interstitial waters of Pacific Ocean cores to contain 1 to 3 orders of magnitude greater radium contents than sea water. Radium release from sedimentary phases with migration into the water column is indicated.

Granger et al. (1961) and Granger (1963) showed that radium had migrated out of Ambrosia Lake, New Mexico, uranium ores and had been partly reconcentrated in barite (BaSO_4) and cryptomelane ($\text{KMn}^{2+}\text{Mn}^{4+}_2 7.25^{0}_{16}\text{H}_2\text{O}$) found in and near some of the ore bodies. The $^{226}\text{Ra}^{2+}$ occurred in the Ba^{2+} position in barite and the Mn^{2+} position in cryptomelane. The high concentrations of ^{226}Ra were not associated with parent uranium, which is good evidence for the recent migration of radium. The strongly to weakly radioactive cryptomelane partially replaced mudstone that occurred near the ore bodies and was relatively low in uranium content and enriched in lead. This suggests that the lead is radiogenic and has also migrated with the ^{226}Ra . The mechanism involved in reconcentration of the ^{226}Ra is the substitution of $^{226}\text{Ra}^{2+}$ for the chemically very similar Ba^{2+} in barite and Mn^{2+} in cryptomelane. Analyses of the outer 5 to 10 cm of mudstone layers near ore disclosed anomalously high radioactivity coupled with an abnormally high lead content. Within mudstone layers, however, the radioactivity was essentially in balance with the uranium content, and the lead content was low.

Hansen and Huntington (1969) determined radium and thorium distributions in a series of morainal soils in Bench Valley, California. Thorium accumulated immediately beneath horizons containing a high amount of organic material. The thorium apparently migrated as organic complexes. Radium was distributed with the uranium in the high organic layers.

The ground and surface water sampling and analyses for radium given by Mruble et al. (1964) and Kaufmann et al. (1975, 1976) for waters of the Colorado Basin and Grants area, New Mexico, respectively, also illustrate the tendency of the radium daughter to become separated from uranium due initially to uranium mining and milling operations, and to continue migrating due to inherent geochemical differences between uranium and radium.

Summary

Radium is present as Ra^{2+} over the normal pH range (4 to 8) and shows little tendency to form complex species. Radium would be expected to substitute for other divalent cations during replacement or precipitation reactions. A direct correlation of cation exchange capacity with adsorption and leaching studies with different types of competing cations suggests that an important reaction mechanism for radium adsorption is cation exchange. Radium could be expected to migrate in much the same manner as strontium.

RUTHENIUM

Natural Sediment and Rock Distributions

Few data on natural distribution of ruthenium are available. Data available on ruthenium in rock-forming minerals are listed in Table 8.65. Platinum group metals, including ruthenium, are known to be concentrated in chromite; but these are older analytical values and may be much higher than modern neutron activation ruthenium analyses. There are no ruthenium data on sandstones and limestones. However, the ruthenium contents are probably very low. The meager data on ruthenium content of shales are given in Table 8.66. The behavior and distribution of natural ruthenium during weathering processes is largely unknown. Estimates for the ruthenium content of marine sediments are given as 20 to 100 ppb.

TABLE 8.65. Abundances of Ruthenium in Igneous Rocks and Rock-Forming Minerals in ppm

<u>Mineral</u>	<u>Ru, ppb</u>	<u>Reference</u>
Olivine	10	Noddack and Noddack, 1931
Chromite, Norway	500	Goldschmidt and Peters, 1932
Chromite, Texas	500	Goldschmidt and Peters, 1932
Chromite, Penn.	500	Goldschmidt and Peters, 1932
Columbite, Norway	10	Noddack and Noddack, 1931
Ilmenite	4	Noddack and Noddack, 1931
Rutile	10	Noddack and Noddack, 1931
Tantalite	2	Noddack and Noddack, 1931
Dunite, Russia	2 to 30 (5 average)	Razin et al., 1965
Dunite, Russia	3 to 6 (4.5 average)	Razin et al., 1965
Apodunite, Russia	0.9 to 4 (2.2 average)	Razin et al., 1965
Mica shonkinite	0.5	Razin et al., 1965

TABLE 8.66. Ruthenium Contents of Shales

<u>Shal.</u>	<u>Ru, ppb</u>	<u>Reference</u>
Kupferschiefer, Mansfeld, Germany	3	Moddack, 1936
Black Shale (3)	60 80 40	Tischendorf, 1959
Bleached Shale (3)	40 5 20	Tischendorf, 1959

Brief Chemistry

The 16 isotopes of ruthenium include the radioactive fission products ^{93}Ru , ^{94}Ru , ^{95}Ru , ^{97}Ru , ^{103}Ru , ^{105}Ru , ^{106}Ru , ^{107}Ru and ^{108}Ru . The natural stable ruthenium isotopes and their abundance are shown in Table 8.67.

TABLE 8.67. Atomic Percentages of Stable Ruthenium Isotopes (Heath, 1976)

	<u>96</u>	<u>98</u>	<u>99</u>	<u>100</u>	<u>101</u>	<u>102</u>	<u>104</u>
Atom %	5.51	1.87	12.72	12.62	17.06	31.61	18.58

Ruthenium-103 with a 39.6-day half-life and ^{106}Ru with a 367-day half-life are the only radioisotopes of ruthenium that persist long enough to be of concern in waste disposal.

Ruthenium exhibits several oxidation states varying from Ru(-II) to Ru(VIII), with Ru(III) and Ru(IV) the most common oxidation states^o in aqueous solutions. Ru(II) is less common. For ruthenium, there is little evidence for simple quo ions. Nearly all aqueous solutions, whatever the anion, may be considered to contain complex ions (Cotton and Wilkinson, 1962). Ru(II), for example, is known to form a unique series of nitrosyl complexes, nitric oxide complexes, ammonia and sulfur complexes, carbonyl complexes, etc.

In an alkaline medium, Ru(IV) forms the insoluble hydrated oxide $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ which does not tend to be reduced to the trivalent state. Ruthenium (III) hydroxide is readily oxidized in air to Ru(IV) (Ginzburg et al., 1975). Ruthenium exists in nitric acid solutions either as the Ru(III) nitrosonitrates $[\text{RuNO}(\text{NO}_3)_n(\text{H}_2\text{O})_{8-3n}]^{3-n}$ or $[\text{RuNO}(\text{NO}_3)_{5-n-m}(\text{OH})_m \cdot (\text{H}_2\text{O})_n]^{p-}$, or as the polymeric Ru(IV) aquohydroxo cations $[\text{Ru}(\text{OH})_x(\text{H}_2\text{O})_{6-x}](\text{NO}_3)_{4-x}$ (Ginzburg et al., 1975). Thus, from acidic nitrate solutions, which are the usual form of fuel reprocessing wastes, ruthenium solutions may be obtained that contain cationic, anionic and neutral complexes. Hence, the chemical forms of soluble ruthenium depend heavily on the chemical history of the solution.

Solution Equilibria

The activity of various solution complexes of ruthenium in equilibrium with RuO_2 (amorphous, hydrated) in oxidizing ($p\text{O}_2 = 0.68$) and other conditions spelled out are given in Figure 8.34. The thermodynamic data used to construct Figure 8.34 were selected from several sources including Sillen and Martell (1964) for RuOH^{3+} , Ru^{4+} and Ru^{3+} , Baes and Mesmer (1976) for $\text{RuO}_4(\text{OH})^-$, and Wagman et al. (1969) for the remaining species. Baes and Mesmer (1976) indicate that the thermodynamic data on ruthenium complexes are either not available or are not very accurate. However, it was decided to construct Figure 8.34 using the existing data to estimate the nature of the species that may be present in solution.

Figure 8.34 indicates that in an oxidizing environment, significant activity of uncomplexed Ru^{4+} will be present only in very acidic conditions ($\text{pH} \leq 2$). Some of the ruthenium species which may be present in solution are RuO_4^- , RuO_4^{2-} , RuO_4^0 , $\text{Ru}(\text{OH})_2^{2+}$, $\text{RuO}_4(\text{OH})^-$, $\text{RuCl}_5(\text{OH})^{2-}$, Ru^{4+} , and Ru^{3+} . Among these species, Ru^{4+} would be predominant in $\text{pH} < 2$, $\text{Ru}(\text{OH})_2^{2+}$ in $\text{pH} 2$ to 5.2 , RuO_4^- in $\text{pH} 5.2$ to 10.5 , and RuO_4^{2-} in $\text{pH} > 10.5$. With an increase in reducing conditions, the activity of Ru^{3+} would increase, the activity of RuO_4^0 .

FIGURE 8.34. The Activity of Various Ruthenium Species in Equilibrium with RuO_2 (amorphous, hydrated) in Oxidizing ($p\text{O}_2 = 0.68$) and Other Conditions

RuO_4^- , RuO_4^{2-} and RuO_4OH^- would decrease and the rest of the species would remain unchanged in activity. The nature of the predominant solution species is highly dependent upon the oxidation-reduction conditions, as is the most stable solid compound. The predominant ruthenium species are cationic below pH 5 and anionic above pH 5. Hence, ion exchange on soils and sediments would be of importance only below pH 5 under these conditions.

Laboratory Adsorption Studies

Aston and Duursma (1973), Dawson and Duursma (1974), Duursma (1973), Duursma and Bosch (1970), Duursma and Eisma (1973), and Duursma and Gross (1971) studied the adsorption of ruthenium into marine sediments. The observed K_d_{Ru} was not affected by the presence on stable carrier ruthenium over the concentration range 0.005 to 0.1 $\mu\text{g/l}$ [using Ru(III) chloride]. K_d_{Ru} for calcareous sediments was less than 7000 ml/g and reached values of 50,000 for sediments containing illite clay. In general, the higher the exchange

capacity of the sediment the larger the observed $K_{d_{Ru}}$. The adsorption of ruthenium follows a Freundlich isotherm. Adsorption versus sediment particle size fraction shows the silt fraction adsorbs more ruthenium than clay. There appears to be greater adsorption of ruthenium under oxidizing conditions than reducing conditions for a Black Sea sediment. The $K_{d_{Ru}}$ under oxidizing conditions was 5.1×10^4 ml/g versus 1.3×10^4 ml/g for reducing conditions. Duursma and coworkers admonished that these results using simple cationic tracers might not accurately predict sorption of the complex distribution of ruthenium species in nature.

A summary of $K_{d_{Ru}}$ values and half-periods of sorption for numerous marine sediments are shown in Table 8.68.

TABLE 8.68. Ru Sorption Data

<u>Sediment</u>	<u>log K</u>	<u>Kd (est.), ml/g</u>	<u>t 1/2 Sorption, days</u>
Atlantic Ocean	4.4 $\pm$ 0.4	3.5×10^4	6.5 $\pm$ 4.6
Pacific Ocean	4.3 $\pm$ 0.6	2.9×10^4	7.1 $\pm$ 1.6
Indian Ocean	4.6 $\pm$ 0.4	8.7×10^4	15.2 $\pm$ 6.5
Baltic Sea	4.5 $\pm$ 0.2	4.7×10^4	9.0
North Sea	4.2 $\pm$ 0.5	2.7×10^4	9.0
Mediterranean Sea	4.3 $\pm$ 0.2	3.0×10^4	8.4 $\pm$ 4.3
Black Sea	4.2 $\pm$ 0.4	2.6×10^4	5.0
Red Sea	4.6 $\pm$	5.4×10^4	5.0

Baranov and Polikarpov (1966, 1968) studied the adsorption of ruthenium onto shallow marine sediments and observed the sorption to be poor compared to Zr, Cs, Ce. The ruthenium which was adsorbed was readily removed by fresh sea water and 0.2N HCl acid.

Collet et al. (1968) studied the adsorption of Ru on Rhine River sediments and separated adsorption values for sand, silt and clay fractions. Doshi et al. (1973) found quantitative removal of Ru from sea water during in situ precipitation of manganese dioxide. Gardner and Skulberg (1964) studied the

adsorption of ruthenium onto sediments from the River Nitelva. Detailed characterization of sediments and river water are given. The sediments were treated with H_2O_2 to remove organic matter, dried and ground to <200 mesh prior to usage. Experiments at 16 to 256 mg/l sediment were performed using ruthenium (III) chloride tracer. At 64 mg/l suspended solids ruthenium adsorption was still slowly increasing after 9 days. The effects of salt composition and sediment concentration are shown in Table 8.69 were Kd_{Ru} (24 hr contact) are shown for river water and distilled water. As the authors show sorption continuing beyond 9 days, these values are not equilibrium values.

TABLE 8.69. Ru Sorption in Fresh Water

Sediment, mg/l	Kd_{Ru} Distilled Water, ml/g	Kd_{Ru} River Water, ml/g
16	11,900	1,600
32	9,600	1,300
64	8,050	1,180
128	6,750	910
256	5,300	690

Gromov (1975) and Gromov and Spitsyn (1974) studied the adsorption and desorption of ruthenium by Pacific Ocean and Indian Ocean sediments. Ruthenium was sorbed readily by the sediments.

Kepak (1966) studied the sorption of ^{106}Ru as the ruthenium (III)- and nitrosylruthenium (II)-ion on hydrated ferric oxide, containing a small amount of silver oxide under dynamic conditions. The sorption of ^{106}Ru was also studied under static conditions and it was observed that the absorption of a small quantity of silver oxide in ferric oxide increased its sorption capacity for the ruthenium (III)- and nitrosylruthenium (II)-ion and the sorption was characterized by high values of the distribution coefficient.

Sorption of Ru from 30.2% saline water by a sandy sediment from the Skagit River estuary (Washington) has been reported by Schell et al. (1979). Ru appears to be rather insoluble in sea water as 78 to 85% of the tracer was filterable from blank solutions. Without blank correction the Kd_{Ru} is 1.7 to 2.9×10^4 ml/g. With blank correction the Kd_{Ru} is 0.8 to 1.1×10^4 .

In a dialysis experiment Schell et al. (1979) show that Ru predominates in soluble forms. The portion which does become bound on particulates shows plankton as stronger sorber than clay or organic detritus. The distributions can be found in Table 8.10 of the americium section.

Schell et al. (1980) report on laboratory determinations of Kd_{Ru} in numerous fresh and marine water environments with actual sediments. Table 8.11 summarizes the results. The Kd_{Ru} values do not appear to be sensitive to salinity effects which suggests Ru sorption is not predominated by ion exchange like processes.

Schell et al. (1980) determined in the laboratory that the sorption of Ru onto a Clinch River (Tennessee) sediment from fresh water increased fivefold between pH 4 and 6. From pH 6 to 10 there was much scatter in observed Kd_{Ru} but no clear trend.

Schell et al. (1980) studied the effects of five organics on ruthenium sorption in a fresh water environment. Four organics significantly increased Kd_{Ru} (see Table 8.12). Care must be exercised in interpreting the significance of these results as unnaturally high concentrations of organics were used.

Schell et al. (1980) continued dialysis experiments using a Lake Michigan freshwater system. After 20 days much of the Ru is found bound to particulates sediments and detritus.

Eichholz et al. (1967) studied the distribution of ruthenium between suspended sediment particles and aqueous solutions. Natural water samples were characterized and used in the adsorption studies as sources of suspended solids, as shown in Table 8.70. A fission product mixture was added to the natural water samples, the system equilibrated and the water and sediments

separated. The adsorption of ^{106}Ru is shown in Table 8.71. A portion of the ^{106}Ru was associated with the suspended sediments, though to a lesser extent than the other radionuclides with the exception of ^{131}I .

TABLE 8.70. Properties of Natural Water Samples
(Eichholz et al., 1967)

<u>Source</u>	<u>Suspended Solids, ppm</u>	<u>Dissolved Solids, ppm</u>	<u>pH</u>	<u>Conductivity μmhos</u>	<u>Solids Composition</u>
Colorado River, Utah	229	350	7.5	540	95% quartz, 5% calcite, feldspar, illite, kaolinite
Camp McCoy, Wisconsin	12	60	6.9	80	30% quartz + feldspar, 6% kaolinite, 24% illite
Bayou Anacoco, Louisiana	24	63	6.2	60	30% quartz, 2% kaolinite, 6% smectite
Lodgepole Creek, Nebraska	965	200	6.8	300	20% illite, 80% smectite
Chattahoochee River, Georgia	131	31	7.3	45	33% quartz, 44% kaolinite, 23% illite
Billy's Lake, Georgia (swamp)	8	68	4.2	45	2% quartz, balance was amorphous and/or organic

TABLE 8.71. Adsorption of ^{106}Ru on Suspended Solids in Natural Waters
(Eichholz et al., 1967)

<u>Source</u>	<u>pH</u>	<u>^{106}Ru Adsorption, %</u>
Colorado River	7.5	25.0
Camp McCoy	6.9	5.7
Bayou Anacoco	6.2	0
Chattahoochee River	7.3	10.4
Billy's Lake	4.2	0

It is obvious that ruthenium adsorption was a function of Ph of the water. The higher percentages of adsorbed ruthenium are directly correlated with water pH.

Peperstraete et al. (1973) performed detailed electrophoretic studies of the distribution of different ruthenium species during their transition from fresh to marine waters. The species distribution was found to be complex with nitroso - (nitrite, chloride, nitrate and hydroxides) all being stable in both fresh and marine environments. With aging the ruthenium complexes appear to form polymers.

The adsorption of trinitratonitrosyl ruthenium on peat as a function of contact time, pH, solids/solution ratio and solution salt content was studied. Ruthenium adsorption was high even above pH 4 where hydrous colloids were present.

Amy (1971) studied the migration rates of different ruthenium forms in calcareous and acidic soil in columns. The nitrodinatrato complexes of ruthenium, $\text{RuNO}_2(\text{NO}_3)_2 (\text{H}_2\text{O})_2$, were much more mobile than cesium in calcareous soils. From 2 to 33% of this ruthenium form passes through the column. For comparison, the fraction from RuCo_3 that migrates down the entire column length varied from 3 to 68%, depending on the soil type. In summary, in calcareous soils maximum ruthenium mobility was attained when the ruthenium was in the form of an anionic complex in permeable soils with a sandy texture and low in organic material.

Champlin and Eichholz (1976) have shown that finely particulate soil materials, such as kaolinite, can adsorb a variety of trace radionuclides including ^{106}Ru and adhere to the soil matrix surface by Van der Waal's forces (Champlin, 1969). Further, these fine particulates were mobilized by laundry detergents and softening agents, so that they were transported quickly through the soil column without reaction with contacting soils.

Nishita et al. (1956) leached ruthenium from soils and clay minerals with water and a salt solution. The ^{106}Ru was the most readily leached radionuclide from the soils with water. The ^{106}Ru also was the most easily water

leached from bentonite and kaolinite. The ruthenium tended to be the least exchangeable in both the soils and the bentonite and kaolinite. A persistent fraction of the bentonite and kaolinite adsorbed ruthenium was nonexchangeable.

Nishita and Essington (1967) continued work on ^{106}Ru migration in different types of soils, comparing the relative movement of ^{65}Zn , ^{85}Sr , ^{91}Y , ^{106}Ru , ^{137}Cs , ^{144}Ce and ^{147}Pm . Irrespective of the soil type, water leaching resulted in the greatest movement for ^{106}Ru .

Rhose (1957) reported the variation in ^{106}Ru distribution coefficients with solution pH on a typical Hanford subsoil. The soil had a cation exchange capacity of 5 meq/100 g, 2 wt% calcium carbonate, with about 2% clays of mainly montmorillonite and less amounts of chlorite. The K_d values for ^{106}Ru are presented in Table 8.72. It should be noted that the ^{106}Ru was obtained from Oak Ridge National Laboratory, probably as RuCl_3 in HCl solution.

The soil adsorption of Ru^{+3} in a chloride medium cannot be similar to the adsorption of the nitro and nitrate complexes of nitrosylruthenium normally present in acidic nitrate waste solutions. Rhodes and Nelson (1957) make this same point when they discuss the soil adsorption of ruthenium present in uranium recovery plant waste. Sampling of ground water beneath a discontinued disposal facility showed that the concentration of ^{106}Ru remained constant for several months. This indicated little adsorption after the initial breakthrough of ^{106}Ru . Klechkovsky (1956) also investigated ^{106}Ru adsorption on soils but did not specify the type of ruthenium or soils used.

According to Schulz (1965), ruthenium tends to react like manganese, cobalt, zinc, iron and chromium in reactions in a soil environment. They are most soluble in acidic conditions and tend to precipitate as hydroxides as the pH rises. Ruthenium tends to form complexes that are uncharged or negatively charged and would therefore tend to be quite mobile in soils.

Bovard and Saas (1968) reported that the free functional groups (carboxylic, phenolic) were the cause of organic matter complexing and fixation of radionuclides. For humic acids, the mean order of complexing was $\text{Ce} > \text{Fe} > \text{Mn} > \text{Co} > \text{Ru} > \text{Sr} > \text{Cs}$. In the case of fulvic acids, no universal order existed. Two

TABLE 8.72. Ruthenium Distribution Coefficients on a Hanford Soil as a Function of pH (Rhodes, 1957)

<u>pH</u>	<u>Kd, ml/g</u>	<u>pH</u>	<u>Kd, ml/g</u>
0	0	9.2	40
1.3	0	10.1	39
2.6	26	10.4	44
4.7	101	11.0	92
6.6	752	11.3	27
7.4	460	13.0	101
8.5	274	14.0	752

types of soils were used in the studies, a calcareous alluvial soil and a humo-ferruginous podzol. Leaching of fission products, particularly ruthenium, by rain water occurred essentially in the form of fulvates.

Essington et al. (1965) and Essington and Nishita (1966) determined the leaching effects of water, chelating agents and HCl on ^{106}Ru adsorbed to soil. Chelating agents (DTPA, CDTA, EDDHA), increased the soluble radionuclides by a small amount as compared to water. The ^{106}Ru tended to remain in the column. Some ^{103}Ru was reported in leachates in CaDTPA-leached soils.

Kulikov (1968) and Kulikov and Molchanova (1972) found EDTA and DTPA could significantly reduce the adsorption of ruthenium by soils.

Wilding and Rhodes (1963) reported that the addition of 100 ppm citrate to a synthetic waste-cationic ruthenium solution reduced the Kd value for ruthenium on Idaho well sediments to 27 ml/g from 275 ml/g. For the same solutions, the reduction on the natural zeolite clinoptilolite was to a Kd value of 4 ml/g from a Kd value of 48 ml/g with no citrate present. Addition of 100 ppm EDTA to the synthetic waste (MTR cooling water) lowered the ruthenium Kd value from about 472 ml/g with no EDTA to 100 ml/g with EDTA. Kepak (1966) reported the adsorption Kd for $\text{Ru}(\text{NO})^{+2}$ and Ru^{+3} on hydrated ferric oxide as 8.4×10^3 and 4.8×10^3 , respectively.

Field Studies

Numerous articles have been published on the observed migration of ruthenium from Oak Ridge National Laboratory waste discharges [Carrigan (1968, 1969), Carrigan et al. (1967), Cowser (1963), Cowser and Parker (1958), Lammers (1968), Lomenick (1963), Pickering (1969, 1970) and Pickering et al. (1965, 1966)]. In general, ruthenium reaching the Clinch and Tennessee rivers is not retained by bottom sediments (<1% retained). The little bit of ruthenium present in the bottom sediments was probably already adsorbed on suspended sediments prior to deposition. Due to the complex and variable pattern of radionuclide distribution in sediments and production, the sediment ruthenium content was not found to correlate with any chemical or physical properties.

Before entering the streams, ruthenium travels through seepage pits and White Oak Lake and Creek. The suspected source is high nitrate waste. Some of the ruthenium is present in the nitrosyl ruthenium hydroxide form $\text{RuNO}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ which is thought to be rather insoluble. Its transport is hypothesized to be as very fine suspended particulates (<0.7 μm) at monitoring stations. At the source, White Oak Dam, ruthenium appears to be predominately in the soluble phase (<0.7 μm) and remains largely in solution all the way down the Tennessee River for distances greater than 100 miles. At the White Dam only 6% of the ruthenium is on suspended particulate, downstream the value fluctuates between 11 and 21% with the majority remaining in solution. Surface runoff in water can move large amounts of suspended radionuclides into White Oak Lake and the rivers downstream. Lomenick (1963) found only small amounts (<15%) of ruthenium are leached from White Oak Lake sediments by tap water and dilute acids when the pH is kept above 6.5. Lomenick hypothesized that the waste is a mixture of nitrosylruthenium hydroxide and mononitrate nitrosylruthenium. The hydroxide is believed to be retained by precipitation in the soil while the nitrate form moves unadsorbed. With time the mononitrate form is slowly converted to the immobile hydroxide form.

Dey and Pillai (1971) studied the migration of ruthenium from the fuel reprocessing plant at Trombay, India.

Subsequent to the appearance of radioactivity above background levels in some wells located near the fuel reprocessing plant detailed studies were undertaken to identify and measure the concentration of radionuclides in the well waters. The measurements indicated that radioruthenium is the most predominant radionuclide in well waters. Radioruthenium measurements in sea water, silt, and bottom sediments in the Bombay Harbor Bay indicated low levels in sea water and high concentration in sediments. The radioruthenium in sediments was limited to the discharge locale. Some benthic organisms collected in the bay from areas close to the effluent discharge locations showed high concentration factors for radioruthenium.

Gloyna et al. (1966), Gromiec and Gloyna (1973), Reynolds and Gloyna (1963) and Yousef, Kudo and Gloyna (1970) studied the adsorption-desorption of ruthenium in model flumes and field tests. RuNO and RuCl_3 dissolved in waters and injected into fresh water flumes do not become adsorbed to bottom sediments. Upon introducing kaolinite clay suspensions into the water as much as 50% of the RuNO became associated with suspended sediments which can ultimately end up in bottom deposits.

Jenne and Wahlberg (1968) examined the sediments present in White Oak Creek, Tennessee, identifying their mineralogy and determining a K_d for several elements. The K_d was determined by analyzing the radionuclide content of White Oak Creek water and sediment, and assuming that an equilibrium between the two was attained. The water contained 230 pCi $^{106}\text{Ru}/\ell$, while no measurable ^{106}Ru was found in the sediment. It was concluded that the ^{106}Ru in White Oak Creek water was not being adsorbed by the sediment.

Liebscher et al. (1961) studied the fission product contents of rain, spring, tap and surface waters. The residence time of ruthenium is much longer than Zr, Nb, and Ce. This was attributed to the ability of ruthenium to form stable soluble anion complexes.

Magno et al. (1970), investigating the radionuclides from the Nuclear Fuel Services plant in western New York that were migrating through the effluent lagooning system, estimated that 70% of the ^{106}Ru passed through the lagoon system and into nearby surface streams.

Brown (1967) gave some profiles of ^{106}Ru at disposal sites. The ^{106}Ru moved at essentially the same velocity as the ground water, with little or no soil adsorption. Radiochemical analyses of the ground water yielded a ruthenium pattern of contamination comparable to the size and shape of the tritium and technetium contamination patterns.

Raymond (1964, 1965) investigated the vertical migration and lateral spread of radionuclides beneath three Hanford waste disposal sites by using scintillation logging of nearby monitoring wells over a period of time. Ruthenium traveled at nearly the same velocity as the soil water.

Perkins et al. (1966) and Robertson et al. (1973) studied the speciation of ruthenium emanating from Hanford reactors and within the Columbia River. Downstream about 50 miles the ruthenium is observed to be distributed on particulates ($>0.3\ \mu\text{m}$) suspended in the river and in an apparent non-ionic form. The non-ionic form predominates (60 to 100%) of the total. In general the percentage of ruthenium on suspended particulates decreases from the reactor source (32%) to the river mouth (15%).

In a later study, Robertson and Perkins (1975) measured the speciation of ruthenium on cooling water emanating from N Reactor and in springs fed by the cooling water after percolation through soil. The mixture leaving the reactor is 66% particulate ($>0.3\ \mu\text{m}$), 16% cationic, 13% anionic and 5% nonionic. At the springs on the bank of the Columbia River the distribution is ~0.3% particulate, ~3% cationic, 92% anionic and 5% nonionic. More than 90% of the ruthenium is retained in the soils between the cooling trench and springs.

Summary

The fate of ruthenium in the environment is very dependent on the source. Nuclear wastes high in nitrates form non-ionic and anionic nitrate complexes which have been observed to migrate rapidly through soils. Cooling water wastes and tracer experiments with Ru(III) have shown large K_d_{Ru} or a strong tendency to adsorb. Without knowledge of the ruthenium speciation it would be difficult to predict ruthenium migration potential. Studies by Schell et al. (1980) do not show significant differences in K_d_{Ru} with type of water (fresh versus marine).

STRONTIUM

Natural Sediment and Rock Distribution

Average strontium contents of igneous and sedimentary rocks are given in Tables 8.73 and 8.74. Note that the strontium contents are often high when compared to the trace concentrations of strontium that may come in contact with them in waste solutions. Vinogradov (1959) reports the average strontium content of soils as 300 ppm. The 300 ppm present as ^{90}Sr in a waste solution would be 42.3 Ci $^{90}\text{Sr}/\ell$, for example. Limestone and other calcium-rich sediments and sedimentary rocks tend to be the highest in strontium content due to rited substitution of strontium for calcium in calcite. Strontium carbonate crystallizes in an aragonite type structure when present in sufficiently high concentrations.

TABLE 8.73. Average Strontium Content of Igneous Rocks (Turekian and Wedepohl, 1961) in ppm

<u>Ultramafic</u>	<u>Basaltic</u>	<u>Granitic</u>		<u>Syenite</u>
		<u>High Ca</u>	<u>Low Ca</u>	
1.0	465	4410	100	200

TABLE 8.74. Average Strontium Content in Sedimentary Rocks and Sediments in ppm

<u>Shale</u>	<u>Sandstone</u>	<u>Limestone</u>	<u>Pelagic</u>	
			<u>Carbonate</u>	<u>Clay</u>
300	20	610	2000	180
<u>Near Shore Sediments</u>		<u>Manganese Nodules</u>	<u>References</u>	
250		1000	Turekian and Wedepohl, 1961 Wedepohl, 1960 Riley and Senhaseni, 1958	

The four naturally-occurring isotopes of strontium include ^{84}Sr (0.55%), ^{86}Sr (9.75%), ^{87}Sr (6.96%) and ^{88}Sr (82.74%). The isotope ^{87}Sr can be

locally variable in abundance because it is a daughter of ^{87}Rb . The other isotopes of strontium between ^{80}Sr and ^{95}Sr are radioisotopes. Only ^{90}Sr fission product (half-life 28.1 years), decaying to ^{90}Y , is of sufficiently high yield and long half-life to be of concern in waste disposal operations. The radionuclides ^{88}Sr and ^{89}Sr also are obtained in high yields but the half-lives are too short to create a persistent disposal problem. The isotope ^{85}Sr (half-life 64 days) is not a fission product, and is usually not encountered except in laboratory waste solutions.

Strontium (II) is the only oxidation state to be encountered in environmental solutions. According to Ahrens (1952) the ionic radius of Sr^{+2} is 1.12 Å, very close to that of Ca^{+2} at 0.99 Å and Ba^{+2} at 1.34 Å. Strontium tends to follow calcium in weathering and other geochemical processes with some exceptions. For example, when present in sufficient concentrations, strontium does form a carbonate that is not isostructural with CaCO_3 . The other main strontium ore mineral, celestite (SrSO_4), is isostructural with its calcium counterpart, anhydrite (CaSO_4). However, limestone or calcite (CaCO_3) can allow the substitution of several hundred parts per million strontium before there is any tendency for strontianite (SrCO_3) to form. As the limestone recrystallizes, there is a tendency for the strontium content to decrease.

There is little, if any, tendency for strontium to form complexes with inorganic ligands. Izrael and Rovinskii (1970), for example, studied by electrodialysis the chemical state of strontium leached by ground water from rubble produced in a nuclear explosion. They found that 100% of the strontium was Sr^{+2} , with no colloidal or anionic strontium present in the leachate.

Solution Equilibria

Strontium is an alkaline-earth and forms several salts. Thermodynamic data for various strontium compounds, SrO , $\text{Sr}(\text{OH})_2$, SrF_2 , SrCl_2 , $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 3\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$, SrHPO_4 , $\text{Sr}_3(\text{PO}_4)_2$, SrSO_4 , $\text{Sr}(\text{NO}_3)_2$, SrCO_3 , SrSiO_3 , SrSiO_4 , SrZrO_3 were considered in order to determine their stability. Except for SrSiO_3 , SrHPO_4 , $\text{Sr}_3(\text{PO}_4)_2$, SrCO_3 , and SrSO_4 , the strontium solid phases are too soluble to show in Figure 8.35. The thermodynamic data for all of

these compounds except $\text{Sr}_3(\text{PO}_4)_2$ were obtained from Parker et al. (1971). The data for $\text{Sr}_3(\text{PO}_4)_2$ were selected from Sillen and Martell (1964). In an acidic environment, most of the strontium solids will be highly soluble, and if the activity of Sr^{2+} in solution exceeds 10^{-4} moles/l, SrSO_4 can precipitate and would be a stable phase. However, in alkaline conditions, SrCO_3 would be the stable phase and the compound that could maintain strontium activity in the aqueous environment.

FIGURE 8.35. The Relative Stability of Various Strontium Solids at $\text{pCa}^{2+} = \text{pSO}_4^{2-} = 2.5$, $\text{pH}_4\text{SiO}_4 = 3.1$, and $\text{pCO}_2(\text{g}) = 1.52$ atm in equilibrium with Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP). Redox potential has little effect on strontium solubilization.

The activity of various solution species in equilibrium with SrCO_3 and at anionic activities of $\text{pCl}^- = \text{pSO}_4^{2-} = 2.5$, $\text{pNO}_3^- = 3.0$, $\text{pF}^- = 4.5$, $\text{pH}_2\text{PO}_4^- = 5$ and $\text{pCO}_2(\text{g}) = 1.52$ atm are plotted in Figure 8.36. The thermodynamic data for SrNO_3^+ and SrPO_4^+ were obtained from Sillen and Martell (1964). All the other data were obtained from Parker et al. (1971). Although strontium forms complexes with the various anions listed above, the solution complexes do not contribute significantly to the total strontium activity in

solution. Sr^{2+} would be the dominant solution species over the environmental pH range of interest and would be expected to be adsorbed by an ion exchange reaction. Izrael et al. (1970) have indicated that strontium was likely to be 100% cationic and that the principal reaction with soils, sediments and rocks is ion exchange.

FIGURE 8.36. The Activities of Various Strontium Species in Equilibrium with $\text{SrCO}_3(\text{s})$ in the Soil at $\text{pCl} = \text{pSO}_4^{2-} = 2.5$, $\text{pNO}_3 = 3.0$, $\text{pF}^- = 4.5$, $\text{pCO}_2(\text{g}) = 1.52 \text{ atm}$ and $\text{pH}_2\text{PO}_4 = 5.0$

Laboratory Adsorption Studies

Baker et al. (1964) determined the distribution coefficients for carrier-free strontium on 17 samples of earth materials collected during July 1961 in the vicinity of Cape Thompson, northwestern Alaska. High percentage uptake was measured under the test conditions. Strontium adsorption was found to be a function of the calcium-plus-magnesium concentration and to be independent of the sodium concentration. In most samples, its equilibrium was reached in less than 1 day.

Baranov and Polikarpov (1966, 1968) studied sorption-desorption of ^{90}Sr in sea water-Black Sea sediments. Among the sediments studied, a large adsorptivity for Sr-90, Zr-95, Ru-106, Cs-137 and Ce-144 was exhibited by shallow-water silts (aleuritic silt with mussel biocoenosis and phaseoline silt). Despite differing mechanical and chemical properties, these silts have similar affinity coefficients for each isotope, an effect for which the size fraction of particles of less than 90 μ was responsible. Phaseoline silt and aleuritic silt with mussel biocoenosis most effectively adsorb Y-91, Zr-95, Cs-137, and Ce-144. Their affinity coefficients for Sr-90 and Ru-106 were low.

Collet et al. (1968) determined the distribution coefficient between river silt and river water (the ratio of the absorbed mass of the element studied per gram silt to the concentration of the same element in the water in equilibrium with the silt) in the laboratory for the elements Ce, Cs, I, P, Ru, and Sr. Altogether 756 individual samples were processed. These samples were separated by a centrifuge method into the three fractions; sand, clay, and organic material; in order to obtain conclusions on the effect of the individual constituents of the silt. The methods were outlined, the results were reported, and the fixation capacities found were related to the activity of the individual fallout nuclides present in the silt.

Duursma and co-workers [Duursma and Bosch (1970), Duursma (1972), Duursma, Parsi, Statham (1974), Duursma and Gross (1971), Duursma and Eisma (1973) and Dawson and Duursma (1974)] have performed and collected data on strontium sorption in marine environments. Strontium was usually the least adsorbed nuclide studied in their experiment with a $K_d \sim 100$ ml/g. The adsorption of Sr on various size fractions of marine sediments is unclear. In one instance all the sorption occurred on particles $< 4 \mu$ in diameter. For a second sediment the adsorption occurred randomly over 5 particle ranges between 64 and $< 4 \mu$. One experiment with a Black Sea sediment showed a 40-fold increase in K_d under anoxic conditions than oxygenated conditions. From thermodynamic considerations these results would not be expected. They do not observe high correlation between $K_{d,\text{Sr}}$ and sediment cation exchange capacity nor with calcium carbonate content. Duursma hypothesized that tracer Sr adsorption is

controlled by isotopic exchange with stable Sr. Table 8.75 shows average $K_{d_{Sr}}$ and $t-1/2$ of sorption for major oceans and seas.

TABLE 8.75. $K_{d_{Sr}}$ and $t-1/2$ Values

Sediment	log K (unitless)	est. K_d ml/g	$t-1/2$ (days)
Atlantic Ocean	2.28 ± 0.74	290	1.8 ± 1.6
Pacific Ocean	2.59 ± 0.85	580	2.5 ± 2.0
Indian Ocean	2.49 ± 0.82	465	0.8 ± 0.2
Baltic Sea	2.37 ± 1.01	350	0.4
North Sea	2.54 ± 0.76	520	3.0
Mediterranean Sea	2.54 ± 1.00	520	3.8 ± 1.7
Black Sea	2.54 ± 0.65	520	5.0
Red Sea	2.11	190	6.0

In leaching experiments of Sr contaminated Mediterranean sediments in (pH 5.4) NH_4 -acetate and in (pH 2.3) acetic acid both removed 100% of adsorbed strontium.

Gardner and Skulbert (1964) studied the adsorption of strontium on a post-glacial marine clay from a Norwegian River using low ionic strength pH 6.7 to 7.6 river water. The sediments were dried and crushed after treatment with hydrogen peroxide. Strontium chloride tracer was added to river water and distilled water and mixed with the dried sediments at various concentrations. The $K_{d_{Sr}}$ after 24 hr contact was dependent on suspended sediment concentration as follows:

<u>Clay Concentration</u>	<u>Distilled Water</u> <u>K_d</u>	<u>River Water</u> <u>K_d</u>
ppm	ml/g	ml/g
16	1600	950
32	1500	800
64	1030	800
128	820	725
256	660	660

At 64 ppm sediment a steady-state adsorption was reached after 40 min; thus, it is doubtful kinetic effects are the cause of the varying K_d .

Ganapathy et al. (1968) studied Sr uptake from seawater by Bombay, India, sediments. The K_d was very small, and they feel the major portions of reactor-released ^{90}Sr introduced into coastal waters and the ocean will likely remain in the aqueous phase.

Gawad et al. (1977) report on sorption experiments of Sr using Ismailia Canal (Egypt) sediments. The mass of Sr/g on sediment adsorbed was found to increase as the particle size distribution of the sediments decreased. For coarse particle sizes $>5\ \mu\text{m}$ changing the pH of the system from 5 to 9 caused little change in sorption. For fines, hand clay ($<5\ \mu\text{m}$) there was an observable increase in sorption as pH increased. If competing ions Na, Mg, Ca were added to the water Sr adsorption decreased with the effect being $\text{Ca} > \text{Mg} > \text{Na}$. Below a Sr concentration of $10^{-4}\ \text{M}$, exchange ($10\ \text{g}\ K_d$ versus $\log$ Sr solution) was linear. Adsorbed strontium was quantitatively removed from sediments by 0.1 N CaCl_2 or 0.1 N SrCl_2 solution after 6 days.

Jenne and Wahlberg (1968) studied Whiteoak Creek, TN, sediments in the field and laboratory and found ^{90}Sr released from Oak Ridge National Laboratory was controlled by in situ precipitation of carbonates.

Juguet et al. (1966) studied the fixation capacity of muds from various French rivers. Sr sorption was between Ce (totally fixed) and I (slightly fixed).

Kawabata (1967) examined factors affecting the sorption of various radionuclides by a river sediment sample in the fresh or saline water; in addition, release of radionuclides in the sediments when it was exposed to the sea water was studied. Water and sediment samples were collected at several places along the Sagami. Uptakes of radionuclides by the sediments were much affected by various competing cations, and the rate of inhibition depends not only on the cationic species but also concentration of cations. The higher the concentration of a competing cation, the more inhibitive to the uptake of radionuclides by river sediments. Release of radionuclides which had been sorbed by the river sediments in the filtered sea water was examined during 12 days storage.

The release of ^{90}Sr , increased for the first 2 days, then gradually decreased, which might be due to the re-absorption of the nuclide by sediments in the sea water. In river environments K_d_{Sr} was 1000 ml/g while in estuarine conditions the K_d dropped to 400.

Meeusen et al. (1975) studied the sorption capacity of Scheldt sediments for Co^{2+} , Sr^{2+} and Cs^+ and their distribution coefficients between sediment and Scheldt water. It was found that clay and silt samples show relatively high sorption capacities for cobalt and cesium, compared with the low fixation rate for strontium.

The selectivity of the sediments for a particular ion, in competition with other ions, was studied and the sequence found was in accordance with the distribution coefficients. From these experiments it may be concluded that the high salt concentrations, present in normal Scheldt water, will limit the risks of radioactive isotopes accumulation in the sediments.

Nagaya and Saiki (1967) and Nakamura and Nagaya (1975) collected 19 samples of sediment from Tokyo Bay and coastal water along Fukushima Prefecture. The HCl-extraction efficiencies of radionuclides in sediment were examined. Recoveries of more than 80% were obtained for ^{144}Ce , ^{106}Ru , and ^{137}Cs in fine mud collected in Tokyo Bay. The sampling device was designed to collect a large amount of sediment of the surface layer of 2 cm thickness. ^{90}Sr , ^{137}Cs , and ^{144}Ce concentrations in fine mud were remarkably higher than those in sandy mud or sand. It was clearly observed that ratios of $^{144}\text{Ce}/^{90}\text{Sr}$ and $^{137}\text{Cs}/^{90}\text{Sr}$ in coastal sediments were substantially higher than those in sea water. Cerium-144 and ^{137}Cs were found to be accumulated more effectively in the surface mud on the bottom of the sea, in comparison with ^{90}Sr .

The concentrations of fission products ^{90}Sr , ^{137}Cs and ^{144}Ce in the marine sediment of Tokyo Bay and of the coastal seas of Ibaraki, Fukushima and Fukui prefectures were determined during 1966 to 1972. The radioactivity ranged 0 to 23.3 pCi/kg-dry for ^{90}Sr , 5.3 to 220 pCi/kg-dry for ^{137}Cs , and 0 to 12.700 pCi/kg-dry for ^{144}Ce . Generally speaking, the ^{90}Sr level is one order of magnitude lower than that of ^{137}Cs , and ^{144}Ce concentration is higher than that of ^{90}Sr by almost two orders of magnitude. The degree of the

radionuclide enrichment in the sediment from sea water is tens for ^{90}Sr , 10^2 for ^{137}Cs and apparently horizontal distribution of ^{144}Ce concentration in the sediment of the areas, but the ^{137}Cs concentration shows fairly small horizontal fluctuation.

Ojima et al. (1965) studied the physicochemical behavior of ^{89}Sr , ^{90}Sr , ^{137}Cs , and ^{60}Co ions in relation to pH of marine water, trace elements dissolved in it, fragments of marine organisms living in it, and sea sediments.

Orlova (1965) found the distribution of ^{90}Sr in a water-bearing stratum is determined to a great extent by the salt content of ground waters. The main cations that may influence the migration of ^{90}Sr are natural strontium, calcium, manganese, and sodium. Investigations, carried out under both static and kinetic conditions, showed that the natural cations in natural water may be classified according to their capacity for decreasing the sorption of ^{90}Sr by minerals in the following order: $\text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$. The presence in the water of the most common anions (Cl^- , NO_3^- , SO_4^{2-}) had practically no effect on the sorption of ^{90}Sr by the sand. On the other hand, the anions (PO_4^{3-} , CO_3^{2-}) with which strontium and calcium form weakly soluble compounds increased the sorption of ^{90}Sr by sand and this tended to reduce the migration capacity of the isotope in the water-bearing stratum.

Puschmann (1970) examined fine-grained sediments from the Weser, Donau, and Elbe Rivers for their sorption behavior in respect to ^{85}Sr , ^{137}Cs , and ^{131}I . The experiments with closed systems give the course of the sorption and the possible sorption rate after the equilibrium has been established. The sorption rates are converted to grams of the element used per m^3 sand as used in the laboratory experiment. The results are compared with the sorption rates dealt with by Weisflog (1968), which were made with low-terrace sediments from the Rhine River.

Schell et al. (1980) report on laboratory determinations of K_d_{Sr} in numerous fresh and marine water environments with sediments. Table 8.11 summarizes the results. The K_d_{Sr} for fresh waters is considerably larger than values for seawater which suggests that ion exchange processes control Sr sorption. Of all elements studied by Schell et al., Sr shows the least affinity for sorption.

In a dialysis experiment using Lake Michigan sediment and water, Sr remains predominantly 97% in the soluble phase in compartments contacting sediment, plankton or organic detritus.

Schneider and Block (1968) and Schneider (1970) performed laboratory experiments on Rhine River sediments and pure minerals. Nuclide sorbability increases in the following order: I^- , Sr(II), Pu(IV), Zn(II), Cs(I). Saturation was reached by sediments after 24 hours at the latest for all nuclides. The sediment samples were taken from Oehningen (Upper Rhine), Koblenz (Middle Rhine), and Wesel (Lower Rhine). Data were compared with the organic content for each sample. The sorption of ^{137}Cs is dependent on grain size but not on organic material. A sudden release by living or dead organic material of radionuclides is not possible, though desorption from mineral suspended material is more rapid, often occurring within a few hours. Less than 1% of transported nuclides in the Rhine under any conceivable conditions would be bound to suspended material or sediments.

The sorptive properties of artificial mono-mineralic fine sands of uniform grain size is investigated. Montmorillonite, kaolinite, muscovite, and biotite have a high sorptive power. The sorptive power of quartz oxides and magnetite and of microcline and albite is low. Hornblende and augite occupy a medium position. The highest affinity for the minerals show the cations ^{137}Cs , ^{90}Sr , and ^{65}Zn . Phosphorus-32, as complex phosphate anion, is less highly absorbed. The sorption of ^{131}I is negligible.

Rhodes (1957) showed the effect of system pH on the adsorption of strontium from a distilled water solution by a fluviatile Hanford soil. A soil paste pH was 8.6, and the calcite content was 2 wt%. The clay fraction of less than $2\text{ }\mu\text{m}$ was 2 wt%, and consisted of primarily montmorillonite, with some mica and chlorite. The system was pH adjusted with NaOH or HCl. The strontium Kd rose from 5 ml/g at pH 6 to 30 ml/g at 8, and 120 ml/g at pH 10. Above pH 10, the sodium added in the NaOH used for pH adjustment began to compete for exchange sites with the strontium, and strontium adsorption began to level off. In 4M NaNO_3 , strontium adsorption was much less affected by pH. At pH 8, for example, strontium Kd was about 5 ml/g and rose to about 10 ml/g at pH 10.

Prout (1958, 1959) showed the effects of pH and strontium concentration on strontium adsorption by Savannah River soil. This soil was 80% sand and 20% clay, chiefly kaolinite. The results were very similar to those of Rhodes (1957) in that a maximum was much higher ($K_d = 700$ to 800 ml/g). The effects of competing cations including several sodium nitrate concentrations were also given. The 30% NaNO_3 solution is about the same as Rhodes (1957) 4M NaNO_3 solution, and the results also are comparable in strontium distribution coefficients. The amount of competing sodium is apparently so high that the soil differences are of lesser importance.

Spitsyn and Gromov (1958) showed that the adsorption of strontium by montmorillonite was an ion exchange process. Various competing cations were added to the strontium-clay system and the strontium distribution coefficient redetermined. These authors also added small amounts of anions such as CO_3^{2-} and $\text{C}_2\text{O}_4^{2-}$ that were said to form radiocolloids with strontium. They believed the enhanced removal of strontium reported by McHenry (1955), when 3×10^{-5} to 3×10^{-4} M PO_4 was added to wastes contacting calcareous soils, could be attributed to the formation of precipitates as a result of the natural calcium on soil exchange sites reacting with the added phosphate ions. This may be true at some phosphate concentrations, but later study also demonstrated a replacement reaction (Ames, 1959) where calcite reacted with the phosphate to form an apatite.

Baker and Beetem (1961) studied the distribution coefficients for carrier-free strontium on an Alaskan wind-blown silt with various concentrations of competing cations which were to be expected at the site. One or two of the K_d values exceed the experimental limits by large amounts, but the remaining values conform to a straight line plot of strontium K_d versus the inverse sum of the competing calcium and magnesium concentration as required by ion exchange theory (Kaufman, 1963).

Cohen and Gailledreau (1961) investigated strontium adsorption on Saclay soil consisting of 45% montmorillonite, 45% kaolinite and 10% illite. The cation exchange capacity was 210 meq/100 g. Graphs were presented of trace strontium-macrocalcium, trace strontium-macrosodium and trace strontium-macropotassium systems. Some work was performed on three-component ion

exchange systems. It was shown that the K_d values plotted versus the strontium concentration for the above Saclay soil yielded a straight line on log scales as required by ion exchange theory.

Kokotov et al. (1961, 1962) gave K_d values for strontium on six Russian soil types as a function of pH. The replacement series $Sr > Cs > Mg > K \geq NH_4 > Na$ was given for strontium competing cation efficiency.

Carlile and Hajek (1967) reported an example of physical transport of strontium. About 0.1% of the ^{85}Sr was found in the first effluent from N-Area soil columns (2 cm diameter by 40 cm in length). Up to 1% random leakage of strontium was reported until 5 column volumes of Columbia River water had passed through the soil. Then leakage fell to below detection limits ($10^{-3}\%$). Columbia River water has an annual mean pH of about 7.8, a mean $CaCO_3$ hardness of 69 mg/l and a mean total dissolved solids of 119 mg/l. Effluent samples were centrifuged at high speeds, treated with H_2O_2 to destroy organic material and recentrifuged. Fifty to 75% of the activity in the leaked effluent was removed. Hydrogen peroxide treatment did not affect removal of strontium by centrifugation, indicating that an organic material was not involved. Leaching a soil system with low ionic strength river water containing trace radionuclides had the result of dispersing the soil colloids on which much of the ^{85}Sr were adsorbed. Column breakthrough was immediate until the dispersed colloids were flushed from the column. Preceding the contaminated river water by a preleach of noncontaminated river water flushed the dispersed colloids and prepared the soil for use. Adding other ions to the system could have accomplished the same thing, but would have competed with adsorption of strontium. Several investigators have studied the interactions of strontium and organic matter. Bovard et al. (1968) found low complexing tendency for Sr with humic and fulvic acids. The complexing order for humic acids was $Ce > Fe > Mn > Co \geq Ru \geq Sr > Cs$. Dunigan and Francis (1972) also found the humic acid-strontium interaction to be weak. Essington and Nishita (1966) and Nishita and Essington (1967) studied the ability of distilled water, irrigation water and the chelating agents (EDTA, DTPA, EDDHA) to leach Sr from soils. Chelating agents did not improve the leaching of Sr sorbed to soil over the waters suggesting little organic interaction.

Four soils varying greatly in organic matter content, cation exchange capacity and texture were studied by Juo and Barber (1970) for their strontium retention characteristics. The adsorption of strontium by soils increased with increasing pH within the pH range 4 to 8. Saturating cations had some effect on strontium adsorption, with influence in the order $\text{Na} > \text{K} > \text{Mg} > \text{Ca} > \text{Ba} > \text{H}$. As the pH increased, an increasing fraction of the adsorbed strontium became nonexchangeable with ammonium acetate. The nonexchangeable portion of the strontium is probably tied up by soil organics and is permanently fixed under favorable pH conditions. In a higher pH environment, a larger portion of the strontium in solution was present as soluble strontium chelates or complexes.

Chelation and movement of strontium in a calcareous soil were evaluated in columns of Mohave sandy loam soil [L'Annunziata and Fuller (1968) and Fuller and L'Annunziata (1969)]. The displacement of ^{89}Sr from the soil columns was 19, 38, 44, 47, and 81% in the order $\text{HEEDTA} < \text{DCyTA} < \text{EDTA} < \text{EGTA} \leq \text{DTPA}$. Only 5% of the ^{89}Sr was removed from the soil with no complexing agents in the leaching solution. The radiostrontium existed in the leachate as a negative complex. Any natural organic chelating agents in the soil did not influence radiostrontium movement.

Mortensen and Marcusiu (1963) incubated a silty clay loam with 40 μCi ^{90}Sr for 60 days and obtained hot water extractions or hydrolyzed with 6N HCl. The supernatant liquid was electrodialyzed with ^{90}Sr migrating to the anode compartment suggesting negatively charged ^{90}Sr -organic matter complexes. Gel filtration showed that ^{90}Sr was complexed or held on exchange sites by high molecular weight polymers. The radioactivity correlated with the presents of polyuronides. Phenols, amino acids and keto acids were separated from the 6N HCl hydrolysate by paper electrophoresis, with no clear correlation between radioactivity and these components.

Mortensen et al. (1963) studied surface organic layers of ten soils for their ability to adsorb strontium. It is apparent that the soils studied, especially those having high exchange capacity and base status, are capable of adsorbing considerable quantities of ^{90}Sr (^{90}Y). Leaching waters from the

more acidic soils release strontium more readily into the drainage waters than in the case of less acid soils. The leaching of fallout Sr from acidic organic soils may occur in a relatively short period of time. Fission product ecology in soils of the area is apparently governed largely by pH and cation exchange.

Szalay and Szilagyi (1964) studied the retention of fission products by humic acids present in peat. Strontium is strongly adsorbed by the peat.

Field Studies

Bowen and others [Bowen (1970), Bowen, Wong and Noshkin (1971), Bowen et al. (1974), Noshkin (1972), Noshkin and Bowen (1973) and Volchok et al. (1971)] have determined the concentrations of fallout ^{90}Sr in ocean sediments and waters. There exist on nonuniformity in surface water ^{90}Sr concentrations which are not understood. Depth profiles down to 700 m in the Atlantic and Pacific show regular decreases. Typical surface concentrations range from 0.1 to 1.5 pCi/l ^{90}Sr . By 1970 only 1% of the total ^{90}Sr delivered to the ocean surface by fallout was adsorbed by bottom sediments using the residence-time concept, ^{90}Sr residence time is about 1×10^3 years, which is at least an order of magnitude less than calculations on stable Sr in land runoff. A possible mechanism, settling of suspended particulates, needs further study.

Brungs (1963, 1964) studied the fate of ^{85}Sr in a 30,000-gal experimental pond with sand substrate, and containing experimental biota. The conditions were comparable to those in an accidental release of radionuclides to an impoundment. Sampling from the pond continued for 80 days. The quantities of radionuclides were determined with a gamma-scintillation spectrometer. Supplemental chemical and biological information on the artificial pond and an adjacent control pond provided a measure of the differences between these two environments.

Of the four radioelements studied, Sr, Co, Cs, Zn, more Sr remained in solution (23% versus <1%) after 80 days. The mass balance of Sr after 80 days was dissolved 23%, adsorbed in sediment 76.5%, incorporated into biota 0.40% and on suspended solids 0.1%. A field Kd for the bottom sediment of 17 to

25 ml/g and for suspended solids 270 ml/g can be calculated from Brung's data. The chemical composition of the pond water was in mg/l: Ca(24), Mg(22), Fe(0.12), Mn(0.06), SO_4 (31), Cl(8) and total hardness (150).

Cerrai et al. (1965, 1967, 1970) measured in fallout concentration of ^{90}Sr in marine sediments and performed some laboratory sorption experiments (1969). The ^{90}Sr content of dried sediment decreased with depth from 0.04 to 0.002 pCi/g between the surface and 40 cm. There was also no large increase in ^{90}Sr concentration on finer size fractions <100 μm versus >100 μm .

Laboratory experiments on Ligurian Sea sediments (200 mg/40 ml traced sea water) were performed for contact times of 1 to 15 hours. At a solids to solution ratio of 100 mg/40 ml after 1 hour $Kd_{Sr} = 6.3$, after 15 hours $Kd_{Sr} = 11.1$ ml/g. Distilled water, macro Sr carrier and Ca sorption experiments proved that the low Kd for Sr was caused by ion exchange competition of alkali and alkaline earth salts.

Dupont (1965) evaluated $^{89,90}Sr$ in water at two locations along the Lower Three Runs Creek, which indirectly receives radioactive material discharged during the operation of the R reactor at Savannah River. These data show that the stream bed acted as an ion exchange system.

Flume, field and laboratory studies of strontium migration have been performed by Gloyna and co-workers at University of Texas. [Clanton (1968), Gloyna et al. (1966, 1971), Gromec and Gloyna (1973), Mahmoud et al. (1968, 1973), Purushothaman (1968, 1971), Purushothaman and Gloyna (1968), Reynolds (1963), Reynolds and Gloyna (1963), Shih and Gloyna (1968), and Yousef et al. (1970).]

In a model flume under riverine conditions a Kd_{Sr} of 85 was obtained for sediment and 600 ml/g for rooted plants. Typically Sr uptake by sediments followed a Freundlich sorption isotherm. When Sr and Cs soluble spikes were added simultaneously with suspended clays they found Sr tended to remain in solution while Cs became much more rapidly bound to the clay. In other experiments as the river water mixed with the brackish San Antonio Bay water some of the Sr and Cs were transferred from the sediments and suspensoids to the saline

water. It was also shown that sediments present in marine waters sorbed less strontium and cesium than sediments in fresh water. The distribution of ^{90}Sr and radiocesium in the lake sediments was dependent upon the grain size. The smaller the grain size the greater the radionuclide content. This suggests ion exchange is controlling Sr adsorption in the aqueous environment.

Lerman (1971), Lerman and Taniguchi (1971, 1972) and Lerman and Lietzke (1975) have constructed models based on field studies and a few experimental sorption studies which describe the distribution of natural fallout ^{90}Sr . Penetration depth of ^{90}Sr in deep-water sediments of Lake Superior and Lake Ontario was 8 to 10 cm by 1969. A detailed picture of the ^{90}Sr -containing layer indicates that the main mechanisms of transport from lake water into sediment are diffusion of ^{90}Sr in interstitial water, and uptake of ^{90}Sr by solid phases in sediment. A diffusional transport model, with diffusion coefficient $D = 2 \times 10^{-6} - 6 \times 10^{-6} \text{ cm}^2, \text{ sec}^{-1}$ and distribution factor $K_d = 30 - 30$ in favor of solids, gives ^{90}Sr concentrations in sediment comparable with observed values. Intensity of diffusional flux into sediment increases with greater uptake by solids (larger values of K). In Lake Ontario, flux into sediment has been removing ^{90}Sr from lake water at the rate of 0.2 to 0.5% per year, during the period 1954 to 1969. The slowness of flux compared with the rate of ^{90}Sr in lake outflow (12% per yr) accounts for the small amount accumulated in sediments (4 to 6% of Sr in lake water) and for the lack of noticeable control of concentrations in lake water by floor sediments. Adsorption of the two tracers by sediment particles, supported by experimental data, can be treated as a linear exchange reaction. ^{90}Sr is adsorbed less strongly than ^{137}Cs by sediments, and this feature accounts for the greater depths of ^{90}Sr occurrence in lake sediments.

Montgomery et al. (1977) surveyed the transport of ^{90}Sr from the Maxey Flats, KY, nuclear burial ground through surface and stream water. The principal radionuclides detected in off-site surface water samples were ^3H and ^{90}Sr . The highest ^3H concentration was 179,000 pCi/l in water from a wash on the west side of the site, outside the exclusion area (i.e., unrestricted area). This corresponds to 6% of the maximum permissible concentration (MPC)

for ^3H in water discharged to unrestricted areas. The highest ^{90}Sr concentration was 80 pCi/ in the Main East Wash, corresponding to 27% of the MPC for ^{90}Sr in water. The ^3H and ^{90}Sr levels in Rock Lick Creek were lower than in the primary drainage pathways; the highest concentrations were 4700 pCi/l and 5.8 pCi/l, respectively. The major aqueous pathways for radionuclides moving from the site were the Main East Wash and the wash on the west side of the site. The principal vehicle of transport appeared to be precipitation run-off from the surface of the burial site. Contamination of the site surface could have resulted from a number of sources, including lateral migration through the soil zone from the trenches to the land surface, spills during burial and trench pumping operations, and deposition from the evaporator plume. However, the relative contribution from these sources could not be determined. Deposition of radionuclides from the evaporator plume, especially ^3H , could be a major source of radioactivity observed in surface water, but additional studies would be necessary to evaluate its significance.

Radionuclides detected in stream bed sediment included ^{54}Mn , ^{60}Co , ^{90}Sr , ^{137}Cs , ^{238}Pu and ^{239}Pu . The highest concentrations were in samples from the Main East Wash which is the major drainage pathway for the burial site. The sediment data supported the conclusion, based on surface water measurements, that the transport of radionuclides from the site surface by suspended solids precipitation run-off was a major source of the radioactivity detected in the drainage pathways.

Nevissi et al. (1975), Noshkin et al. (1974, 1975) studied the distribution of ^{90}Sr in the Enewetak and Bikini Atolls after bomb testing. Up to 371 pCi/g soil of ^{90}Sr are reported for surface soils on Bikini Atoll while well water samples contained from 0.01 to 19 pCi/l, depending on location. Pacific Ocean waters (unfiltered) contained 0.07 to 0.15 pCi/l. Unfiltered Enewetak lagoon waters ranged from 0.09 to 1.07 pCi/l ^{90}Sr while water directly in bomb craters ranged from 0.1 to 48 pCi/l. Filtered (1 μm) lagoon and crater water from Bikini Atoll contained 0.3 to 1.7 pCi/l ^{90}Sr . The average concentrations for surface waters are Enewetak 0.3, Bikini 0.6, and north equatorial Pacific 0.07 pCi/l.

Ophel, Fraser and Judd (1972) and Ophel (1973) have studied the cycling of ^{90}Sr in a fresh water lake. The strontium content of bottom sediments is strongly correlated with the amount of organic matter they contain. The specific activity of the strontium ($\text{dpm } ^{90}\text{Sr}/\mu\text{g}$) appears to be uniform throughout the water and the lake biota, i.e., biological availability of the stable isotope and radioisotope is the same. In the upper 10 cm of bottom sediments, however, specific activity of the exchangeable strontium and of total strontium is only half that in biota and water indicating incomplete exchange of radio-nuclide and stable element in this layer even after 15 years of exposure.

Rovinskii (1967) studied the migration of ^{90}Sr in lake waters by determining the content of ^{90}Sr , stable Sr^{2+} , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} ions both in waters of 13 lakes and in the lake bed grounds. The migration of ^{90}Sr in stagnant waters is attributed to the ion-exchange reaction between the water and the lake bed ground. The redistribution of ^{90}Sr in the lakes proceeds mainly by ion-exchange reactions with Ca^{2+} . Equations for predicting the level of contamination of lake waters by ^{90}Sr were derived. Comparable results were also obtained under laboratory conditions using synthetic lake water samples.

Ruf (1968) found the artificial radioactivity of fresh water in Bavaria differed in the years between 1957 and 1966 within a range of less than $1 \mu\text{Ci}/\text{l}$ up to $140 \mu\text{Ci}/\text{l}$. The water activity showed a direct dependence on the activity of rain, and the effects of nuclear power plants. Radioactivity in surface waters was caused by typical fallout products such as: ^{90}Sr , ^{89}Sr , ^{137}Cs , ^{103}Ru , ^{106}Ru , ^{141}Ce , ^{144}Ce , ^{95}Zr , ^{95}Nb , ^{54}Mn , ^{125}Sb . Since the 237-MW-KRB-reactor Gundremmingen reached its full capacity in November 1966, more waste has been passed into the River Danube. So radioactivity corrosion products (Co-, Fe-, Mn- and Cr-isotopes) of low concentrations could be analyzed besides fission products (especially I-131). Radioactive substances were, to a large extent, concentrated in the sludge of river dams, in consequence of the increased sedimentation of seston particles. In this case the ^{137}Cs and ^{144}Ce activity reached a 12- to 15,000 fold concentration of the water activity. In different fish of the River Isar and Danube a ^{137}Cs activity 3,000 times higher than water activity was found.

Safronova (1974) found a previously proposed diffusion model of the self-purification of natural water as a result of the absorption of ^{90}Sr by the bottom deposits agrees with the experimental data on the kinetics of the change in the concentration of ^{90}Sr in the water of an experimental lake. Together with the diffusion mechanism of self-purification, a factor of self-purification that can be considered within the framework of the model operates in the lake. Simple computation formulas for the dependence of the concentration of ^{90}Sr in the water on the time were obtained, permitting a long-range prognosis for the experimental lake.

Tritrenmel et al. (1966) studied the behavior of various radionuclides in surface water by field experiments in the Leitha-Mühl Canal and by complementary experiments in the laboratory. The boundary and profile characteristics of the stream were ascertained and flow rate calculated. Suspensions were examined for size and mineral or organic content in relation to current velocities, and core samples were collected from the bed at selected regions of deposition. Experiments were carried out on dispersion and transport of wastes under varying outlet conditions and the diffusion constant was measured. In the laboratory, sedimentation and uptake experiments were conducted on mineral and organic suspensions in conjunction with nuclides such as ^{90}Sr , ^{131}I , ^{140}La , ^{24}Na and mixed-fission products. Uptake was found to be dependent on mineral species and varied inversely with particle size. Elution experiments were also carried out on accumulated sediments. From these results it is possible to assess the radioactive content and frequency of batch discharges of effluents that may be released to a river without causing unacceptably high concentrations.

The unitless K sorption of Sr versus particle size was:

grain size	K
<15	500
30	65
56	40
75 to 150	15
150 to 500	8

Sorption was complete after 15 minutes whereas desorption of Sr into clean river water continued longer than 1 hour. Wahlgren and Nelson (1973) and Wahlgren and Marshall (1974) measured fallout ^{90}Sr in the water column of Lake Michigan and bottom sediments during studies on Pu cycling.

Many field studies and a few laboratory studies have been performed to determine the transport of ^{90}Sr from Oak Ridge National Laboratory disposal grounds to the surface discharges in White Oak Creek, Clinch and Tennessee Rivers.

Duguid (1974a, 1974b, 1975, 1976 and 1977) reports on the groundwater transport of ^{90}Sr from burial ground to White Oak Creek. One to two curies of ^{90}Sr are leaving the burial trenches with groundwater flow each year.

The $K_{d_{\text{Sr}}}$ is very sensitive to pH, leading Duguid to hypothesize sorption by hydrous oxides is important. Contaminated groundwaters with ^{90}Sr concentrations as high as 6.4 pCi/ml have been recorded. Soils with ^{90}Sr concentrations as high as 810 pCi/g yield an estimate field $K_{d_{\text{Sr}}}$ of 100 to 150 ml/g.

Carrigan (1968, 1969), Carrigan et al. (1967), Morton (1961), Nelson et al. (1961), Pickering (1969, 1970) and Pickering et al. (1965, 1966) report on the fate of ^{90}Sr once it reaches White Oak Creek, Clinch and Tennessee Rivers. Most all >99% of the Sr entering the Clinch River remain soluble and are washed from the area. The sediments contain on the average 1.6 to 3.0 pCi/g of ^{90}Sr . Less than 5% of the ^{90}Sr in water samples resides on suspended matter. Bottom sediment and standard clay sorption experiments show the $K_{d_{\text{Sr}}}$ to be a function of pH and contact time. The Clinch River sediment contained 60% illite, 15% kaolinite, 10 to 15% vermiculite, and 10 to 15% quartz.

After 7 days the $K_{d_{\text{Sr}}}$ for the river sediment appears higher than one would expect assuming additive portions based on the mineral distributions. Sorathesn et al. (1960) obtained some strontium distribution coefficients on Clinch River sediments that were in the ten thousands, much higher than for standard clays equilibrated with the same solution. The difference was thought to be due to the organic material in the river sediment.

Studies of the specific activity in clams shows that ^{90}Sr released to a surface water stream moves downstream in solution and there is little or no ionic exchange between the strontium in solution and that in the bottom sediments.

Average Kd of Strontium-85 Sorbed by Clays

<u>Material</u>	<u>Contact Time</u>	<u>Average Kd</u>		<u>Ratio of Clay to Master Solution</u>
		<u>pH 6</u>	<u>pH 9</u>	
Illite	1 hr	310	320	0.1 g/100 ml
	3 days	360	700	
	7 days	370	760	
Kaolinite	1 hr	3400	5000	0.1 g/200 ml
	3 days	4200	4400	
	7 days	4000	3900	
Montmorillonite	1 hr	2400	2600	0.1 g/100 ml
	3 days	4200	4400	
	7 days	2100	2200	
Vermiculite	1 hr	170	100	1 g/50 ml
	2 days	1600	1400	
	8 days	1800	3900	
River Sediment	1 hr	540	660	0.1 g/200 ml
	3 days	1700	3500	
	7 days	1400	4000	

Contaminated bottom sediments release 11% of the ^{90}Sr when sog (dry) are contacted with 400 ml of solution for 24 hours. If the water is acidified to pH 2 80 to 90% of the Sr is released. Salt solutions (0.1 to 1 M) of Ca, K, Na chloride also remove 40 to 70% of the absorbed ^{90}Sr . Calcium is most effective followed by K then Na.

The migration of ^{90}Sr as seepage from Oak Ridge burial pits was investigated by Lomenick et al. (1967). They reported that most of the strontium on the side walls and bottom of the pit in Conasauga shale was tied up in the precipitated calcite (calcium carbonate). Water moved 0.15 m/day while the ^{90}Sr moved 0.24 m/yr.

Magno et al. (1970) investigated the migration of strontium through the effluent lagooning system of the Nuclear Fuel Services plant in western New York State. They estimated on the basis of analyses that approximately 90% of the ^{90}Sr passed through the lagoon system and into nearby surface streams. Further, only 12% of the ^{90}Sr discharged from the lagoon system was associated with suspended solids. Thus 78% of the ^{90}Sr discharged from the lagoon system was in solution. The low adsorption of ^{90}Sr was apparently due to a combination of pH and competing cations lower ion exchange loading of solids. For example, when the plant effluent pH was 11 during one sampling period, 75% of the ^{90}Sr was removed in the lagoon system. At another sampling period, plant effluent was pH 7 and only 10% of the ^{90}Sr was removed by the lagoon system.

Summary

Most of the strontium chemical compounds for which data are available are very soluble. Only in highly alkaline environments could SrCO_3 control strontium activity in solutions. Strontium in solution is expected to be predominantly present as Sr^{2+} and to be exchangeable on sediments. Laboratory studies show that ion exchange is the principal mechanism of strontium adsorption by soils and rocks sediments. Strontium K_d values are usually directly correlated with cation exchange capacity of the sediment, but not invariably Duursma (1973). A direct correlation between solution pH and strontium K_d has also been reported (Rhodes, 1957; Prout, 1958, 1959; Juo and Barber, 1970), which suggests hydrogen ion competition with Sr^{2+} for exchange sites. Strontium K_d values fall rapidly from 100 to 200 ml/g or more in low ionic strength salt solutions to less than 5 ml/g in high ionic strength salt solutions. Strontium and calcium most readily replace trace strontium (Kokotov et al., 1961, 1962) and cause strontium radioisotopes to migrate rapidly when present in ground

water with the strontium. Low pH also results in a relatively high strontium migration velocity in ground water (Parsons, 1953; Baetsle et al., 1964) with the strontium and ground-water velocity identical at pH 3. Calcium competition is the probable cause of the 90% soluble strontium migration from the lagoons of the Nuclear Fuel Services plant (Magno et al., 1970); although strontium also migrates on soil particulates (Carlile and Hajek, 1967). The many strontium Kd values determined demonstrate that secondary minerals, such as clays and zeolites, are much better strontium adsorbers, and are more selective for strontium from solutions containing strontium and calcium than are the primary minerals, such as quartz, feldspars and pyroxenes. Another mechanism for strontium removal from solution is its coprecipitation with calcite (Jenne and Wahlberg, 1968). Weak strontium organic complexes are known and result in a measure of strontium fixation (Mortensen and Marcusiu, 1963). The tendency for soluble organic complexation is low.

TECHNETIUM

Natural Sediment and Rock Distributions

There are no published values for technetium in aquatic sediments. According to Boyd and Larson (1956), technetium occurs in most abundance in molybdenite (MoS_2), a common molybdenum ore, as shown in Table 8.76. The technetium content of all materials except pitchblende is of secondary origin, formed by the action of cosmic radiation on molybdenum, ruthenium or niobium. The ^{99}Tc in pitchblende is a product of ^{238}U spontaneous fissioning. Not everyone accepts the existence of the natural ^{99}Tc as having been proven (see Handbook of Chemistry and Physics, 57th Edition, p. B-50).

TABLE 8.76. Technetium Content of Some Natural Materials
(Boyd and Larson, 1956)

Material	Tc, g/kg	Determination Method
Molybdenite, Climax, CO	$<4 \times 10^{-10}$	Spectroscopic
Molybdenite, NV	$<1.5 \times 10^{-9}$	Spectroscopic
Molybdenite, Miami, AZ	$<1.8 \times 10^{-7}$ 8.3×10^{-11} , 1.3×10^{-11}	Activation
Molybdenite, NV	1.3×10^{-10}	Activation
Osmium-iridium concentrate	$<1.6 \times 10^{-8}$	Spectroscopic
Yttriotantalite, West Africa	$<6 \times 10^{-11}$	Mass Spectroscopic
Iron-nickel Meteorite	$<4.5 \times 10^{-10}$	Spectroscopic
K ReO_4 , pure	$<8 \times 10^{-9}$	Spectroscopic
Pitchblende (~50 uranium)	$2.5 \times 10^{10} \text{ } ^{99}\text{Tc}$	

Brief Chemistry

There are 16 isotopes and 6 isomers of technetium presently known (Lavrukhina and Pozdnyakov, 1970). Several technetium isotopes are obtained by the fissioning of nuclear fuels of uranium in the reactor. The fission product technetium isotopes and their yields include: ^{99}Tc , 6.06%; ^{101}Tc , 5.6%; ^{102}Tc , 4.3%; ^{103}Tc , 3.0%; ^{104}Tc , 1.8%; ^{105}Tc , 0.9%; ^{107}Tc , 0.19% (Katcoff, 1958). According to Boyd (1959), the technetium content of first cycle Purex waste is 41 mg/l. Of the several fission product technetium isotopes, only ^{99}Tc is long half-lived (2.12×10^5 years), and hence is a potential hazard.

Technetium exists in valence states from (VII) to (-I). The most stable state in aqueous solutions is heptavalent, usually corresponding to the TcO_4^- (pertechnetate) ion, with other valences encountered chiefly in complex compounds. The ionic radius of Tc^{+7} is 0.56 Å, while its geochemical relative, Re^{+7} , is 0.46 Å. The corresponding radius of the solvated TcO_4^- ion is 4.6 Å (Smith et al., 1953). In weakly acid, neutral and alkaline solutions, Tc(IV) , the second most stable state of technetium, is oxidized by atmospheric oxygen to Tc(VII) . The solubility of KTcO_4 in water at 20°C is 21.3 g/l (Busey and Larson, 1958). Technetium (IV) and Tc(V) form halogen complexes such as $(\text{TcCl}_6)^{-2}$, and Tc(II) , (III) and (V) form diarsine complexes and cyanide complexes.

Solution Equilibria

Baes and Mesmer (1976) reported that technetium (VII) forms strong peracids (HMO_4), and that its oxides are very soluble. No information is available concerning the soluble complexes of technetium or the solubility of its salts (Pourbaix, 1966). Pertechnetate ion, TcO_4^- , is the most stable species of the element in aqueous solutions (Boyd, 1959). Under extremely reducing conditions Tc^{2+} may be the predominant solution species (Pourbaix, 1966).

Laboratory Adsorption Results

Gromov and Spitsyn (1974) and Gromov (1975) investigate the adsorption of microamounts of ^{99}Tc by Pacific Ocean sediments red clay, carbonates, diatomaceous ooze. Technetium was not absorbed to any significant degree. It appeared that the TcO_4^- added was stable in sea water. Contaminated sediments were used in desorption experiments in fresh water.

Spitsyn et al. (1969) showed that 2 mg/l TcO_4^- could be added to sea water between the pH's 2 and 8 without any observable precipitation or colloid formation $>0.1 \mu\text{m}$. Even after 30 days the TcO_4^- was not filterable.

Wildung et al. (1975) used a batch equilibrium technique to determine pertechnetate ion adsorption on soils. The range of the 22 soil type properties used in the study are given in Table 8.77. The K_d values for pertechnetate

TABLE 8.77. Range of Properties of 22 Surface Soils Used in the Pertechmetate Adsorption Studies (Wildung et al., 1975)

Cation Exchange Capacity, meq/100 g	Soil Paste pH	Contents, wt%				
		Carbonate	Organic Carbon	Sand	Silt	Clay
5.5 - 90.0	3.6 - 8.9	0 - 6.5	0.23-28.8	14.1-73.1	17.6-58.0	38-46.6

ranged from 0.007 to 2.8. The K_d values were positively correlated with soil organic carbon content and negatively correlated with soil pH. The positive charge on soil organic colloids is probably an important factor in technetium adsorption by soils. The soil carbon-pertechmetate ion removal correlation was the only one significant at the 1% confidence level. Cation exchange capacity-pertechmetate ion removal also was positively correlated but at a 5% confidence level. Negatively correlated at the 5% confidence level was pH-pertechmetate ion removal, probably because as pH decreases, positive charge increases with decreased ionization of acidic groups of soil organic colloids and increased protonation of basic groups. A regression equation was given for pertechmetate distribution coefficient determination within the range of significant independent variables. This was $Y_1 = 0.08X_3 - 0.09X_4$, where Y_1 is the pertechmetate distribution coefficient (based on the ranges shown in Table 8.77), X_3 is the soil organic carbon content and X_4 is the soil-solution pH. The soil silt content (X_1) and clay content (X_2) correlations with K_d were not statistically significant at the 5% confidence level and did not, therefore, appear in the regression equation.

Gast (1975) studied several Minnesota soils and their abilities to adsorb percertechmetate ions. The soil characteristics are outlined in Table 8.78. From 2 to 5 weeks of contact time between soil and solution were required for equilibrium to be established. Nicollet C and Zimmerman soils, both low in organic carbon content, adsorbed very little ^{99}Tc , while up to 98% of the technetium was adsorbed from solution by the remaining soils corresponding to a ^{99}Tc K_d value of 857.5 ml/g. When the organic carbon was removed by

hydrogen peroxide treatment from two soils originally high in carbon content, the adsorption of technetium was greatly reduced.

TABLE 8.78. Properties of Soils Used in Technetium Adsorption Studies (Gast, 1975)

Soil	wt%			pH, H ₂ O	Organic C, wt%	CaCO ₃ , wt%	% Fe ₂ O ₃	CEC, meq/100 g
	Sand	Silt	Clay					
Bearden	9.1	63.7	27.2	7.68	5.39	16.29	0.09	16.9
Hegne	1.9	37.6	60.5	8.00	2.20	12.79	0.29	36.1
Hibbing	3.3	79.5	17.2	5.48	2.29	---	1.40	11.3
Nicollet A	24.4	42.9	29.7	5.91	2.39	---	0.86	19.3
Nicollet C	23.9	48.6	27.5	8.40	0.12	15.21	1.35	15.7
Omega	61.5	30.7	7.9	7.87	1.26	1.21	1.20	6.0
Bergland	14.0	25.1	60.9	6.35	5.67	---	2.39	32.3
Arveson	47.1	24.6	28.3	7.70	2.80	15.58	0.21	14.9
Waukegan	10.0	69.2	20.7	6.25	2.36	---	1.03	15.1
Zimmerman	69.4	24.9	5.7	5.74	0.80	---	0.47	2.7
Peat	---	---	---	7.83	45.95	7.58	0.40	50.9

Gast also mentioned that anaerobic conditions prevailed in the soil-solution environment which may have led to the precipitation of technetium heptasulfide, rather than technetium removal by adsorption processes.

Routson et al. (1976, 1977) determined distribution coefficients on technetium with Washington and South Carolina soils. Soil properties are given in Table 8.79. The organic carbon content was not given. The technetium K_d values obtained were very low, as seen in Table 8.80, when competing bicarbonate ions were present in the system. All K_d values were essentially zero.

TABLE 8.79. Properties of Soil Samples (Routson et al., 1977)

Soil	CaCO ₃ , mg/g	wt%		CEC, meq/100 g	pH, H ₂ O
		Silt	Clay		
Washington	0.8	10.1	0.5	4.9	7.0
South Carolina	0.2	3.6	37.2	2.5	5.1

TABLE 8.80. Technetium Kd as a Function of NaHCO₃ Concentration for a South Carolina Soil Characterized in Table 8.79 (Routson et al., 1977)

<u>NaHCO₃, M</u>	<u>Average Kd, ml/g</u>
0.002	0.019 ± 0.06
0.008	0.0 ± 0.01
0.020	0.0 ± 0.01
0.200	0.010 ± 0.04

Field Studies

There are no field studies of technetium migration in rivers, lakes or oceans. Brown (1967) traced the movement of technetium discharged to the ground near the chemical separations plant at Hanford via an extensive network of monitoring wells. Based on analytical results, a map of the contamination pattern at the surface of the ground water was given for 1966 at limits defined by the 0.01 pCi ⁹⁹Tc/cm³ isoconcentration contour. The contamination pattern was very similar in shape and size to that for tritium. Technetium-99 was reported to be moving at essentially the same rate as the ground water, and was detectable in the ground water at below public drinking water limits all the way to the Columbia River.

Summary

Pertechnetate ion, TcO₄⁻, is the most stable species of technetium in aqueous solutions (Boyd, 1959). A major portion of the ion exchange capacity of soils and sediments is cation exchange capacity at the usual near-neutral pH conditions. Therefore, a negatively charged TcO₄⁻ would hardly be exchanged, and hence show little adsorption by soils and rocks (Routson et al., 1976, 1977). Gast (1975) reported high Kd values (800 to 900) for soils with high organic matter. He also reported the presence of H₂S in his equilibrating samples, and suggested that the high Kd values were due to precipitation of technetium as Tc₂S₇ in the presence of H₂S or another reduced form such as TcO₂ (Kotegov, 1968). In conditions where the soil

contains appreciable organic matter, the Tc(VII) may be reduced to Tc(IV) or Tc(II) and adsorbed (Wildung et al., 1975). Tc(IV) can coprecipitate with ferric hydroxide (Anders, 1960). Hence, technetium Kd values of close to zero would normally be encountered in oxidizing conditions and in sediments that are relatively low in organic matter. More study is required to determine the nature of the organic matter-pertechnetate ion reaction, and the influence of redox conditions on adsorption of technetium by sediments.

THORIUM

Natural Sediment and Rock Distributions

The content of thorium in rocks and sediments is given in Table 8.81. The thorium in sedimentary rocks may be due either to the selective adsorption of thorium on clays or its retention in heavy resistate minerals such as monazite. Concentrations of thorium in metamorphic rocks are highly variable. The thorium content of igneous rocks increases from basalts to granites.

TABLE 8.81. Thorium Content of Common Rocks and Sediments

<u>Rock</u>	<u>Thorium Average or Range, ppm</u>	<u>Reference</u>
<u>Igneous Rocks</u>		
Granites	10-20	Rogers, 1964
Intermediate	2-10	Heier and Carter, 1964
Basalt and Gabbros	0.5-2	Heier and Rogers, 1963
<u>Sedimentary Rocks</u>		
Shales, North America	10-15	Adams and Weaver, 1958
Bauxites	49	Adams and Richardson, 1960
Bentonites	24	Adams and Weaver, 1958
Limestones	1.1	Adams and Weaver, 1958
Sandstones	1.7	Murray and Adams, 1958
Soils	6	Vinogradov, 1959
<u>Sediments</u>		
Pelagic Carbonates	1	Turekian and Wedepohl, 1961
Pelagic Clays	5-48	El Wakeel and Rilely, 1961
<u>Metamorphic Rocks</u>		
Marble	0.03	Pliler, 1956
Slate	7.5	Pliler, 1956
Phyllite	5.5	Pliler, 1956
Schist	7.5	Pliler, 1956
Gneiss	13.1	Billings, 1962

Brief Chemistry

There are 13 isotopes of thorium with six of them found in nature. Of the six natural thorium isotopes, five are relatively quantitatively unimportant members of the ^{238}U , ^{235}U or ^{232}Th decay series. Thorium-232 is the major isotope, with a half-life of 1.39×10^{10} years (Ryabchikov and Golbraikh, 1969).

Although other oxidation states of thorium are known in the laboratory, only Th(IV) is found in nature. Th(IV) is found as Th^{+4} . The atomic radius of Th^{+4} is 0.99 Å (Ahrens, 1952).

Common insoluble thorium compounds include the hydroxide, fluoride and phosphate. Soluble compounds include the chloride, nitrate and sulfate. Thorium in solution is a small, highly charged ion that undergoes extensive interaction with water and many anions. The solution chemistry of thorium is largely a study of its complex ions. Common anions that form strong complexes with thorium include fluoride, chloride, nitrate, phosphate and sulfate. At pH values about 3, thorium undergoes hydrolysis in aqueous solutions. During the sedimentary cycle, thorium usually becomes separated from uranium because the uranium tends to mobilize in its U(VI) oxidation state until encountering a reducing environment to become immobilized as U(IV). Thorium does not undergo a comparable oxidation state change.

Solution Equilibria

The relative activity of solution species of thorium in equilibrium with $\text{ThO}_2(\text{s})$ at assumed activities of various ions is plotted in Figure 8.37. The thermodynamic data for all the hydrolysis species except $\text{Th}(\text{OH})_5^-$ were obtained from Sillen and Martell (1964). In general, the total concentration of thorium in solution decreases with an increase of pH from zero to 5. Above 5, pH does not affect thorium concentration in solution due to the formation of $\text{Th}(\text{OH})_4^0$. The activity of all positively charged species decreases with an increase in pH, while the activity of the negatively charged species increases with the increase in pH. Under the conditions assumed for Figure 8.37, the total activity of thorium in solution would be expected to be approximately $10^{-9.6}$ moles/l above pH 5.

FIGURE 8.37. Activity of Various Thorium Species in Soil in Equilibrium with $\text{ThO}_2(\text{s})$, $\text{pCl}^- = \text{pNO}_3^- = \text{pSO}_4^{2-} = 3.0$, $\text{pF}^- = 4.5$ and $\text{pH}_2\text{PO}_4^- = 5.0$

In addition to OH^- , thorium forms various complexes with SO_4^{2-} , PO_4^{3-} , Cl^- , NO_3^- , and F^- . Various anions in increasing order of their importance to forming complexes are: NO_3^- , Cl^- , H_2PO_4^- , and F^- . Figure 8.37 shows that thorium exists as Th^{4+} only in very acidic solutions ($\text{pH} < 3$). Above pH 3, Th^{4+} hydrolyzes very rapidly and it does not contribute significantly to the total thorium concentration. Under the conditions assumed for Figure 8.37, ThF^{3+} would be a dominant solution species at $\text{pH} < 5$, and Th(OH)_4^0 would be a dominant solution species at $\text{pH} < 5$. If fluoride ion is absent from the solution, or its concentration is extremely low, Th(OH)_2^{2+} would mainly control the thorium concentration in solution at $\text{pH} < 5$.

Laboratory Adsorption Studies

Antal (1966) found that the acid leachable ^{230}Th content of Caribbean Sea sediments decreased with depth in cores. It was suggested that the initially soluble precipitate of ^{230}Th is transformed in the sediment to a more acid-resistant state, with an apparent half-life of 24,000 years at 3°C .

Holland and Kulp (1954) studied the adsorption and base exchange of thorium on deep-sea red clay, globigerina ooze, and green clay. At equilibrium the fraction of radioactivity remaining in the seawater solution is independent of the total quantity of tracer added. Extrapolation of the data to actual concentrations of thorium in sea water indicates that the concentrations of thorium in sediments is comparable to that of these experiments. It is concluded that base exchange is the method by which thorium is taken up by the sediments.

Koczy (1949) described experiments which show the precipitation of thorium in sea water. The adsorption of isotopes of radium and thorium on red clay, powdered manganous dioxide, and a powdered manganese nodule was determined. Radium adsorbed on all three powders, which is not the case with thorium. The thorium content of a few samples of marine sediments has been measured. They contain about 1×10^{-7} g Th/g. One manganese nodule investigated was found to hold as much as 1.3×10^{-6} g Th/g. The geochemistry of thorium and uranium in sea water is briefly discussed. An attempt is made to estimate the thorium content of sea water with the aid of the ratio Io:Th in the sediments. The thorium content of sea water is calculated to be 1 to 10×10^{-9} g Th/l.

Thorium incorporation into sediments by precipitation mechanisms is documented. Koczy (1949) performed experiments in which thorium directly precipitated in sea water. Pettersson (1949) also hypothesized thorium precipitation to the sea bottom to explain the distribution of thorium and radium.

Nishiwaki et al. (1972) spiked sea water and sea water-distilled water mixtures with Th^{+4} and measured the adsorption on a medium sand, very fine

sand and silt-clay. Twenty grams of soil were contacted with 4 l of spiked water and mixed until equilibrium was reached. The K_d for thorium increased as the particle size of the soil decreased. Chlorosity of the water did not appear to consistently affect the thorium K_d for the fine sand or silt-clay. The K_d for the medium sand increased as the chlorosity of the water decreased. The chlorosity effect was compounded by a variable pH of the various salt solutions, so that the exact cause of the trend was not determinable. K_d values for the medium sand, very fine sand and silt-clay were 40 to 130, 310 to 470, and 2700 to 10,000 ml/g, respectively.

Katsurayama (1968) determined the distribution coefficient of thorium ($K_{d_{Th}}$) but data are not presented in the available abstract.

Desai and Ganguly (1970) showed humic acids from a coastal marine sediment solubilized 100% of the thorium added to an ammonia solution (2.5N). Thorium in this solution without humic acid was observed to predominantly precipitate (95%). The humic acid-thorium complex was noncationic. In an identical experiment, fulvic acid extract was shown to solubilize 59% of thorium added to an ammonia solution. Again, the solubilized organic-thorium fraction was noncationic.

Sugimura (1964) leached ocean sediments with cold HCl and found 60 to 70% of the thorium was extracted. Imahashi (1970) observed hydrothermal weathering of rocks in a Japanese hot spring area. Sixty percent of the thorium and 50% of the uranium was weathered from the rock. Dementev and Syromyatnikov (1965) concluded that thorium migration in ground waters occurred in both colloidal suspension and anionic complexes probably with organic acids.

Adams et al. (1959) suggest that thorium is concentrated by clay minerals. Schulz (1965) found the thorium in soils which he studied to be strongly adsorbed by clay particles or present as insoluble oxides and hydroxides. Rubtsov (1966, 1972) found thorium to be associated with the fine-grained particles during soil weathering. Ritchie et al. (1972) found the thorium content of sediments in a freshwater environment to increase with decreasing particle size distribution.

Rancon (1973) measured the thorium Kd for a soil developed on a schist consisting of quartz and clay with no calcite or organic matter, for a mixed quartz-clay-calcite-organic matter soil and for illite with 100 mg Th/l versus solution pH. For the quartz-clay soil, at pH 6 the Kd was 5×10^5 ml/g, at pH 4 the Kd was about 1×10^3 ml/g, and at pH 2 the Kd was about 5 ml/g. The mixed quartz-clay-calcite-organic matter soil could not be lowered in pH without removal of soil calcite, but above pH 8, the thorium Kd dropped from 10^6 ml/g to 1000 ml/g at pH 10. Dissolution of humic acids in the soil probably resulted in thorium complexation and a decreased Kd with rising pH. Illite behaved similarly to the quartz-clay soil, but the thorium Kd at pH 1 was about 500 ml/g and about 1×10^5 ml/g at pH 6.5. For soils without calcite or organic material, the thorium Kd decreased as the thorium concentration in solution initially increased. Calcareous soils neutralized even high strength thorium solutions to precipitate $\text{Th}(\text{OH})_4$. The quartz-clay soil and illite, for example, gave thorium Kd values of 8 ml/g and 1000 ml/g, respectively, in a 0.1 g Th/l solution. The drop in thorium Kd was caused by saturation of available exchange sites as a result of increased thorium concentration. There was evidence for the concentration dependence of the thorium Kd down to 1 mg Th/l in the initial contacting solution. In general, three types of soil-thorium adsorption reactions were found: 1) $\text{Th}(\text{OH})_4$ precipitation as a result of soil calcite buffering, 2) strong adsorption on clay-containing soils and dilute thorium (<1 g/l) solutions at a pH above 2, and 3) strong adsorption on organic-containing soils at the neutral to acid pH range, but diminishing adsorption into the alkaline pH range.

Bondietti (1974) studied the adsorption of hydrolyzed thorium from waters at pH 6.5 by calcium saturated reference clays (montmorillonite and kaolinite) and calcium humate and found 95% and 99.9+% adsorption, respectively. Desorption studies utilizing calcium citrate removed 10 to 30% of the thorium from the clays but only 1% from the humate. Stronger complexers (DTPA and EDTA) removed 20 to 30% of the thorium from the humate. A mixed organic-hydroxy complex was proposed for the reaction of thorium with humic substances.

Field Studies

Baranov and Khristiansova (1963), Baranov et al. (1962), Baturin et al. (1971), Bernat and Goldberg (1969), Bonatti et al. (1971), and Kuznetsov et al. (1964, 1968, 1969, 1971) reported on the distribution of thorium in marine sediments.

The distribution of the two thorium isotopes, ^{230}Th and ^{232}Th , are quite different in the marine environment. In suspended particulates and bed sediments ^{230}Th associated with phosphates, hydroxide precipitates, organics and calcium carbonates. Thorium-232 was associated in sedimentary detrital particles. Thorium-232 present in the cores is of continental or volcanic origin. Most of the ^{230}Th was formed from uranium in the sea water and only 25% of it is of continental origin. The clay fraction in all types of ocean sediments has a $^{230}\text{Th}:\text{Th}$ ratio increasing from 30 in terrigenous to 50 in pelitic formations. Increase of the $^{230}\text{Th}:\text{Th}$ ratio from sands, to silts, and to muds indicates that the ^{230}Th in sea water is in a form more easily sorbed than thorium. A similar effect was observed with radium; the clayey fractions are 10 times richer in radium than sands. The behavior of uranium is quite different. Its content in all types of sediments is about the same and does not depend on the granulometric composition of sediment. The $\text{Th}:\text{U}$ ratio in all types of sediments is ≤ 1.7 to 1.8 in clay fractions and ≤ 0.3 to 0.7 in sands and silts. The $^{230}\text{Th}:\text{U}$ ratio in all types and all fractions (in silts it is 4 and in clay 7 to 10) indicates a distinct radioactive disequilibrium caused by predominance of ^{230}Th over uranium. The $\text{Ra}:\text{U}$ ratio has the same character as the $^{230}\text{Th}:\text{U}$ ratio. Thorium distributions in cores shows no migration occurs during diagenesis but Somayajula and Church (1973) did find thorium (^{230}Th and ^{232}Th) concentrations in interstitial waters of a Pacific Ocean sediment to be higher by a factor of 10 to 1000 over their concentrations in sea water which suggest migration. Lazarev et al. (1961) and Kimura et al. (1968) studied the fate of thorium in sea water. Both studies show thorium in sea water is bound to colloidal suspended particles. El Nadi and Ammar (1960) found the thorium content of the Nile River to be 150 $\mu\text{g}/\text{l}$.

Nikolaev et al. (1969) measured the concentrations of thorium and ionium (^{230}Th) in the water and suspensions of the main rivers in the basin of the Black and Azov Seas. On the basis of the data obtained, the main elements of balance and the reserves of thorium and ionium in the Black and Azov Seas were determined. The amounts precipitated in deep and shallow water zones in the Black Sea annually are 143 and 691 tons of thorium and 19,100 and 10,400 g of ionium. It was calculated that the residence time of thorium in the aqueous phase is 56.5 years for the Black Sea and 160 days in the Azov Sea; for ionium the values are 365 years and 172 days, respectively. Kurokawa (1971) gives the range of thorium content in 40 Japanese soils to be 2.8 to 20 ppm and in ten rivers 2.7×10^{-2} ppb. These values yield an apparent Kd_{Th} of 10^3 to 10^4 .

Sugima (1964) reviews the distribution of natural radioactive elements in sea water and sediment. Sea waters contain 2×10^{-9} to 1×10^{-7} g Th/l and $n \times 10^{-11}$ - $n \times 10^{-14}$ g ^{230}Th /l. Sea sediments contain 6 to 13 ppm Th; 60 to 70% of the thorium is leached with cold HCl. Studies were made to determine the sedimentation rate of sediment from the contents of ^{232}Th and $^{230}\text{Th}(\text{Io})$. Iskra et al. (1969) studied an interior-drained freshwater basin and determined the main sinks for thorium were the plant detritus and soils. Pashneva et al. (1965) found the thorium content in Tomsk region Russian soils to increase with increasing humus content. Hansen and Huntington (1969) found a similar correlation with organic matter in Sierra Mountain soils. In contrast, Tyuruykanova and Kalugina (1971) found low thorium in peats and forest podzol soils compared to alluvial soils.

Two Soviet articles by Yakobenchuck (1968) and Pokidin et al. (1972) found thorium to be associated with the calcium carbonate content of a podzolic soil and Caspian Sea sediment, respectively.

The thorium content of ground water was reported by Dementyev and Syromyatnikov (1965) to be highest in low salinity, low hardness, low pH, high organic content ground waters. These characteristics suggest transport of thorium as colloidal suspensions and anionic complexes involving soil acids.

Summary

Under alkaline conditions, $\text{Th}(\text{OH})_4$ and ThO_2 maintain low activities in solution and these compounds could form and govern thorium concentration. Thorium hydrolyzes readily even in moderately acidic environments (Figure 8.36) so that Th^{4+} would be present only in very acidic solutions. Laboratory studies also show that thorium tends to precipitate as thorium hydroxide and hydrated thorium oxide.

An increase in thorium content with increases in CaCO_3 , phosphate and humus content of soils and sediments has been reported (Kuznetsov et al., 1968; Pashneva et al., 1965; Menzel, 1968; Yakobenchuck, 1968; Hansen and Huntington, 1969; Pokidin et al., 1972). However, Tyuryukanova and Kalugina (1971) reported low thorium concentrations in high humus soils (peats and forest podzols) compared with alluvial soils. Thorium adsorption increases with increase in pH (Rancon, 1973) and decrease in soil particle size (Hansen and Huntington, 1969; Hanse, 1970; Nishiwaki et al., 1972; Rubtsov, 1966, 1972; Bondiotti, 1974). Strong humic and fulvic acid complexes with thorium occur in the neutral to acidic range (Rancon, 1973; Bondiotti, 1974) which are noncationic (desai and Ganguly, 1970) and mobile. It has been reported also that thorium migrates primarily in the colloidal form (polymeric) in the natural environment (Baranov et al., 1956; Lazarev et al., 1961; Kimura et al., 1968). Observed K_d_{Th} for fresh and marine environments are typically 10^3 to 10^5 ml/g.

TRITIUM

Natural Sediment and Rock Distributions

Natural tritium concentrations vary geographically from about 10 T.U. for northern and southern midlatitude precipitation to 1 T.U. for equatorial precipitation. The background tritium content of deep ocean and ground water is essentially zero (Fairbridge, 1972). Hence, the tritium content of rocks, minerals and deeper sediments also is nearly zero unless contacted by tritium-contaminated ground water.

Brief Chemistry

Tritium (^3H or T) is an isotope of hydrogen with a half-life of 12.16 yr. Tritium occurs naturally in the upper atmosphere, chiefly by the interaction of fast neutrons with nitrogen (Kaufman and Libby, 1954). The amount of natural tritium is about one part in 10^{17} parts of normal hydrogen (^1H) (Cotton and Wilkinson, 1962).

It was a fairly recent discovery that tritium also is a product of uranium fission (Albenesius, 1959; Albenesius and Ondrejcin, 1960). Several years prior to the identification of tritium as a uranium fission product, the Environmental Monitoring Group at Savannah River plant recognized tritium as occurring in Purex separations process wastes, and was using it as a ground-water tracer (Horton and Ross, 1960). Tritium yields of 3.8 to 20.3 curies/ton uranium were obtained for exposures between 300 and 1600 megawatt-days/ton uranium.

Tritium oxidizes rapidly to HTO , existing essentially as water, and its distribution in ground and surface waters is controlled by the operation of the hydrological cycle. Tritium is measured in tritium units, T.U., where $\text{T.U.} = \text{T}/10^{18}\text{H}$, or expressed as picocuries/l. Natural background levels have risen since weapons testing of nuclear devices from 1 to 10 T.U. to several hundred T.U. up to the 1963 atmospheric detonation moratorium. Most of the tritium added to the hydrological cycle by fusion devices was due to residual tritium ($\sim 6.7 \times 10^6 \text{ Ci } ^3\text{H/megaton fusion device}$, Stead, 1963).

Solution Equilibria

Tritium (H^3) is a radioactive isotope of hydrogen. Thus, tritium behavior in the environment would be expected either to be similar to hydrogen or to exist as an ion, gas and liquid (tritiated water). Except for the slight differences in vapor pressure, tritiated water behaves the same as ordinary water (Jacobs, 1974). Although no discrete solid phases of tritium are expected in sediments, it could associate itself with organic components containing hydrogen or with some minerals as mobile water, water of hydration, or as part of structural hydroxyl groups (Jacobs, 1974; Stewart, 1967).

Tritium rapidly travels at about the same velocity as the ground water in the form of HTO. Some replacement of nontritiated water on clays and other hydrated soil constituents occurs, but the reaction is of marginal value as far as tritium retention is concerned. Tritium can move in a vapor phase through the soil under certain conditions as well.

Laboratory Adsorption Studies

Tritium ultimately exists in aquatic environments as a tritiated water molecule. Theoretically, tritium ions are capable of exchanging for hydrogen and other ions. However, the tritium is usually in an aqueous solution before contacting sediment, so that isotopic exchange and replacement of hydroxyl water molecules is the most common mechanism of tritium removal. Little quantitative work on tritium distribution has been reported. Most of the field studies indicate that tritium distribution has been reported. Most of the field studies indicate that tritium distribution coefficients were very low because tritium migration velocities were essentially the same as those of the accompanying ground water (Brown and Haney, 1964; Brown, 1967; and Hawkins, 1975). Hawkins (1975) and Hayes (1976) have studied the migration of 3H from Savannah River Plant burial grounds and adjacent estuary.

Field Studies

Haney, Brown and Reisenauer (1962) and Brown and Haney (1964) estimated by studying the rate and direction of ground-water flow that movement of tritium disposed to the ground at the Hanford Purex Plant would require 6 or

7 years travel time to the Columbia River, approximately 17 miles from the Purex Plant. The half-life of tritium allowed about 70% of the total tritium discharged to reach the river. The tritium content of Columbia River water was not expected to rise over 50% higher than the present background because of tritium dispersion during travel and the large dilution represented by the Columbia River (80,000 to 200,000 ft³/sec).

Brown (1967) reviewed the hydrology and geology of the Hanford area, and showed the 1966 limits of the areas defined by 3000 pCi/cm³ and 10 pCi/cm³ of tritium based on well water analytical results. The 10 pCi³H/cm³ area was 3 km from the Columbia River in 1966. The concentration of tritium added at the Purex Plant disposal sites was 10,000 pCi³H/cm³. Tritium moved at essentially the same rate as the ground water.

Kline and Jordan (1968) reported a field experiment on a Puerto Rican clayey soil where 1 l of 20 mCi/l tritiated water was applied to a plot with about 1 m² area, and sampled via a lysimeter installed horizontally, without disturbing the plot surface soil, 18 cm below the soil surface. The sampling program lasted 210 days during time 137 cm of rain fell on the plot. Runoff surface water was collected as well. The soil remained saturated, or close to saturation for the sampling period. Most of the tritium passed through the profile as a peak or front 16 days after application, and declined in concentration exponentially during the remainder of the experiment. The surface runoff peaked in 1.9 days, with another change in decline of specific activity at 35.6 days. Because of the loss rate curve of tritium in the free soil water, the authors suggested that tritium movement through soils must be modified to allow for the existence in clay soils of isolated compartments of immobile water that does not have free interchange with the more rapidly moving water.

Jordan et al. (1971) monitored tritium movement through a soil near Argonne, Illinois. They concluded from the results that a pulse of tritium moves downward at a rate determined by precipitation entering the top of the soil column. The tritium peak broadens and flattens from diffusion and will become immobilized if the upper soil layers dry out. Loss of tritium occurred

both by evapotranspiration and deep drainage. Deviation of the field results from a model of tritiated water movement proposed by Sasscer et al. (1971) was explained as due to parameters that were difficult to quantify such as root holes and hydroxyl exchanges.

Ehhalt (1973) pointed out that triated molecular hydrogen in the atmosphere was oxidized by soil microorganisms. He also estimated from the tritium content of H_2 of 2×10^6 T.U., steady since 1962, that the HT input rate was about 5.4 T atoms/cm² sec into the soil from the action of soil microorganisms.

Purtymun (1973) investigated the underground movement of tritium from solid waste storage shafts in rhyolite tuff at Los Alamos. Levels of 100 pCi ³H/ml had moved a distance of 105 ft in 4 years. Core samples of tuff were collected, water was distilled from them and tritium in the water was determined. Asphalt coatings on containers and shaft walls were suggested to control tritium migration from the shafts.

In contrast, Wheeler and Warren (1975) reported that a later comparison between asphalted and nonasphalted shafts showed that the asphalt containment techniques used were ineffective in slowing tritium migration from the shafts. Double containment and complete encapsulation of the 210-2 disposal drums in roofing asphalt was suggested to flow tritium movement from the storage shafts.

Because soil water and ground-water systems are similar, it would be expected that tritium oxide would move through these systems at essentially the same rate as light water. However, in comparing chloride ions and tritium breakthrough curves for various soil types, the tritium curve lags behind that for chloride ions in soils containing clays and silt (Kaufman and Orlob, 1955). This behavior was reported as caused by the tritiated water molecule entering the clays and replacing nontritiated water adsorbed on clay surfaces or interlayers.

Haney (1963, 1964) reported a laboratory study where actual ground water containing complexed ¹⁰⁶Ru and tritium was passed through several Hanford project soils. In silty soils, the ruthenium breakthrough curve was slightly

behind that for tritium, but in sandy soil columns, the breakthrough curves were essentially identical. Several retention mechanisms of tritium on clays are possible. For example: 1) exchange of tritium ions for hydrogen ions in exchange positions, 2) tritiated water molecules exchanged for hydroxyl water or water of crystallization, 3) exchange of tritium ions for exchangeable cations other than hydrogen, and 4) replacement of aluminum in lattice sites by tritium, with the aluminum ions moving into exchangeable cation positions. In the last case, the tritium may be more or less "fixed" in its octahedral position. This "fixation" has been considered to be minimal by some investigations (Higgins, 1959; Halevy, 1964; Corey and Horton, 1968; Teller et al., 1968).

It has been hypothesized by others (Corey and Fenimore, 1968) that the chloride ions are repelled from negatively charged soil particles into the central region of the soil pore where ground-water velocity is greatest (anion exclusion). This would be most effective in high cation exchange capacity soils which do not retain anions. Also, Corey and Fenimore (1968) showed that chloride ions lag far behind tritium in acid kaolinitic soil due to anion exchange of the chloride ions.

Corey and Horton (1958) reported no appreciable tritium "fixation" upon investigation of the movement of tritiated and deuterated water through acidic, kaolinitic soil. The work of other investigators, however, indicates that hydrogen isotopes may be selectively fixed (Rosenqvist, 1963; Koranda, 1965; Clayton et al., 1966; Savin, 1967; Stewart, 1967). The work of Rabinowitz (1969) and Rabinowitz et al. (1973) with forced exchange of tritiated water on clays also supports the view that part of the tritium can be "fixed" on clays. The isotopic exchange and fixation was forced with a mild form of electro-dialysis (2 V/cm) resulting in an increase in the reaction rate of about five times the rate without electrodialysis. Aluminum and other basing cations were determined after each experiment. The presence of exchangeable Al^{+3} correlated with tritium loss from the water resulting from tritium "fixation". A mass balance on the tritium also was determined for each experiment. The analytical data for tritium facilitated the differentiation of isotopic exchange and the "fixation" of tritium by kaolinite and illite.

Summary

Tritium substitutes readily for the hydrogen in water and thus becomes a part of the hydrological cycle (Jacobs, 1974). Migration of tritium in the aquatic environment takes place at the same velocity as the ground water (Haney 1963, 1964; Haney et al., 1962); Brown and Haney, 1964; Brown, 1967). Some investigators have reported the selective fixation of tritiated water on clays and other hydrated minerals (Rosenqvist, 1963; Koranda, 1965; Clayton et al., 1966; Savin, 1967; Stewart, 1967; Rabinowitz, 1969; Rabinowitz et al., 1973) while other investigators have considered tritium fixation to be minimal (Higgins, 1959; Halevy, 1964; Corey and Horton, 1968; Teller et al., 1968). However, all of the field studies have indicated that tritium movement is synonymous with water movement (Brown, 1967).

URANIUM

Natural Sediment and Rock Distributions

The range in abundance of uranium in nature is given in Table 8.82. Vinogradov (1959) reported 1 ppm uranium as the average content of uranium in soils. The oxidation of organic matter in black shales tends to precipitate U(IV). Consequently, the black shales usually contain more uranium than red, green or gray shales.

TABLE 8.82. Abundances of Uranium in Natural Materials

<u>Material</u>	<u>U Concentration Range, ppm</u>		<u>Reference</u>
	<u>Igneous</u>		
Dunites and Peridotites	0.001-0.8		Adams et al., 1959
Gabbro and Diabase	0.3-3.4	Median 0.5	"
Intermediate (diorite and quartz diorite)	0.1-11.0	Median 1.7	"
Sialic (granite, syenite, monazite)	0.15-21.0	Median 3.9	"
	<u>Sedimentary</u>		
Black shales	3.05-25.0	Median 8.0	"
Red, gray and green shales	1.2-12.0	Median 3.2	"
Orthoquartzite	0.2-0.6	Median 0.45	"
Limestone and dolomite	0.1-9.0	Median 2.2	"
Bentonite	1.0-21.0	Median 5.0	"
Bauxite	3.0-27.0	Median 8.0	"
Halite	0.01-0.02	Median 0.013	"
Anhydrite	0.25-0.43	Median 0.37	"
Pelagic carbonates	0.1		Turekian and Wedepohl, 1961
Pelagic clays	0.7-4.3		Sugimara and Sugimara, 1962
Manganese nodule	3.6-5.0		Tatsumoto and Goldberg, 1959
Beach Sand	0.3-0.6		Mahdavi, 1964
	<u>Metamorphic</u>		
Marble	0.11-0.24		Clark et al., 1966
Slate	1.2-6.1		"
Phyllite	1.0-2.7		"
Schist	1.8-2.9		"
Gneiss	4.5-15.0		"
Amphibolite	2.6-4.1		"
Granulite	3.2-7.0		"

Brief Chemistry

There are 15 known isotopes of uranium from ^{227}U to ^{240}U and one uranium isomer (^{235}U) (Fairbridge, 1972). The half-lives of the uranium isotopes vary from a few minutes to over 4 billion years. Only three of the isotopes occur naturally, and two of these (^{235}U and ^{238}U) are parents of series that end in lead isotopes. The nuclear data on the three natural uranium isotopes are given in Table 8.83. The common oxidation states of uranium are U(III), U(IV), U(V) and U(VI) (Udaltsova, 1963). U(III) is easily oxidized in air to U(IV). The U(IV) state is fairly stable in aqueous solutions if they are very acidic. Uranium (V) disproportionates to U(IV) and U(VI): $2\text{UO}_2^+ + 4\text{H}_3\text{O}^+ \rightarrow \text{UO}_2^{+2} + \text{U}^{+4} + 6\text{H}_2\text{O}$ (Udaltsova, 1963). U(VI), as UO_2^{+2} (Uranyl) at $\text{pH} \leq 2.5$, is the most stable state of uranium in aerated aqueous solutions (Seaborg and Katz, 1954). At higher pH values, hydrolyzed uranyl ions predominate. Approximately 103 uranium minerals have been confirmed. Uraninite (ideally UO_2) is the primary ore mineral of uranium, but other secondary minerals include carbonates, sulfates, molybdates, phosphates, vanadates, silicates and multiple oxides. Uranyl ions readily form many complexes with anions ordinarily found in water environments such as carbonate, sulfate and fluoride.

TABLE 8.83. Nuclear Properties of Natural Uranium Isotopes (Fairbridge, 1972)

<u>Isotopes</u>	<u>% Abundance</u>	<u>Half-Life, yr</u>	<u>Decay Series Parent</u>
^{234}U	0.0056	2.48×10^5	---
^{235}U	0.72	7.13×10^8	4N + 3
^{238}U	99.27	4.51×10^9	4N + 2

Solution Equilibria

The common oxidation states of uranium are U(III), U(IV), U(V), and U(VI) (Udaltsova, 1963). However, in the geologic environment U(IV) and U(VI) are the most important oxidation states. In an oxidizing environment U(III),

U(IV), and U(V) species are very low in concentration and do not contribute significantly to the total uranium concentration. U(VI) species entirely control the total uranium concentration in oxidizing environments (Ames and Rai, 1978). UO_2^{2+} and the $\text{UO}_2^{\text{F}+}$ are the predominant solution species up to a pH of approximately 6. The predominant solution species over pH ranges of from 6 to 8 and >8 are $\text{UO}_2(\text{OH})_2$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, respectively. In oxidizing and high chloride environment such as sea water the UO_2Cl^+ will become among the most predominant solution species below pH 6. In extremely reducing conditions, UOH^{3+} and to a lesser extent UO_2^+ species would be most important.

The thermodynamic data for UO_2F^+ and $\text{UO}_2\text{H}_2\text{PO}_4^+$ were selected from Palei (1970) and selected data from Sillen and Martell (1964) were used for the remaining species in Figure 8.38. All the species except UO_2^+ shown in Figure 8.38 are of U(VI). Since equilibrium is assumed with Na_2UO_4 , a U(VI) compound, a change in oxidation-reduction conditions will affect the position of the curves. In an oxidizing environment ($p\text{O}_2 = 0.68 \text{ atm}$), the U(IV) species are very low in concentration ($\log a_i < 38$) and fall outside of the boundaries of Figure 8.38.

Laboratory Adsorption Studies

Bell (1960) and Dall'Aglio and Casentini (1970) found uranium in desiccating salt basins to remain in solution under oxidizing, low organic matter substrate conditions.

Masuda and Yamamoto (1971) examined the desorption of uranium from alluvial, sand and volcanic ash soils. The cation exchange capacities were 13.7, 7.7 and 33.0 meq/100 g, respectively, for the alluvial, sand and volcanic ash soils. Strong salt solutions and distilled water were used as leachates. Loads of more than 2000 $\mu\text{g U/g}$ of soil were required before desorption by distilled water was 1% of the uranium on the soils. The uranium was amended to the soils as uranyl nitrate before the desorption work. Desorption of uranium was higher with 0.5M $(\text{NH}_4)_2\text{SO}_4$, 1.34M KCl and 1.44M K_2HPO_4 salt solutions, but reached 50% removal only for the alluvial soil with a high adsorbed uranium content in 1.44M K_2HPO_4 solution. The volcanic ash soil did not attain 5% uranium desorbed in any of the salt solutions.

FIGURE 8.38. Activity of Various Uranium Species in Equilibrium with Na_2UO_4 in an Oxidizing Soil Environment [$p\text{O}_2(\text{g}) = 0.68 \text{ atm}$], $p\text{CO}_2(\text{g}) = 3.52 \text{ atm}$, $p\text{Cl}^- = p\text{SO}_4^{2-} = 3.0$, $p\text{F}^- = 4.5$ and $p\text{H}_2\text{PO}_3 = 5.0$

The effects of carbonate ions on uranium desorption from soils was examined by Yamamoto et al. (1973). They used an alluvial soil, a volcanic ash soil and a sandy soil containing up to 500 $\mu\text{g U/g}$ air-dried in their desorption experiments. The desorption of uranium declined as a power function of the amount of uranium on the soil. Desorption results are shown in Table 8.83. Ten grams of soil were magnetically stirred with 100 ml of potassium carbonate solution for 30 min and stood overnight before filtering and fluoremetric

uranium analysis. As can be seen in Table 8.84, uranium desorption was very low in the presence of low to moderate environmental carbonate concentrations.

TABLE 8.84. Desorption of Uranium from Soils with Distilled Water and Carbonate Solutions (Yamamoto, 1973)

Soil	U Content, μg/g	Distilled Water, %	Carbonate Solution, %	
			4.3 mg CO ₃ ²⁻ /l	43.5 mg CO ₃ ²⁻ /l
Alluvial	7.1	0.31	0.62	1.20
	485.0	0.22	0.25	0.41
Sandy	10.1	0.14	0.27	0.90
	488.2	0.12	0.13	0.46
Volcanic Ash	8.3	0.18	0.57	1.15
	500.0	0.09	0.10	0.20

Rancon (1973) studied the adsorption behavior of uranium added to soils to simulate nuclear energy discharges as compared to natural weathering events. Rancon chose four soils: a) a river sediment containing a mixture of clay, calcium carbonate and organic matter; b) a highly organic riverine peat; c) a clay-calcium carbonate soil; and d) a clay and pure illite, calcite and quartz. The first two soils were exposed to river water containing uranium while the latter two solutions were exposed to their respective ground waters both at 10 ppm U. The K_d in ml/g are shown in Table 8.85.

An increase in initial uranium concentration above 1 ppm U which causes a subsequent pH decrease in the water causes the K_d to drop. At 10,000 ppm U (pH 2.5) the K_d is nil for the first two soils. A saturation of the adsorbate sites is proposed as a partial cause of the drop in K_d . Rancon also presents data on the variation of K_d with pH at 1 ppm U. For the clay soil, three peaks were observed; around pH 5.5 ($K_d = 300$), a larger peak at pH 10 ($K_d = 2000$), and a peak at pH 12 ($K_d = 270$). Since soils are of variable composition, Rancon concludes the peaks correspond to sorption maxima corresponding to electrokinetic potential (surface charge) maxima for certain

TABLE 8.85. Kd Values for Uranium

<u>Adsorbate</u>	<u>K_d</u>
Clay-Carbonate-Organic Mix	39
Alkaline Peat	33
Clay-Carbonate	16
Clay	270
Pure Quartz	0
Pure Calcite	7
Illite	139

constituents. The uranyl ion UO_2^{++} is electrostatically adsorbed at these points. Other explanations for carbonate and humic bearing soils are discussed. The K_{dU} for the alkaline peat is very low compared to the K_{dU} for acidic peats.

Calvo (1974) reported a short experiment on the metallogenetic aspects of the uranium-organic matter reported a short experiment on the metallogenetic aspects of the uranium-organic matter association in nature. The author carried out several experiments on uranium fixation by organic matter with different degrees of maturity. Although further studies are considered necessary, the results already obtained lead to the following conclusion: when uraniferous solutions come into contact with humic organic matter, the efficiency and nature of the uranium-organic matter association thus established depends on the degree of carbonization attained by the humic material. At the beginning of the development process, the organic matter has high chemical activity and the uranium tends to occur in stable organic phases. As the process continues, a stage is reached from which uranium tends to form its own minerals independently of organic matter. From the coalification stage onward the tendency toward uranium-organic matter association becomes increasingly less in any form. Petrographically, the humic constituents to which uranium is closely and positively related belong to the huminite maceral group. Lastly, it is considered that when the organic matter is present as an accessory constituent in other sedimentary rocks and with quite low maturity indices, there is greater favorability for the formation of uranium deposits.

result because the pH 6 region is a boundary between anionic and cationic uranium forms and corresponds to: $[UO_2^{+2}] + [UO_2OH^+] = [UO_2(CO_3)_2^{-2}]$, an equality between cation and anion uranium forms in solution.

Kovalevskii (1967) found the uranium content of noncultivated soils in western Siberia increased with the clay content of the soils. Clay soils contained at least three times as much uranium as sands. Yakobenchuck (1968) correlated the total uranium content in Russian sodpodzolic soils from the Ukraine with other soil constituents. Uranium showed correlation with the oxidizes of silicon, iron, and aluminum suggesting coprecipitation or inclusion.

Grandstaff (1976) arrived at a rate expression for the effects of surface area and uraninite composition, oxygen content of the solution, carbonate content, organics content, pH and system temperature on uraninite dissolution:

$$R, \text{ the rate of uraninite (UO}_2\text{) dissolution} = \frac{-d(\text{uran})}{dt} = 10^{20.25} (SS)(RF)^{-1} \\ (10^{3.38-20.8 \text{ NOC}}) (a_{CO_2}) (D.O.) (a_{H^+}) \exp (-7045/T_{day}^{-1})$$

where

SS = the specific surface area (cm^2/g),

RF = an organic retardation factor,

NOC = the mole fraction of nonuranium cations in the uraninite,

D.O. = the dissolved oxygen content of the water (ppm),

CO_2 = the total dissolved carbonate, and

T = the absolute temperature.

The rate expression was used to predict UO_2 dissolution rates under varying conditions in the absence of organics in the contacting water with good results. Dissolved inorganic species in artificial sea water other than hydrogen ion activity (pH), total carbonate and dissolved oxygen did not appreciably affect the UO_2 dissolution rate. The organic retardation factor

must be determined experimentally for each organic-containing solution by comparing the calculated UO_2 dissolution rate without organics in the environment with the observed dissolution rate, or $\text{RF} = R_{\text{calculated}}/R_{\text{observed}}$. Retardation values of up to 420 were obtained. The magnitude of the effects of the several factors in the expression on the oxidation rate of U(IV) to U(VI) could be of assistance in understanding uranium mobility in natural environments.

Schulz (1965) suggested that uranium may be present in the soil as the divalent uranyl ion, UO_2^{2+} , and will be mobile in soils if present as the uranyl ion.

Alberti et al. (1959) leached uranium ore deposits with water and found the percentage leached to depend on the acidity of the solution. On the average, 18% of the total uranium solubilized in water, while 20% sulfuric acid leached 60% of the total uranium.

Armands and Landergren (1960) report on a uranium rich peat bog. Leaching experiments on iron ore that contained 0.05% uranium showed that 12 to 26% of the uranium could be leached by NaHCO_3 solutions in 4 days; the uranium in the bog probably came from leaching the iron ore by ground-water bicarbonate solutions.

Goldsztein and Ros (1963) leached Mediterranean Sea sediments with 2N nitric acid and found 60% of the uranium in continental shelf sediment and 36% of the uranium in abyssal plain sediments to be leachable.

Imahashi (1970) removed 50% of the uranium content of hydrothermally-altered rocks. Leaching performed under acid weathering conditions is more rapid than weathering processes under neutral conditions.

Legin, Kuznetsov and Lazarev (1966) leached sulfide bearing sediments from the Black Sea and sediments from the Azov Sea with 0.7N sodium bicarbonate. The sulfide rich Black Sea sediment's uranium quantitatively leached whereas only 4 to 6% of the uranium in the Azov Sea sediment mobilized.

Titaeva and Veksler (1969, 1969) found uranium leached from metamorphic gneiss and crystalline schists by ground waters from the Russian permafrost area. The waters contained high organic loads, oxygen and carbon dioxide contents which from a geochemical standpoint all favor uranium mobilization. Uranium migrated fastest, radium slower and thorium slowest in the extremely cold ground waters. Baturin, Illyina and Popov (1971) found the same order of migration in a marine sedimentary regime.

Field Studies

There is a large amount of literature on the geochemistry of uranium because of its great value as a fuel for nuclear reactors. The uranium chemistry in the natural environment has been well studied with the practical objective to better predict the occurrence of ores.

Several investigators have observed correlation between uranium content and sediment Eh, organic carbon content, particle size, phosphorous content, and hydrous oxide content. Many of these characteristics are interdependent such that a clear understanding of the controlling mechanism for uranium adsorption is not possible. For instance one observer will claim Eh controls uranium adsorption while another believes organic carbon is the active adsorbate. Since it is common to find high organic matter and reducing conditions present together the correlation of each parameter with uranium content is possible.

Among the investigators who have found uranium to be immobilized by reducing conditions in rocks and sediments are Adams et al. (1959), Agamirov (1963), Baturin (1966), Baturin et al. (1966), Bonatti et al. (1971), Dorta and Rona (1971), and Veek (1967). Sediments from the Black Sea, Caspian Sea, Cariaco Trench, Pacific Ocean, Gulf of California, a Norwegian Fjord and Terrestrial rocks were studied. Reduced sediments contained 1 to 39 ppm uranium versus oxidized deep sea clay values averaging 3 ppm. Koliadin et al. (1960) based on the observance of U(VI) carbonate complexes in solution just above anoxic Black Sea sediments believed uranium reduction was not occurring. As mentioned in the section on mechanisms, the Eh of sediments can vary

rapidly over small distances. It is very likely that U(VI) can exist in solution directly above reducing sediments yet become adsorbed as U(IV) into the sediments within a reducing film around the sediment particles.

Amiel et al. (1972), Armands and Landergren (1960), Baranov and Titaeva (1961), Baturin (1968, 1969, 1971, 1973), Baturin and co-workers (1966, 1967, 1969, 1971, 1973), Calvo (1974), Kochenov et al. (1967), Kolodny and Kaplan (1970) and Mo et al. (1973) found the total uranium content of sediments to correlate with organic content suggesting organic matter adsorbs significant amounts of uranium. Sediments which were included are fresh water peat, Lena River (Russia), Baltic Sea, Black Sea, Indian Ocean, Mediterranean Sea, Gulf of Mexico, Saanich Inlet (British Columbia), and Pettaquamscutt River (Rhode Island). In one study of sediments offshore of Japan, Mizuno and Mochizuki (1970) found no correlation of uranium content with organic carbon. Instead they found uranium correlated with fine particle size sediments.

Kochenov and Baturin (1967) found the uranium in Aral Sea sediments to correlate with both organic matter and particle size. Sand and silt ooze contained only 1 to 2 ppm Uranium, arvillaceous (clay sediments and organic rich sediments) contained over 10 ppm uranium.

Baturin (1969), Baturin et al. (1971), Bell (1960), Habashi (1962), Kolodny (1969), Kolodny and Kaplan (1970), Kuznetsov et al. (1968), Mihalik (1968) and Sakanoue (1960) all present field data correlating high uranium contents with high phosphorus suggesting phosphate mineral formation scavenges uranium.

Haglund (1968), Haglund et al. (1969), Lambet and Nikolaev (1962), Kuznetsov et al. (1967), Ermolaev et al. (1965) and Pyalling (1970) have studied the uranium content in waters and find soluble carbonate complexes of U(VI) increase its solubility and mobility in waters.

Baturin (1971, 1973a, 1973b) and Baturin and Kochenov (1973) concluded after studies on Atlantic, Pacific, Azov Sea, Black Sea, and various river sediments that all the above mentioned mechanisms (Eh, organic matter, P, carbonate) all play a role in the adsorption affinity of uranium.

From the several field measurements observed, K_d values can be calculated. Typical marine sediments of high organic or reducing potential contain 1.80 ppm uranium while the overlying sea waters contain 1 to 10 g/ uranium which yield an average range in K_d of 10^2 to 8×10^4 ml/g with 10^3 being median values [Baturin and Emelianov (1973), Kochenov and Baturin (1967), Sugimura (1964)].

Bhat and Krishnaswamy (1969) measured Indian River water uranium concentrations at 0.01 to 7 $\mu\text{g/l}$ dependent upon the source rock over which the rivers flow. Koczy et al. (1957) report a range of 0.5 to 12.8 $\mu\text{g/l}$ for rivers entering the Baltic Sea.

Baturin and Kochenov (1969) report that 50% of the uranium entering the oceans from river runoff is soluble and 50% is adsorbed on suspended matter.

From field measurements Kennedy et al. (1977) have calculated K_d s for U in the Great Miami River (Ohio) for suspended particles to be 1.0 to 1.6×10^3 .

Kurokawa (1971) reports the range of uranium content in 40 Japanese soils as 0.48 to 2.89 ppm while the average uranium content in 10 rivers was 0.57 $\mu\text{g/l}$. The K_d for rivers would be about 1 to 6×10^3 ml/g.

Krylov and Shats (1958) studied the uranium contents in northwestern Russian water bodies and concluded that uranium precipitation was controlled by iron hydroxide and humic compounds.

Ritchie, Hawaks, and McHenry (1972) also found the uranium content of sediments from the Little Tallahatchie River to increase with decreasing particle size.

Yabuki and Shima (1973) measured the metal concentrations of carbonaceous ooze and nearby manganese nodules and concluded that the 20 times smaller concentration of uranium in the nodules in comparison with other metals meant that the UO_2^{++} ion in sea water rarely coprecipitated with manganese and iron. The uranium present in nodules probably represented surface adsorbed uranyl carbonate complexes.

Summary

The common oxidation states of uranium are U(III), U(IV), U(V) and U(VI). However, in the geologic environment U(IV) and U(VI) are the most important oxidation states. In oxidizing environments U(VI) will predominate. U(IV) would precipitate as UO_2 in a reducing environment. U(VI) solution species govern uranium concentrations and movement in oxidizing environments. Uranium retention by soils and sediments in oxidizing and alkaline conditions is poor because the predominant uranium species at pH 6 in oxidizing environments are either neutral or negatively charged. An increase in CO_2 pressure in solutions reduces uranium adsorption and can increase uranium concentration. The cation exchange properties of sediments could contribute to the adsorption of uranium in the neutral to acidic pH range due to the presence of UO_2^{2+} . Oxidation-reduction conditions and pH would be important parameters of uranium mobilization and immobilization.

The above theoretically based predictions are substantiated by experimental results. Uranium has been reported to be solubilized and highly mobile in carbonate-containing waters (Brown and Keller, 1951; Naumov, 1961; Ermolaev et al., 1965; Legin et al., 1966; Haglund, 1968, 1969). Soluble uranium [U(VI)] can:

1. precipitate in the presence of phosphorus as evidenced by a direct correlation of uranium and phosphate content in soils and sediments (Bell, 1960; Sakanoue, 1960; Habashi, 1962; Kuznetsov et al., 1968; Menzel, 1968; Mihalik, 1968), and
2. be adsorbed by the soil organic component and/or reduced to U(IV) followed by precipitation (Breger et al., 1955; Kolodny, 1969; Kolodny and Kaplan, 1970; Baturin, 1971; Dall'Aglio, 1971; Dorta and Rona, 1971; Gabelman, 1971; Baturin and Kochenov, 1973; Mo et al., 1973).

An increase in uranium content with a decrease in sediment particle size was reported by several workers (Kovalevskii, 1967; Mizuno and Mochizuki, 1970; Ritchie et al., 1972).

The uranyl ion can be adsorbed on clay minerals (Goldsztanu and Wey, 1955; Kovalevskii, 1967; Rubtsov, 1972; Ritchie et al., 1972; Rancon, 1973) and other adsorbent materials (Masuda and Yamamoto, 1971; Yamamoto et al., 1973), but also is inclined to form complexes with anions, such as carbonate, that are commonly found in the solution. Uranyl salts also have been shown to substitute for Ca^{2+} during replacement of calcite by apatite (Ames, 1960), and Ca^{2+} competes with UO_2^{2+} for available sites during ion exchange reactions on inorganics such as calcite (Rancon, 1973) resulting in low uranium Kd values. However, uranyl ion adsorption on organic materials and humic substances is quite high (Szalay, 1954, 1957; Manskaya et al., 1956; Rozhkova et al., 1959; Rancon, 1973) especially at acid pH values. The most important parameters of uranium migration and retention are system Eh and pH.

ZINC

Natural Sediment Distribution

Some average values for zinc in marine and fresh water clays are found in Table 8.86.

TABLE 8.86. Zinc Concentration in Sediments

<u>Type</u>	<u>Concentration, ppm</u>	<u>Reference</u>
General Ocean Sediment	80 - 250	Duursma, 1974
Pelagic Carbonates	35	Turekian and Wedepohl, 1961
Pelagic Clay	165	Turekian and Wedepohl, 1961
Manganese Nodule	6600	Riley and Sunhaseni, 1958
Freshwater Clays	80 - 230	Lundearth, 1947
Soils	50	Vinogradov, 1959

Brief Chemistry

There are five stable isotopes of zinc with the following abundances ^{64}Zn (48.87%), ^{66}Zn (27.62%), ^{67}Zn (4.12%) and ^{68}Zn (18.71%). The only radioactive zinc isotope of consequence to nuclear waste disposal ^{65}Zn has a 250-day half-life.

Solution Equilibria

Zinc exists exclusively in Zn(II) oxidation state. The predominant zinc species in solution below approximately pH 8 is Zn^{2+} , and between pH 8 and 11.5 is Zn(OH)_2 in both fresh and salt water (Baes and Mesmer, 1976; Lindsay, 1972; Zirino and Healy, 1970; Zirino and Yamamoto, 1972).

Laboratory Adsorption

Aston and Duursma (1973), Dawson and Duursma (1974), Duursma and Bosch (1970), Duursma and Eisma (1973), Duursma and Gross (1971) and Duursma et al., (1974) report on sorption-desorption studies on zinc in the marine environment.

The addition of stable zinc between 50 to 1000 $\mu\text{g/l}$ did not consistently alter $K_d\text{Zn}$ for four marine sediments but below 35 $\mu\text{g/l}$ additional zinc the K_d was larger. The natural zinc concentration in sea water is 5 $\mu\text{g/l}$. It was also noted that 25% of zinc added to sea water was filterable after 50 hr suggesting colloid formation or precipitation. The $K_d\text{Zn}$ was dependent upon sediment concentration below 200 mg/l for 3 of 4 sediments studied. Very high K_d values ($>40,000$) occurred at sediment loads below 200 mg/l . Above 200 mg/l $K_d\text{Zn}$ leveled off at about 20,000 ml/g . This suggests nucleation of colloids or precipitates and inflates the sorption. For one sediment, sorption studies were performed as a function of salinity. The adsorption was independent of salinity suggesting ion exchange does not control zinc adsorption. In later experiments on world ocean sediments the $K_d\text{Zn}$ was shown to correlate with sediment cation-exchange capacity suggesting exchange does play a role in zinc adsorption. For two marine sediments which were split into six size fractions the $K_d\text{Zn}$ was higher for silt ranges 8 to 16 μm , 4 to 8 μm , 16 to 32 μm than the clay fraction $<4 \mu\text{m}$ suggesting sorption on hydrous oxides might play a role in zinc adsorption. For a Black Sea sediment the $K_d\text{Zn}$ under anoxic conditions was 11 times larger than the $K_d\text{Zn}$ for oxic conditions (4.8×10^4 versus $4.5 \times 10^3 \text{ ml/g}$). This suggests sulfides present in reducing sediments could immobilize zinc. Table 8.87 lists average values for the zinc distribution coefficient and half period of sorption for sediments studied by Duursma and co-workers.

In one long-term, 7-month experiment 50 g of Mediterranean Sea sediment was shaken with 10 liters of sea water traced with 1 $\mu\text{Ci/l}$ ^{65}Zn . After 7 months the adsorbed zinc was leached with 1N acetic acid-ammonium acetate (pH 5.4) and 1N acetic acid (pH 2.3). In the first instance 4 to 33% of the adsorbed zinc was leached, in the latter case 10 to 80% was removed. Strontium which adsorbs by ion exchange was completely leached in both cases. Thus there is more than simple ion exchange controlling zinc adsorption. Onishi et al. (1973) found that zinc present in sea water was quantitatively removed by in situ precipitation of manganese dioxide.

TABLE 8.87. Zinc Sorption in Marine Environments

<u>Sediment</u>	<u>log K</u>	<u>est. Kd ml/g</u>	<u>t^{1/2} Sorption, days</u>
Atlantic Ocean	3.8 ± 0.9	9.2 ± 10 ³	2.5 ± 2.7
Pacific Ocean	3.6 ± 0.5	6.3 ± 10 ³	1.1 ± 1.0
Indian Ocean	3.6 ± 0.4	6.6 ± 10 ³	2.4 ± 1.7
Baltic Sea	3.6 ± 0.7	6.7 ± 10 ³	5
North Sea	3.8 ± 0.1	9.5 ± 10 ³	2
Mediterranean Sea	3.8 ± 0.8	8.8 ± 10 ³	0.9 ± 0.7
Black Sea	4.0 ± 0.7	1.5 ± 10 ⁴	3
Red Sea	4.3	3.0 ± 10 ⁴	2.5

Murray and Murray (1973) adsorbed zinc on river sediments and studied its subsequent removal by seawater as a function of pH, time and sediment concentration. Using 800 mg/l river sediment, zinc adsorption was observed to reach steady state in from 1 to 3 days. Desorption steady state was reached after one day. In blank experiments without sediment only 3% of the total zinc became particulate (>0.45 μ m) in river or sea water, but if Fe(OH)₃ was precipitated 50% of the zinc was removed also.

The adsorption and desorption of zinc is rather sensitive to pH changes as shown in Figures 8.39 and 8.40. Between pH 7 and 8 adsorption doubles for the river conditions studied. Between pH 8 and 9.5 the adsorption is constant. Conversely for desorption by sea water the removal zinc steadily decreases as pH increases. For the river environment calculated KdZm is 850 at pH 7 and 5000 at pH 8. The desorption KdZm are 380 at pH 7 and 3750 at pH 8. The values are low because the desorption took place in sea water. The adsorption-desorption also appeared to be a function of sediment concentration. For adsorption increasing sediment from 200 mg/l to 800 mg/l load increased total adsorption but decreased per unit weight adsorption i.e., KdZm decreased 33%. For desorption increasing contaminated sediment load leads to proportionally less zinc release/unit weight.

FIGURE 8.39. Adsorption of Zinc at Constant Carrier Concentration and Sediment Lead with Varying pH

FIGURE 8.40. Desorption of Zinc at Constant Adsorbed Trace Element Concentration and Sediment Load with Varying pH

The effect of salinity on desorption of zinc from contaminated river sediments is small compared to the pH effect for salinities 25 to 38‰ as shown in Figure 8.41.

FIGURE 8.41. Variation of Desorption of Zinc in Sea Water of Different Salinities at Different pH

Piro et al. (1975) describes an interesting experimental study using anodic stripping voltammetry which permits the simultaneous determination of stable and radioactive ionic zinc in aqueous solution. With this apparatus it is possible to investigate the exchange reactions between stable ionic and complexed zinc and radioactive ionic zinc in NaCl solution and sea water. In NaCl (34‰ S), in presence of a complexing agent, after about one hour the ^{65}Zn is distributed between the noncomplexed and complexed fractions in the same way as the stable isotope, indicating a complete exchange reaction. On the other hand, adding ionic ^{65}Zn to sea water, the radioactive isotope is not uniformly distributed in all physico-chemical states present in the sea water but is diluted only in the ionic and particulated fractions. Even one year after the addition of ^{65}Zn , the radioactive zinc has not entered the complexed fraction. The consequences of this fractionation for the interpretation of tracer experiments and hazard evaluation are discussed.

These results raise an important question on the validity of all sorption-desorption experimentation in which added tracers are used.

Schneider and Block (1968) studied the adsorption of Zn(II) ions onto Rhine River sediments. Steady state adsorption was reached within 1 day.

Seymour et al. (1979) measured the KdZn for three sediments which had been sterilized by ^{60}Co treatment. An anoxic silty marine clay/seawater slurry gave a KdZn of $1.96 \pm 0.47 \times 10^3 \text{ ml/g}$. A marine silty sand/seawater slurry gave a value $\sim 7.5 \times 10^2 \text{ ml/g}$. A freshwater clay/lake water slurry gave a value of $5.16 \pm 0.77 \times 10^3 \text{ ml/g}$.

In two dialysis experiments Schell et al. (1979) studied the distribution of zinc in seawater and its reaction with sediments, plankton and organic detritus. Zinc which passed through dialysis bags holding sediments and plankton (see Table 8.9, Am Section) shows strong sorption tendencies. On the other hand a second dialysis experiment shows zinc remaining predominantly in solution (see Table 8.10, Am Section).

Essington and Nishita (1966), Kulikov (1968) and Salo and Saxen (1974) have investigated the effects of natural organics and chelating agents on the interactions of zinc with soils and sediments. The chelating agents DTPA, EDDHA and EDTA were shown to decrease zinc adsorption. CDTA had no effect on zinc interactions. Natural humic substances with high molecular weight were strongly associated with zinc in an estuarine environment. Soluble organic compounds of zinc would be expected in coastal waters.

Field Studies

Brungs (1963, 1964) added radiotracers to a 30,000-gal artificial pond and monitored their fate 80 days. Within one day of addition the soluble zinc content was about 10% of the spike addition and continued to slowly decrease over the 80 day period. Suspended solids accumulated most of the zinc and eventually settled to the bottom where after 80 days 98% of the zinc resided. After 80 days the observed KdZn for suspended and bottom sediments were 3.1×10^5 and 1.0 to $3.9 \times 10^3 \text{ ml/g}$, respectively.

Gloyna et al. (1966) and Yousef et al. (1970) report on the fate of ^{65}Zn in model river and estuary flumes. Numerous investigators have studied the fate of zinc present in the cooling waters of the Hanford reactors as it travels down the Columbia River to the Pacific Ocean. To better understand the interactions with sediments several laboratory experiments were also performed. Their results will also be described in this section as they relate specifically to the field studies.

Delaplane et al. (1969) and Glenn (1971) report on a detailed study of ^{65}Zn content of Columbia River sediments versus particle size, cation exchange capacity, C.E.C. and carbon content and mineralogy. As particle size decreases zinc content generally increases with some anomalies explained by valuable C.E.C. and carbon content. On a mass basis through the ubiquitous fine to medium sand contains 45% of the adsorbed zinc while the clay contains 16%.

Haushild et al. (1971, 1973a, 1973b) and Nelson and Haushild (1970) report on the second and spatial variations in ^{65}Zn concentrations in suspended and soluble fractions. During transit from Pasco to Vancouver (240 miles) the soluble fraction of zinc decreases 30 to 50% depending upon the year. At Pasco the soluble fraction ($<0.3\ \mu\text{m}$) accounts for 55 to 70% of zinc while at Vancouver the value is 18 to 23%. Gross (1966, 1967, 1972) and Gross et al. (1963), Carey et al. (1973), Forster and Hanson (1964) and Hanson (1967) studied the deposition of ^{65}Zn along the Columbia River mouth and coast of Washington and Oregon.

Nelson et al. (1966), Perkins et al. (1966), Robertson et al. (1973) and Battelle, Pacific Northwest Laboratories (1972) report on the speciation of ^{65}Zn found in the Columbia River water. In general the ^{65}Zn percentage particulate increased downstream from the reactors as shown in Table 8.88 although large variations occur depending on source. Evans (1973), Evans and Cutshall (1973), Johnson et al. (1967), Nelson et al. (1966), Osterberg et al. (1966) and Robertson et al. (1973) performed leaching experiments to determine the fate of adsorbed ^{65}Zn upon contact with sea water.

TABLE 8.88. Distribution of ^{65}Zn in Columbia River Water

	Distance from Reactor	% Particulate >0.3 μm	% Cationic	% Anionic	% Monionic	Source
Effluent	0	16	84	0	0	Nelson et al. (1966)
(N Reactor)	0	84	75	<1	<1	Robertson and Perkins (1975)
300 Area	25	51	47	0.5	1.5	Nelson et al. (1966)
Pasco	50	14	--	--	--	Perkins et al. (1966)
McNary Dam	90	77	22.6	0.2	0.2	Nelson et al. (1966)
		99	0.6	<0.1	0.5	Robertson et al. (1973)
Dalles Dam	175	84	15.4	0.3	0.3	Nelson et al. (1966)
Hood River	215	64	--	--	--	Perkins et al. (1966)
Vancouver	275	76	--	--	--	
		80	16.6	2.4	1.0	Nelson et al. (1966)

Robertson et al. loaded McNary Dam sediments (30 g) into a column and leached with eight liters of sea water. At most each liter removed about 1% of the total adsorbed zinc. Nelson et al. (1966) leached bed sediments with 1M ammonium acetate and removed only 1.6% of the adsorbed zinc. Acetic acid (pH 3) removed 19% of the zinc. Osterberg et al. (1966) found less than 5% of the ^{65}Zn adsorbed on Columbia River sediments to be ion exchangeable. Johnson et al. (1967) leached nine Columbia River bed sediments with sea water and 0.05M Cu SO_4 solution. The sediments were from the Columbia River estuary up to McNary Dam (290 miles inland). Sea water leaching 150 ml/15 g sediment released typically less than 1% of the ^{65}Zn , whereas greater than 25% of ^{54}Mn was released. In contrast an equal volume of copper sulfate solution leached 35 to 50% of the zinc. The other suggest "specific adsorption" as the binding mechanism for zinc. Specific adsorption was defined as the metal adsorbed and cannot be displaced by alkali, alkaline earth or ammonia ions, but can be displaced by other transition metal.

Evans (1973) and Evans and Cutshall (1973) found seawater did not remove ^{65}Zn from bed sediments even after 11 weeks contact but would remove 15 to

45% of the zinc adsorbed to suspended solids after 4 hr. Three hypotheses were suggested for the differing behavior: 1) the large surface area/volume ratio of the suspended particulates favored surface exchange reactions, 2) possible significant compositional differences between suspended solids and bed sediments, and 3) aging effect allowing surface bound zinc to slowly diffuse into internal lattices of bed sediment.

Summary

In water zinc is found in the cationic and at high pH neutral hydrolyzed form. Laboratory experiments suggest colloid formation and precipitation is a dominant adsorption mechanism. Other experiments suggest cation-exchange like mechanisms and hydrous oxide sorption play a role in zinc adsorption. In all instances the zinc K_d in marine environment was quite large, 10^3 to 10^4 . In fresh water environments the K_d is very sensitive to pH changes being in one instance 850 at pH 7 and 5000 ml/g at pH 8.

Organic chelation may affect the fate of zinc because of highly stable complexes.

ZIRCONIUM

Natural Sediment and Rock Distributions

The zirconium distribution and content in igneous and sedimentary materials are shown in Table 8.89. It should be noted that much of the zirconium contained in sedimentary rocks is present as resistate material such as zircon (ZrSiO_4), which is only very slightly soluble in any aqueous solution. The average content of worldwide soils is given by Vinogradov (1959) as 300 ppm zirconium.

TABLE 8.89. The Average Zirconium Content of Rocks
(Turekian and Wedepohl, 1961)

<u>Rock Type</u>	<u>Zr, ppm</u>
<u>Igneous Rocks</u>	
Ultramafic	45
Basaltic	140
Granitic, high Ca	140
Granitic, low Ca	175
Syenite	500
<u>Sedimentary Material</u>	
Shale	160
Sandstone	220
Limestone-dolomite	19
Pelagic clay	150 to 180
Pelagic carbonates	20
Manganese nodule	340

Brief Chemistry

Eighteen isotopes and two isomers of zirconium are shown. The naturally occurring isotopes are listed in Table 8.90. All are stable except ^{96}Zr which has a half-life listed as 3.6×10^{17} years (Weast, 1976). For all practical purposes, ^{96}Zr also is a stable isotope.

The immediate concern in radioactive waste disposal is for ^{95}Zr with a relatively short half-life of 65 days. Also obtained in much smaller yields as a fission product is the longer-lived ^{93}Zr (half-life 1.5×10^6 years), which is of long-term interest (Schneider and Platt, 1974). Zirconium-95 decays by β^- emission to ^{95}Nb which also emits a β^- and decays to stable ^{95}Mo .

TABLE 8.90. Natural Isotopes of Zirconium and Their Abundances (Weast, 1976)

Isotope	Abundance, %
^{90}Zr	51.46
^{91}Zr	11.23
^{92}Zr	17.11
^{94}Zr	17.40
^{96}Zr	2.80

The most stable and common form of zirconium in rocks is as the simple orthosilicate zircon, ZrSiO_4 . The only oxidation state of zirconium of any importance in aqueous solutions is Zr(IV) , though usually not as Zr^{+4} cations. Due to the high charge and a small atomic radius (0.72 Å in six-fold coordination, 0.84 Å in octahedral coordination (Shannon and Prewitt, 1969), zirconium ions are readily hydrolyzed in aqueous solutions. When an acid solution is neutralized with a base such as NH_4OH , hydrous zirconium oxide is precipitated rather than zirconium hydroxide. Zirconium compounds, such as ZrCl_4 , react violently with water, producing high acidity solutions. A zirconyl salt ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) is produced with liberation of hydrogen ions. A solution 0.05M in $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, for example, has a pH of 1. The equilibrium established is $\text{Zr}^{+4} + n\text{H}_2\text{O} \rightarrow \text{Zr(OH)}_n^{4-n} + n\text{H}^+$ and depends on the solution acidity.

According to Connick and McVey (1949), in 2.0 to 0.2M perchloric acid at 25°C, zirconium exists as Zr^{+4} and Zr(OH)^{+3} ions. At concentrations of perchloric acid of less than 0.2M, the zirconium species was probably Zr(OH)_2^{+2} . At or above 2.0M HClO_4 , zirconium exists exclusively as Zr^{+4} ions (Larsen and

Wang, 1954). When zirconium hydroxides are acidified with HCl, oxo cations (ZrO^{+2}) first appear, and not until the solution is 2N in HCl or higher, do appreciable amounts of Zr^{+4} ions appear (Lister and McDonald, 1951).

Zirconium forms very stable complexes with halogens of the type M_2ZrG_6 where M is a univalent metal and G is a halogen. Zirconium also forms a series of complexes with fluoride phosphate and sulfate ions and many of the organic ligands. Electrolysis of a solution of $\text{Zr}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, for example, produces hydrogen at the cathode and zirconium sulfate at the anode. Hence, the compound was $\text{H}_2 [\text{ZrO}(\text{SO}_4)_2]$, with zirconium in the complex anion $[\text{ZrO}(\text{SO}_4)_2]^{1-2}$. Since most of the waste solutions containing zirconium are near-neutral solutions, no Zr^{+4} ion should exist in solution. Only charged to neutral polymers and complexes of zirconium exist in the pH range of most radioactive waste solutions.

Solution Equilibria

The activity of various solution species with a change in pH and in equilibrium with zircon (ZrSiO_4) and soil SiO_2 is given in Figure 8.42. The thermodynamic data for all the hydrolysis species were selected from Baes and Mesmer (1976). Other solution species data were selected from Sillen and Martell (1964). Zirconium forms complexes with the common anions (F^- , Cl^- , SO_4^{2-} , NO_3^-). The significance of complexation of zirconium with these anions decreases in the following order: F^- , SO_4^{2-} , Cl^- , NO_3^- . Although zirconium forms complexes with common anions, ZrF^{3+} complex would be the only one which could contribute significantly in acidic environments (pH 3.5) to the total zirconium in solution. It can be seen from the diagram that the uncomplexed zirconium (Zr^{4+}) would exist in significant amounts only in very acidic solutions (pH < 1). The zirconium ions are hydrolyzed in solutions with pH values of greater than 1.0. The most dominant zirconium solution species with the conditions assumed in Figure 8.42 are ZrF^{3+} , $\text{Zr}(\text{OH})_4^0$, and $\text{Zr}(\text{OH})_5^-$ in pH ranges of <3.5, 3.5 to 6.25, and >6.25, respectively.

FIGURE 8.42. The Activity of Various Zirconium Species in Equilibrium with Zircon $[\text{ZrSiO}_4(\text{s})]$ and Soil Solution Silica ($\text{pH}_4\text{SiO}_4 = 3.1$) at $\text{PC}^- = \text{PSO}_4^- = 2.5$, $\text{pNO}_3^- = 3.0$ and $\text{pF}^- = 4.5$

If a waste solution containing zirconium is assumed to be in equilibrium with zircon and the conditions assumed in Figure 8.42, then the total activity of zirconium in solution would be lower than 10^{-14} over a pH range of 3.5 to 8.

The Zr^{4+} ion becomes increasingly hydrolyzed above pH 1. The Zr^{4+} content of the solution falls rapidly, as does the content of fluoride complex ZrF^{3+} , in favor of hydrolyzed species at higher pH values. Only at relatively low pH values of less than four do positively charged species of zirconium predominate. Because most soils and sediments buffer waters contacting them to pH 5 or higher, ion exchange probably plays a relatively minor role in zirconium retention by soils and sediments. Because of the formation of negatively charged complexes in solutions of pH > 6.5, zirconium adsorption would be expected to decrease with an increase in pH above 6.5.

Laboratory Adsorption Studies

Baranova and Polikarpov (1966, 1968) studied the adsorption of zirconium on shallow water marine muds. Adsorption was quite large.

Doshi et al. (1973) found zirconium was quantitatively adsorbed by manganese dioxide formed in situ in sea water.

Duursma and Gross (1971) and Duursma and Eisma (1973) summarize their work on zirconium adsorption in marine environments. They believe the adsorption is controlled by hydrolysis product $[Zr(OH)_n]^{4-n}$ precipitation. Their KD_{Zr} values determined are for initial concentrations of 1 ppm zirconium which is much higher than natural sea water concentrations of 0.03 ppb. The values reported in Table 8.91 may thus be overestimated because of precipitation. For Dutch (Wadden) Sea and Mediterranean Sea sediments the fine silt fractions 4 to 10 μm adsorb more zirconium than smaller clay fractions which suggests ion exchange is not the controlling mechanism. For a Black Sea sediment adsorption under oxidizing conditions was 33% greater than under reducing conditions ($KD_{Zr} \sim 1.8 \times 10^4$ versus 1.35×10^4).

TABLE 8.91. Zirconium Adsorption on Marine Sediments

Sediment	log K	est. Kd, ml/g	t _{1/2} Sorption, days
Atlantic Ocean	4.0 $\pm$ 0.6	1.5×10^4	4 $\pm$ 2
Pacific Ocean	4.2 $\pm$ 0.6	2.1×10^4	6 $\pm$ 3
Indian Ocean	4.2 $\pm$ 0.3	2.6×10^4	8 $\pm$ 2
Baltic Sea	4.9 $\pm$ 0.2	1.1×10^5	9.4
North Sea	4.2 $\pm$ 0.4	2.4×10^4	5
Mediterranean Sea	4.3 $\pm$ 0.6	2.7×10^4	5 $\pm$ 3
Black Sea	4.0 $\pm$ 0.1	1.6×10^4	8
Red Sea	4.3	2.7×10^4	6

Garder and Skulberg (1964) studied the adsorption of ^{95}Zr oxalate tracer (1.2 $\mu c/ml$) added to distilled water on to glacial clays. Detailed characterization of sediment water is given. For a sediment concentration of 64 mg/l it took three days for the percentage Zr-Nb adsorbed to stabilize. The KD_{Zr} after one day contact was dependent on the sediment concentration. At 16, 32,

64, 128 and 256 mg/l sediment concentration, the K_d was 5400, 4500, 3800, 2350 and 2400 ml/g, respectively. In the natural environment zirconium would not be expected to be present as an oxalate complex so the usefulness of these values should be questioned.

Klingeman (1965) and Klingeman and Kaufman (1965) studied the desorption of Zr-Nb traced clay-silt suspensions upon mixing of fresh water with sea water. Zirconium was found to be irreversibly adsorbed on the suspended solids suggesting ion exchange is not controlling zirconium sorption.

Rhodes (1957) determined the effect of pH on the distribution coefficient of zirconium-niobium on a Hanford soil. The soil was made up of 2% CaCO_3 with >2 mm diameter material, 6%; 2 to 0.2 mm diameter material, 67%; 0.02 to 0.2 mm diameter material, 19%; 0.02 to 0.002 mm diameter material, 6%; and <0.002 mm diameter material, 2%. The cation exchange capacity was 5 meq/100 g and the water past pH was 8.6. The bulk of the soil consisted of quartz, feldspars, augite, olivine and mica. The clay fraction contained mainly montmorillonite. The K_d values for zirconium as a function of pH are given in Table 8.92.

TABLE 8.92. Zircon-Niobium K_d Values as a Function of pH (Rhodes, 1957)

<u>pH</u>	<u>K_d, ml/g</u>	<u>pH</u>	<u>K_d, ml/g</u>
0	82	8.3	282
1	1028	9.6	90
2.6	1340	10.2	104
4.1	>1980	11.0	180
6.4	>1980	12.2	1980
7.7	>1980	14.0	1980

Rhodes considered that the dips in zirconium K_d for pH 8 to 12 were due to a charge alteration of the zirconium polymer or colloid within this pH range.

Benson (1960) reported a visible, white precipitate in systems containing $3 \times 10^{-2} M$ zirconium. The uptake of trace ^{95}Zr was not appreciably different from that noted in the presence of carrier indicating that precipitation also occurred at the trace concentration. Zirconium was not appreciably affected by the presence of other cations unless the pH was below 2. Benson also reported that carbonate, oxalate and citrate ions inhibited zirconium uptake on soil over a wide pH range, probably because of the formation of complex anionic species.

Sorathesn et al. (1960) stated that ^{95}Zr behaved like a colloid at pH 6 to 9. They reported the zirconium Kd on illite at 7 days equilibration time to be 24,470 ml/g.

Prout (1959) reported that tests made at pH 4 with $10^{-3} M C_2O_4^{2-}$ showed adsorption of zirconium-niobium on soil to be inhibited, but at pH 8, the oxalate did not seriously affect the removal of zirconium-niobium. Schulz (1965) reported that zirconium and niobium were two of the elements that were adsorbed by soil in a very immobile form.

Fallout material on soil from an underground nuclear explosion was used by Essington et al. (1965) to determine the leaching effects of water, HCl and chelating agents. The soil was suspended in 25 ml of solution and equilibrated for up to 106 days. The 10^{-4} molar chelating agents in solution included sodium-diethylenetriaminepentaacetate, sodium-cyclohexane-1,2-diaminetetraacetate, sodium-ethylenediamine di(o-hydroxyphenylacetate) and 0.1M HCl. Zirconium-95/Niobium-95 was identified in the original soil. Chelating agents, HCl and water equilibrations did not appreciably increase ^{95}Zr - ^{95}Nb solubility. In column studies with Yolo soil (pH 7.9), Sorrento soil (pH 7.8) and Hanford soil (pH 6.6), water and calcium-diethylene-triaminepentaacetate ($10^{-4} M$) leaches of 7 days produced no detectable ^{95}Zr - ^{95}Nb in the effluent solution. The dominant clay minerals in the Hanford, Sorrento and Yolo soils were illite, kaolinite and montmorillonite.

According to Schulz (1965), the zirconium in soils is either very strongly adsorbed by the clay particles or is present as an insoluble oxide or hydroxide. In either case, the zirconium in the soil is immobile.

Harrison (1969), using nuclear debris contaminated with ^{95}Zr - ^{95}Nb as a source, approached equilibrium from the direction of starting with the radionuclide on the solid. The leaching produced ^{95}Zr - ^{95}Nb Kd values of 5,200 to 17,000 ml/g in distilled water as a function of particle size range (<4000 to <62 μm), 790 to 2700 ml/g in synthetic sea water for the same particle-size range and 270 to 1200 ml/g in 1M ammonium acetate for that particle size range. An implication of this work is that cation exchange is involved because the ^{95}Zr - ^{95}Nb Kd values are sensitive to competing ion concentrations.

Field Studies

Eichholz et al. (1967) investigated the partitioning of dissolved radionuclides between suspended sediment particles and aqueous solutions. Several natural water samples were characterized and used in the adsorption studies as suspended solids sources (see Table 8.93). A fission product mixture was added to the natural water samples, the system equilibrated and the water recovered and filtered. The adsorption of ^{95}Zr and daughter ^{95}Nb are shown in Table 8.92. A large portion of the zirconium was associated with the particulate matter in a highly concentrated form.

Adsorption does not appear to be a direct function of suspended solids content but has to include a consideration of dissolved solids content, pH and solids composition before the adsorption results begin to make any sense. The high ^{95}Zr adsorption on Chattahoochee River suspended solids was due to the low dissolved solids content (31 ppm), which suggests that a positively charged zirconium species was involved.

Magno et al. (1970) investigated radionuclides from the Nuclear Fuel Services Plant in Western New York that were migrating through the plant effluent lagooning system. They estimated that greater than 90% of the ^{95}Zr discharged from the plant was deposited by sedimentation in the lagoon system.

TABLE 8.93. Adsorption of ^{95}Zr and ^{95}Nb on Suspended Solids in Natural Waters (Eichholz et al., 1967)

Source	Suspended Solids, mg/l	^{95}Zr Adsorption, %	^{95}Nb Adsorption, %
Colorado River	229	61.1	33.3
Camp McCoy	12	50.0	4.7
Bayou Anacoco	24	80.5	23.8
Lodgepole Creek	965	81.3	---
Chattahoochee River	131	88.4	18.9
Billy's Lake	8	53.9	8.9

Perkins et al. (1966) and Nelson et al. (1966) found about 70% of the $^{95}\text{Zr-Nb}$ in the Columbia River at Hanford was on particulate matter ($>0.3\ \mu\text{m}$). The percentage did not change downriver all the way to the Pacific Ocean suggesting further significant dissolution-precipitation was not occurring.

Robertson and Perkins (1975) studied the distribution of ^{95}Zr between particulate, cationic, anionic and nonionic species for cooling water leaving N Reactor at Hanford. The zirconium was 81% particulate, 11% anionic, 6% cationic and 2% nonionic. After percolating through alkaline sandy soil less than 10^{-4} of the original zirconium was observed in springs along the bank of the Columbia River.

Spitsyn et. al. (1958) used an alkaline solution (4 to 8 g NaOH/l , 200 g NaNO_3/l) and an acidic solution [6 to 8 g HNO_3/l , 200 g $\text{Al}(\text{NO}_3)_3/\text{l}$] in laboratory and field studies of radionuclide migration rates. Zirconium was adsorbed and retained by a sand in field tests near the point of injection of the waste solutions for both acidic and alkaline solutions. Little movement was indicated even under acidic conditions.

Summary

Trace concentrations of zirconium are strongly adsorbed on sediments. Rhodes (1957) did observe a dip in K_d values between pH 8 to 12, probably due

to the prevalence of uncharged or anionic zirconium species over this pH range (Figure 8.42). There are some evidence for affects caused by competing cations at near-neutral pH, suggesting at least partial removal by an ion exchange mechanism of polymerized or colloidal species (Eichholz et al., 1967; Harrison, 1969). Zirconium is well-adsorbed by the sediment over the normal pH range of 6 to 8. Carbonate, oxalate and citrate complexes of zirconium have been reported to migrate rapidly through soil columns (Bensen, 1960), but the concentrations of the hazards used in these experiments were inordinately large and they would not be expected in nature. In general zirconium can be assumed to be bound strongly to sediments and suspended solids.

CONCLUSIONS AND EVALUATION

The solution ions exist in dynamic equilibrium with bed sediment and suspended sediment. Many factors that are inherent to the solid matrix and the solution can influence the concentration of the element and its species in solution. These factors include pH, Eh, CEC, type and amount of soil minerals, solid phases of the element, complexing ligands, and competing ions. In order to determine the distribution of the element between solution and solid and its reactions with the solid matrix, the identity and relative magnitude of the various factors are required. Such information would help predict the solution concentrations of the element and help extrapolate the results to other situations. However, the data presented in the Element Literature Review section indicate that there is a general lack of systematic evaluation of various factors that determine element-solid matrix interactions, and little information at present is available to quantify the importance of the various factors. At best, the available data suggest trends for the influence of some of the factors that control solution concentrations and interaction with solid matrices. This type of information would not be very useful for quantitatively predicting the general fate of radionuclides in the environment. Additional research required for general understanding of the behavior of radionuclides is outlined at the end of this section.

Factors Influencing Adsorption of Radionuclides on Geologic Media

Some of the factors that have been reported to influence the adsorption of elements by geologic media are listed for the studied elements in Table 8.94.

An "X" indicates that a given factor was reported to influence adsorption of that element (present as a radionuclide). The results reported in Table 8.94 are qualitative only. In most cases, the authors did not definitively show that a specific factor was operative, but hypothesizes that it was. Since these data cannot be used for quantitative predictions, they are mainly presented for use as guidelines in future experiments or environmental assessments. The probable principal adsorption mechanisms were deduced from an examination of the factors reported for each element. For example, colloid formation is a good indication of precipitation, as pH also may be. An

TABLE 8.94. Factors Reported to Affect Adsorption of Radioelements over the pH Range of 4 to 9

Element	pH	Eh	CEC(a)	Competing Ions	Selectively Adsorbed On	Factors			Probable Adsorption Mechanisms(b)
						Inorganic Ligands	Complex Ions Organic Constituents	Colloid Formation	
Am	X		X	X		X			IE, PPT
Sb		X			Iron Oxides	X	X	X	PPT, OX
C					OM		X		BIO
Ce	X					X	X	X	IE, PPT
Cs			X		Zeolites, Micas				IE
Co	X				Illite, Iron Oxide	X	X	X	PPT, OX
Cm	X					X		X	PPT
Eu	X			X		X		X	IE, PPT
Fe	X	X		X		X	X	PPT, OX	
I					OM		X		OM
Mn		X	X	X	Hydrous oxides		X		OX
Np						X		X	UNK
P	X	X			Hydrous oxides, OM		X		OX, BIO
Pu	X	X	X			X	X	X	IE, PPT
Pm	X			X			X		IE, PPT
Ra			X	X	Zeolites, Barite				IE
Ru	X				OM	X	X		PPT
Sr	X		X	X	calcite, Zeolites	X	X		IE
Tc							X		UNK
Th	X		X		OM	X	X	X	IE, PPT
³ H					H ₂ O				NONE
U	X	X	X		OM	X	X		PPT, IE
-Zn			X		Hydrous Oxide		X	X	IE, PPT
Zr	X				OM	X	X	X	PPT

(a) CEC = Cation Exchange Capacity

(b) IE = Ion exchange, OM = Organic matter adsorption, PPT = Precipitation Hydrolysis Colloids, UNK = Unknown, OX = Hydrous Oxides, BIO = Biological

adsorption sensitivity to cation exchange capacity, competing ions and system pH usually indicates an ion exchange adsorption mechanism. There is, admittedly, a certain amount of value judgment that went into the summation process because in some cases the literature was ambiguous and vague concerning adsorption-influencing factors, and in other cases, the experimental work has yet to be done.

In addition to concentration, the nature of the solution species would have a tremendous effect on the radionuclide interaction with the geologic media and on the mobility of the radionuclides. Very few data are available in the literature delineating species that have been identified in natural environments. Thermodynamic data were used to develop solution species diagrams to predict the predominant solution species. There are several limitations and drawbacks to this approach and the author admonishes the reader to place minor emphasis on such projections. The predicted nature of the predominant solution species of various elements are reported in Table 8.95. The environmental conditions assumed for Table 8.95 data include a pH range of 4 to 9, pO_2 range of 0.68 to 80 atmospheres, pCO_2 of 1.52 to 3.52 atmospheres, pCl of 0.45 to 3.0 and $pNO_3 = pSO_4^{2-} = 3.0$, pF^- 4.5, and pH_2PO_4 5.0. It should be pointed out that a change in environmental conditions, in addition to the ligands not considered in the above assumptions, may change the nature of the solution species. Depending upon the given chemical environment, several species of an element can exist in solution. Cesium, cobalt, promethium, radium, strontium, and tritium would be expected to exist predominantly as uncomplexed solution species as Cs^+ , Co^{2+} , Pm^{3+} , Ra^{2+} , Sr^{2+} , and $^3H^+$. Certain elements such as plutonium, neptunium and uranium can exist in acidic solutions in an oxidizing environment as uncomplexed solution ions (PuO_2^{2+} , PuO_2^+ , NpO_2^+ , UO_2^{2+}). Some of the elements such as curium, thorium and zirconium hydrolyze very readily even in acidic environments, so they mainly exist as hydrolyzed species $CmOH^{2+}$, $Cm(OH)_2^+$, $Th(OH)_3^+$, $Zr(OH)_4^0$, $Zr(OH)_5^-$. Some of the common inorganic ligands (CO_3^{2-} , SO_4^{2-}) form strong complexes with americium, curium, europium, neptunium, plutonium and uranium so that these ligands would influence the concentration of these elements in solutions.

TABLE 8.95. Predominant Solution Species of Elements in a pH 4 to 9, pO_2 0.68 to 80, pCO_2 1.52 to 3.52, pCl^- 0.45 to 3/0, $pNO_3 = pSO_4^{2-} = 3.0$, pH^- 4.5 and pH_2PO_4 5.0 Environment Without Organic Ligands

Elements	Predominant Solution Species of Elements		
	Little Affected by Oxidation-Reduction	In an Oxidizing Environment	In a Reducing Environment
As	As^{3+} , $AsSO_4^+$, $As(OH)^{2+}$, $AsCl^{2+}$		
Sb		$HSbO_2^0$, $Sb(OH)_3^0$, $SbOF^0$	SbO^+
C	HCO_3^- , organic matter	$Sb(OH)_4$	
Ce	Ce^{3+} , $CeSO_4^+$		
Cr		CrO_4^{2-} , Cr^{3+} , $Cr(OH)^{2+}$, $Cr(OH)_2^+$	Cr^{3+} , $Cr(OH)^{2+}$, $Cr(OH)_2^+$
Cs	Cs^+	$Cr_3(OH)_4^{5+}$	$Cr_3(OH)_4^{5+}$
Co	Co^{2+} , $Co(OH)_2^+$		
Cm	Cm^{3+} , $CmOH^{2+}$, $Cm(OH)_2^+$		
Eu	Eu^{3+} , $EuSO_4^+$, $Eu_2P_2O_7^{2+}$		
Fe		$Fe(OH)_2^+$, $Fe(OH)_3^0$	Fe^{2+}
I	I^- , IO_3^-		
Mn	Mn^{2+}		
Np		NpO_2^+ , $NpO_2HPO_4^-$, NpO_2HCO_3	$NpOH^{3+}$, Np^{4+}
P	HPO_4^{2-} , $H_2PO_4^{1-}$, PO_4^{3-} , organic		
Pu		PuO_2^{2+} , $PuO_2(CO_3)(OH)_2^{2-}$, PuO_2	$PuOH^{2+}$, Pu^{3+} , $PuCl^{2+}$
Pm	Pm^{3+}		
Ra	Ra^{2+}		
Ru		$Ru(OH)_2^{2+}$, RuO_4^- , RuO_4^{2-}	RuO_4^-
Sr	Sr^{2+}		
Tc		TcO_4^-	Tc^{2+}
Th	ThF^{3+} , $Th(OH)_3^+$		
3H	$^3H-O-H$		
U		UO_2^{2+} , UO_2F^+ , $UO_2(OH)_2^0$, $UO_2(CO_3)_3^{4-}$, UO_2Cl^+	UO_2^{2+} , UOH^{3+} , UO_2^+ , $UO_2(CO_3)_3^{4-}$
Zn	Zn^{2+} , $Zn(OH)_2^0$		
Zr	$Zr(OH)_4^0$, $Zr(OH)_5^-$, ZrF^{3+}		

Oxidation-reduction conditions would predominantly influence the nature of the solution species of antimony, chromium, iron, neptunium, plutonium, technetium and uranium.

Based upon the nature of the predominant solution species, qualitative predictions regarding the adsorption and movement of various elements can be made. Bed and suspended sediments mainly show cation exchange capacities (since they carry a large net negative charge) and to a limited extent, anion exchange capacities. Thus, most cations would react with sediments and transport at speeds slower than the water. Relative to each other, the trivalent cations generally move the slowest, the divalent cations at intermediate velocities and the monovalent cations most rapidly. Tritium is unique in that it readily substitutes for hydrogen in water and migrates, therefore, at the same velocity as water. Complicating factors include a higher selectivity of a sediment component for a given cation or a more successful hydrogen ion competition with one cation relative to another. The relative mobilities of strontium and cesium at low pH is a good example of the latter effect. Strontium is much more mobile at low pH than is cesium.

The simple anions tend to migrate with little reaction because usually a pH of less than 4 is required to activate a significant anion exchange capacity. However, both I and Tc which exist predominantly as anions (I^- , TcO_4^-) undergo other reactions with organic ligands that can greatly slow their migration.

The migration and retention of inorganic complex species (mononuclear and polynuclear) would also be dependent upon the charge and size of the species. Positively charged species would move slower than the negative charged species. The highly charged metal ions tend to polymerize or form colloidal size, charged precipitates. The trivalent metal ions (Am, Cm, Sb, Ru) and quadrivalent or higher charged metal ions (Pu, Th, U, Zr) are known to form polymers. Initially, at lower pH, the polymers are positively charged and at pH 9 become increasingly negatively charged. The result is good adsorption and very slow movement at acidic to neutral pH, and greatly lessened adsorption and rapid migration from pH 9 upward.

The behavior of organic complexed species of elements is difficult to predict because of the lack of knowledge regarding the exact nature of the organic ligands, a wide variation in amounts and types of organic ligands, and the size and solubility of these organics. These organic materials can either retain the element or complex it in a form that migrates readily. The source of these organic ligands can be the radioactive waste solutions containing the synthetic organic ligands such as TBP and/or the organic ligands produced by flora and fauna.

The metal ions that take part in replacement reactions depend upon the size and charge of the species involved and the ability of the final mineral product to accept that species into its growing structure. Apatite, for example, accepts into its structure a wide range of metal ions such as strontium, uranium and probably americium and cerium. Cobalt replaces calcium in calcite, and radium and strontium replace barium in barite. These metal ions are buried in the replacement product crystal structure and are effectively retained unless a changing chemical environment causes instability and dissolution of the crystal.

Additional Research Needs

The areas that require more work to better understand radionuclide interactions with sediments include:

1. Determination of radionuclide adsorption mechanisms.

Additional work is required in the area of radionuclide adsorption, mechanisms (ion exchange, precipitation, coprecipitation, hydrolysis and colloid formation). There are many K_d values that include several sediment adsorption mechanisms operating simultaneously for a range of elemental species. Definitive experimental data that would allow deduction of probable adsorption mechanisms for most elements are lacking in the literature. In addition, the environment in which a given adsorption mechanism predominates should be delineated as well.

2. Factors that influence radionuclide/geologic media interactions.

The influence of different factors (such as pH, Eh, complexing ligands, competing ions, CEC, type and amount of minerals, solid phases of element) on the magnitude and extent of adsorption of radionuclides by the geologic media needs to be evaluated.

3. An experimental consideration of the effects of redox potential on radionuclide migration.

Stagnant conditions present in bed sediments, especially organic rich lake and estuarine, usually form reducing conditions. There has been little examination of the effects of radionuclide migration in the low oxygen environments which will be encountered under these conditions. It should be mentioned though that suspended sediments and the thin layer in contact with the water column are very seldom anoxic. The water column and sediment interface is the region of biological interest and thus for environmental assessments results for oxidizing environments would be most relevant (although diffusion from anoxic bed sediments can act as a slow release source term).

4. Characterization and influence of organic ligands on radionuclide migration.

The existing thermodynamic data on species are incomplete in many cases, and of dubious quality in other cases. The thermodynamic data should be confirmed by experimental evidence on radionuclide adsorption and migration. Thermodynamic data on the radionuclide complexes with natural water organic components are essentially nonexistent. Note in Table 8.95 that radionuclide reactions with organic material were reported for 17 of the 25 radionuclides reviewed. Hence, what may prove to be a most important influence on radionuclide adsorption and migration is one of the least understood. The sources of organic materials in the environment capable of forming complexed species with radionuclides include the many industrial wastes from various manufacturing processes disposed to the atmosphere and surface waters, the organics included in municipal sewage treatment effluents also disposed to surface waters, the various pesticides and herbicides used during farming operations

contained in the atmosphere and irrigation runoff, humic substances and decaying plant and animal remains already present in the aquatic environment along with the associated living microflora and fauna. With such varied sources and types of organic ligands, a large quantity of work remains to be done in even identifying the metal ligand species involved in radionuclide migration on the land surface. For carbon and phosphorus which are intimately tied to biological cycling this point is most germane.

5. Thermodynamic data determinations for several solution species.

Thermodynamic data are badly needed for several complex solution species of different elements. For example, the ruthenium complexes $\text{RuNO}(\text{NO}_2)_2\text{OH}(\text{H}_2\text{O})_2$ and $\text{RuONO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ were reported as very stable and commonly found in nuclear waste solutions by several authors. Yet no firm thermodynamic data for these two complexes were located in the literature. When the data are determined, they may drastically change the order and specification for ruthenium solution species reported.

6. The generation of Kd data that can be used in a comparative mode.

The experimental conditions, including sediment and solution characterization, were only sketchily given in most references, or not given at all in most cases. Hence, the Kd values reported are the best available, but evaluation of these data by any objective methodology would result in discarding a large number of them. The requirements for determination of a Kd value that could be used in a comparative mode were listed in the laundry list functional dependency section. A program to determine such Kd values for terrestrial environments is now underway by the Office of Nuclear Waste Isolation (Serne, 1978).

7. Maintenance of a bank of such Kd data.

A bank of the Kd data should be maintained and kept current. The data could be computer-stored and made available to all personnel concerned with waste management and environmental assessment upon request. The present system has resulted in using unevaluated Kd values that are often not applicable to the case in point.

8. Determination of radionuclide adsorption and desorption reaction kinetics with sediments.

Several authors that have equilibrated solutions containing radionuclides with sediments for several weeks have reported that a considerable period of time was required to attain equilibrium. Kinetic studies 1) could indicate radionuclide adsorption mechanisms, 2) could help in separating adsorption rates due to different mechanisms, and 3) would help in increasing the confidence in extrapolating the predicted results into the future. Kinetic or time dependent information is especially important in the transport of radionuclides in flowing bodies of water such as streams, rivers, estuaries and near shore or coastal zones. The rate of water and suspended solids movement in these environments may be quite high compared to the rate of approach to chemical equilibrium for some radionuclides. If one is striving to attain a quantitative transport model with a relatively fine spatial grid, the fact that non-equilibrium adsorption may predominate needs to be addressed. A critical assessment is needed to evaluate typical mixing times or contact times between nuclear wastes and bed and suspended sediments in the field. As most laboratory determinations of K_d are performed in a closed batch system at solids to solution ratios much higher than found in nature the rate of approach to equilibrium in the laboratory may differ significantly from the field situation. Actual field verification studies would be quite complicated and expensive; thus, it is suggested that more attention be given to attempts to simulate field conditions in the laboratory. As it is typically soil or earth science chemists who perform K_d experiments and these disciplines usually are not familiar with hydraulics or sediment transport, some multidisciplinary cross talk would be fruitful. If physical oceanographers and hydraulics engineers and the chemists would sit down and familiarize themselves with the total field system, more relevant experiments would result.

Although it is impossible to generalize and establish one K_d for each nuclide, computer modelers request input values constantly. Thus to satisfy the needs of modelers the following table was constructed, albeit rather arbitrarily from the literature review in this document. Fresh water and

marine environments were separated to show the importance of cation competition for those nuclides which adsorb by ion exchange reactions. Also marine environments have a very narrow pH range around the mean value of pH 8.1. For elements which adsorb by hydrolysis and colloidal polymer precipitation Kd values in sea water are often larger than fresh water, which shows a wider pH range and less tendency to promote coagulation.

Table 8.96 is only for gross generalizations. Median Kd values should be considered to vary $\pm$ an order of magnitude for those values greater than 10^2 .

TABLE 8.96. Gross Average Kd ml/g for Studied Elements with Emphasis on Oxidizing Conditions

Elements	Fresh Water		Sa Water	
	Range	Median	Range	Median
Am	85-40,000	5×10^3	97-650,000	10^4
Sb*	--conflicting data--		--conflicting data--	
C	--no available data--		--no available data--	
Ce	7,800-140,000	10^4	9,000- 10^7	5×10^4
Cr*	0- 10^3	low	0- 10^3	low
Cs	$50-8 \times 10^4$	10^3	$17-10^4$	3×10^2
Co	1,000-71,000	5×10^3	7,000-300,000	10^4
Cm	100-70,000	5×10^3	--no data--	
Eu	200-800	5×10^2	5,000-130,000	10^4
Fe*	$10^3 - 10^4$	5×10^3	20,000-450,000	5×10^4
I	0-75	10	0-100	10
Mn*	$10^2 - 10^4$	10^3	$10^2 - 10^4$	10^3
Np*	0.2-127 10		--no data--	
P*	---	High	---	High
Pu	$10^2 - 10^7$	10^5	$10^2 - 10^5$	5×10^4
Pm	$10^3 - 10^4$	5×10^3	$10^3 - 10^5$	10^4
Ra	$10^2 - 10^3$	5×10^2	$10^1 - 10^3$	10^2
Ru	complicated chemistry (multiple species)	variable	complicated chemistry (multiple species)	variable
Sr	8-4,000	1,000	6-400	50
Tc*	0- 10^2	5	0	0
Th	$10^3 - 10^6$	10^4	$10^4 - 10^5$	5×10^4
^3H	0	0	0	0
U*	$16-10^3$	5×10^1	$10^2 - 10^4$	5×10^2
Zn	$10^2 - 10^3$	5×10^2	$10^3 - 10^4$	5×10^3
Zr	$10^3 - 10^4$	10^3	$10^3 - 10^5$	10^4

*Very dependent on oxidation - reduction conditions.

REFERENCES FOR CHAPTER 8

- Aarkrog, A. 1971. "Radioecological Investigations of Plutonium in an Arctic Marine Environment." Health Physics. 20:31-47.
- Aarkrog, A. 1972. "Re-examination of Plutonium at Thule, Greenland, in 1970." EUR-4800. 1&2:1213-19.
- Adams, J. A. S. and C. E. Weaver. 1958. "Thorium-to-Uranium Ratios as Indicators of Sedimentary Processes -- An Example of Geochemical Facies." Bull. Am. Petrol. Geol. 42:387.
- Adams, J. A. S., J. K. Osmond, and J. J. W. Rogers. 1959. "The Geochemistry of Thorium and Uranium." In: Physics and Chemistry of the Earth. 3. L. H. Ahrens, F. Press, K. Rankama, and S. K. Runcorn (eds.), pp. 298-348.
- Adams, J. A. S. and K. A. Richardson. 1960. "Thorium, Uranium, and Zirconium Concentrations in Bauxite." Econ. Geol. 55:1653.
- Adams, J. A. S., J. K. Osmond, and J. J. W. Rogers. 1959. "The Geochemistry of Uranium and Thorium." Phys. Chem. Earth. 3:298.
- Adams, W. H. 1971. Solubility of Plutonium-238 Labeled PuO₂ in Los Alamos Tap Water. LADC-12900.
- Agamirov, S. S. 1963. "Precipitation of U in Black Sea." Geokhimiya. 1:92-3 (in Russian).
- Ahlstrom, S. W. and H. P. Foor. 1976. Multicomponent Mass Transport Model: Theory and Numerical Implementation (Discrete-Parcel-Random-Walk Version). Battelle, Pacific Northwest Laboratories, Richland, WA.
- Ahrens, L. H. 1952. "The Use of Ionization Potentials. Part I. Ionic Radii of the Elements." Geochim. et Cosmochim. Acta. 2:155.
- Albenesius, E. L. and R. S. Ondrecin. 1960. "Nuclear Fission Produces Tritium." Nucleonics. 18:100.
- Albenesius, E. L. 1959. "Tritium as a Product of Fission." Physics Review Letters. 3:274.
- Alberti, G., C. Bettinali, G. Grassini and F. Silvestro. 1959. "Leaching Tests of Uranium of Canale Monterano." In: Studia Ricerche Della Divisione Geomineraria. 2:129-53.
- Alberts, J. J., M. A. Wahlgren, C. A. Reeve, and P. J. Jehn. 1974a. Sedimentary ^{239,240}Pu Phase Distributions in Lake Michigan Sediments.

- Alberts, J. J., M. A. Wahlgren, P. J. Jehn, D. M. Nelson, and K. A. Orlandini. 1974b. Chemical Speciation of $^{239,240}\text{Pu}$ and ^{137}Cs in Lake Michigan Waters. AML-75-3 (Pt. 3), pp. 89-96.
- Ames, L. L. and D. Rai. 1978. Radionuclide Interactions with Soil and Rock Media, Vol. 1: Processes Influencing Radionuclide Mobility and Retention. Draft Report to Office of Radiation Programs U.S.E.P.A.
- Ames, L. L., Jr. 1961a. "Anion Metasomatic Replacement Reactions." Economic Geology. 56:521-532.
- Ames, L. L., Jr. 1961b. "The Metasomatic Replacement of Limestones by Alkaline, Fluoride-Bearing Solutions." Economic Geology. 56:730-739.
- Ames, L. L., Jr. 1961c. "Cation Metasomatic Replacement Reactions." Economic Geology. 56:1017-1024.
- Ames, L. L., Jr. 1960a. Anion Replacement Reactions for the Removal of Strontium from Aqueous Solutions. HW-66383.
- Ames, L. L., Jr. 1960b. "Some Cation Substitutions During the Formation of Phosphorite from Calcite." Economic Geology. 55:354-362.
- Ames, L. L., Jr. 1959a. The Removal of the "Bone-Seeking" Group of Radioisotopes from Solution by a Calcite-Phosphate Reaction. HW-60412.
- Ames, L. L., Jr. 1959b. Zeolite Extraction of Cesium from Aqueous Solutions. HW-62607.
- Amiel, A. J., D. S. Miller, and G. M. Friedman. 1972. "Uranium Distribution in Carbonate Sediments of a Hypersaline Pool, Gulf of Elat, Red Sea." Isr. J. Earth Sci. 21:187-91.
- Amy, J. P. 1971. Contribution to the Study of the Migration of Ruthenium-106 in Soils. RFP-Trans-140.
- Andelman, J. B. and T. C. Rozzell. 1970. "Plutonium in the Water Environment. I. Characteristics of Aqueous Plutonium." In: Radionuclides in the Environment. Adv. in Chem. Ser. No. 93. Amer. Chem. Soc., Washington, DC, pp. 118-137.
- Anders, E. 1960. The Radiochemistry of Technetium. Nuclear Sci. Ser. Nat. Acad. Sci. - Nat. Res. Council. NAS-NS 3021.
- Anonymous. 1960. Summary Report on I. The Control of Radium and Thorium in the Uranium Milling Industry, II. Radium-226 Analysis Principles, Interference and Practice, III. Current Winchester Laboratory Projects. WIN-112.

- Anonymous. 1968. Radioactivity Transport in Water. Interaction Between Flowing Water and Bed Sediments. ORO-490-17. 165 p.
- Anonymous. 1973. 241-T-106 Tank Leak Investigation. ARH-2874.
- Antal, P. S. 1966. "Diagenesis of Thorium Isotopes in Deep Sea Sediments." Limnol. Oceanog. 11:278-92
- Armands, G. and S. Landergrén. 1960. "Geochemical Prospecting for Uranium in Northern Sweden: The Enrichment of Uranium in Peat." Intern. Geol. Congr., Rept. 21st Session, Copenhagen, Part 15:51-66.
- Armstrong, M. E., L. W. Canter, and E. F. Gloyna. 1968. "Transport of Organic and Radioactive Wastes." Water Wastes Eng. 5:54-6.
- Arnold, W. D. and D. J. Crouse. 1971. Radioactive Contamination of Copper Recovered from Ore Fractured with Nuclear Explosions. ORNL-4677.
- Arnold, W. D. and D. J. Crouse. 1964. "Radium Removal from Uranium Mill Effluents with Inorganic Ion Exchangers." I&EC Process Design and Development. 4:335-337.
- Ashizawa, F. T. and P. K. Kuroda. 1957. "The Occurrence of the Short-Lived Iodine Isotopes in Natural and in Depleted Uranium Salts." J. Inorg. Nucl. Chem. 5:12-22.
- Aston, S. R. and E. K. Duursma. 1973. "Concentration Effects on ^{137}Cs , ^{65}Zn , ^{60}Co , and ^{106}Ru Sorption by Marine Sediments with Geochemical Implications." Netherlands Journal of Sea Research. 6:225-240.
- Baes, C. F., Jr. and R. E. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.
- Baetsle, L. and P. Dejonghe. 1962. "Investigations on the Movement of Radioactive Substances in the Ground. Part III: Practical Aspects of the Program and Physiocochemical Considerations." In: Ground Disposal of Radioactive Wastes. TID-7628, pp. 198-210.
- Baetsle, L. H., P. Dejonghe, W. Maes, W. E. Simpson, J. Souffriau, and P. Staner. 1964. Underground Radionuclide Movement. EURAEC-703.
- Baker, J. H., W. A. Beetem, and J. S. Wahlberg. 1964. Adsorption Equilibria Between Earth Materials and Radionuclides, Cape Thompson, Alaska. TID-20638.
- Balashov, U. A., et al. 1964. "The Effects of Climate and Facies Environment on the Fractionation of the Rare Earths During Sedimentation." Geochemistry International. 10:951-969.

- Baranov, V. I. and L. A. Khristianova. 1963. "Radioactivity of Ocean Sediments." Khim. Zemnoi Kory, Akad. Nauk SSSR, Tr. Geokhim. Konf. 1:401-8.
- Baranov, V. I., A. B. Ronov, and K. G. Kinashova. 1956. "On Geochemistry of Dispersed Thorium and Uranium in Clays and Carbonate Rocks of Russian Platform." Geokhimiya. No. 3:3-8.
- Baranov, V. I. and N. I. Titaeva. 1961. "Uranium, Thorium, Radium, and Ionium Content in the Quaternary Deposits of the River Lena." Geokhimiya. No. 2:110-14 (in Russian).
- Baranova, D. D. and G. G. Polikarpov. 1968. "Sorption and Desorption of Radionuclides by Shallow-water Sediments of the Black Sea." Okeanologiya. 8:427-30 (in Russian).
- Baranova, D. D. and G. G. Polikarpov. 1966. Adsorption and Desorption of Radionuclides by Shallow-water Sediments of the Black Sea. Oceanology of the Academy of Sciences of the USSR, pp. 341-344.
- Bartlett, R. J. and J. M. Kimble. 1976. "Behavior of Chromium in Soils: I. Trivalent Forms." J. Environ. Qual. 5(4):379-386.
- Baturin, G. N. 1968. "Geochemistry of Uranium in the Baltic Sea." Geokhimiya. 3:377-81 (in Russian).
- Baturin, G. N. 1966. "Uranium Content in Caspian Sea Sediments." At. Energ. 21:515-16 (in Russian).
- Baturin, G. N. 1969. "Uranium in the Surface Layer of Sediments in the Northwestern Part of the Indian Ocean." Okeanologiya. 9:1031-7 (in Russian).
- Baturin, G. N. 1971. "Uranium in Solutions of Ooze Deposits in the Southeastern Atlantic." Dokl. Akad. Nauk. SSSR. 198:1186-1188 (in Russian).
- Baturin, G. N. 1973a. "Uranium in the Contemporaneous Sedimentary Cycle of the Sea." Geokhimiya. 9:1362-1372 (in Russian).
- Baturin, G. N. 1973b. "Uranium During Sedimentation in the Black and Azov Seas." Litol. Polez. Iskop. 5:21-32 (in Russian).
- Baturin, G. N. and E. M. Emel'anov. 1973. "Distribution of Uranium in the Sediments of the Mediterranean Sea." Okeanologiya. 13:814-20 (in Russian).
- Baturin, G. N., T. D. Ilyina, and N. I. Popov. 1971. "Soviet Investigations of Natural Radionuclides in Marine and Ocean Sediments." Proc. Roy. Soc. Edinburgh, Section B. 72:183-91.

- Baturin, G. N. and A. V. Kochenov. 1969. "Migration of Uranium in Rivers and the Duration of Its Presence in Waters of the World's Oceans, Seas, and Lakes." Geokhimiya. 6:715-23 (in Russian).
- Baturin, G. N. and A. V. Kochenov. 1973. "Uranium in Interstitial Waters of Marine and Oceanic Sediments." Geokhimiya. 10:1529-1536 (in Russian).
- Baturin, G. N., A. V. Kochenov, and S. A. Kovaleva. 1966. "Some Aspects of the Distribution of Uranium in Black Sea Waters." Dokl. Akad. Nauk SSSR. 166:698-700 (in Russian).
- Baturin, G. N., A. V. Kochenov, and Y. M. Senin. 1971. "Uranium Concentration in Recent Oceanic Sediments of Water Uprise Zones." Geokhimiya. 4:456-62 (in Russian).
- Baturin, G. N., A. V. Kochenov, and K. M. Shimkus. 1967. "Uranium and Minor Metals in Columns of Bottom Sediments of the Black and Mediterranean Seas." Geokhimiya. 1:41-50 (in Russian).
- Becker, V. J., J. H. Bennett, and O. K. Manuel. 1972. "Iodine and Uranium in Sedimentary Rocks." Chem. Geol. 9:133.
- Becker, V. J. and O. K. Manuel. 1972. "Chlorine, Bromine, Iodine, and Uranium in Tektites, Obsidians and Impact Glasses." J. Geophys. Res. 77:6353.
- Bell, K. G. 1960. Deposition of Uranium in Salt-Pan Basins. U.S.G.S. Professional Paper No. 354-G:161-169.
- Bell, K. G., C. Goodman and W. L. Whitehead. 1940. "Radioactivity of Sedimentary Rocks and Associated Petroleum." Bull. Am. Assoc. Petroleum Geol. 24:1529.
- Belousdva, M. Ya and I. V. Melikhov. 1972. "Study of the Trapping of Impurities by Hydroxides XV. Two Independent Examples of the Segregation of Cobalt." Sov. Radiochem. 14, 1:7-11.
- Benes, P. 1969. "(W73-04126) On the State of Mercury (II) Traces in Aqueous Solutions. Colloidal Behavior of Mercury." Journal of Inorganic Nuclear Chemistry, 31:(7)1923-1928.
- Bennett, J. H. and O. K. Manuel. 1968. "Iodine Abundances in Deep-Sea Sediments." J. Geophys. Res. 73:2302-3.
- Bensen, D. W. 1960. Review of Soil Chemistry Research at Hanford. HW-67201.
- Bensen, D. W. 1961. Mineral Adsorption of Radionuclides in Reactor Effluent. HW-69225.

- Bernat, M. and E. D. Goldberg. 1969. "Thorium Isotopes in the Marine Environment." Earth Planet. Sci. Lett. 5:308-12.
- Berner, R. A. 1975. Kinetic Models for the Early Diagenesis of Nitrogen, Sulfur, Phosphorus, and Silicon in Anoxic Marine Sediments in the Sea. Volume 5 edited by E. D. Goldberg, Wiley-Interscience Publications, New York.
- Bernovskaya, R. N. and Bogdanov, Yu. A. 1971. "Influence of Iron on the Physicochemical State of Radioelements in Sea Water." Soviet Radiochemistry. 13(1):158-160.
- Betenekov, M. D., Yu. V. Egorov, V. D. Puzako. 1973. "Radiocolloids in Sorption Systems XI. Nature of Maximum on E-pH Isotherm Relation of Sorption and Colloidal Properties of a Radioisotope in the Formation of True Colloids." Radiokhimiya. 16(1):20-26.
- Beus, A. A. and E. A. Fabrikova. 1961. "Distribution of Cesium in the Granites of the USSR." Geochemistry. 1961-970-976.
- Bhat, S. G. and S. Krishnaswamy. 1969. "Isotopes of Uranium and Radium in Indian Rivers." Proc. Indian Acad. Sci. Section A, No. 1:1-17.
- Billings, G. K. 1962. "A Geochemical Investigation of the Valley Spring Gneiss and Packsaddle Schist, Llano Uplift, Texas." Texas J. Sci. 9:328.
- Blaine, D. E., R. A. Schwind, H. W. Kirby and E. L. Murphy. 1974. "New-Process for Removing Plutonium from Waste Water_A Progress Report." Proceedings of the Second AEC Environmental Protection Conference. Albuquerque, New Mexico. April 16-19, 1974. WASH-1332-74-V-1: 321-338.
- Bonatti, E., D. E. Fisher, O. Joensuu, and H. S. Rydell. 1971. "Post-Depositional Mobility of Some Transition Elements, Phosphorus, Uranium, and Thorium in Deep Sea Sediments." Geochim. et Cosmochim. Acta. 35:189-201.
- Bondietti, E. A. 1974. "Adsorption of Pu(IV) and Th(IV) by Soil Colloids." Agronomy Abstracts.
- Bondietti, E. A. and S. A. Reynolds. 1977. Field and Laboratory Observations on Plutonium Oxidation States. BNWL-2117, Pacific Northwest Laboratory, Richland, WA, pp. 505-533.
- Bondietti, E. A., S. A. Reynolds, and M. H. Shanks. 1975. Interactions of Plutonium with Complexing Substances in Soils and Natural Waters. IAEA-SM-199/51.
- Booth, R. A. 1975. "A Systems Analysis Model for Calculating Radionuclide Transport Between Receiving Waters and Bottom Sediments." Chapter 7 of Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms. Ann Arbor Science, pp. 135-159.

- Bovard, P., A. Grauby and A. Saas. 1968. "Chelating Effect of Organic Matter and Its Influence on the Migration of Fission Products." In: Isotopes and Radiation in Soil Organic Matter Studies. CONF-680275, pp. 471-495.
- Bowen, V. T. 1971. General Summary of Progress, 1970-1971. NYO-2174-129.
- Bowen, V. T. 1974a. Plutonium and Americium Concentration Along Freshwater Food Chains of the Great Lakes, U.S.A. COO-3568-4.
- Bowen, V. T. 1974b. Radioelement Studies in the Oceans. Progress Report, COO-3563-28.
- Bowen, V. T. 1975. Transuranic Elements in Marine Environments. HASL-291.
- Bowen, V. T., H. D. Livingston and J. C. Burke. 1975. Distributions of Transuranium Nuclides in Sediment and Biota of the North Atlantic Ocean. IAEA-SM-199/96.
- Bowen, V. T. and V. E. Moshkin. 1973. Plutonium Concentration Along Fresh Water Food Chains of the Great Lakes, U.S.A. General Summary of Progress, 1972-1973. COO-3568-3.
- Bowen, V. T., V. E. Moshkin, H. L. Volchok, H. D. Livingston, and K. M. Wong. 1974. "¹³⁷Cs to ⁹⁰Sr Ratios in the Atlantic Ocean, 1966 through 1972." Limnol. Oceanogr. 19:670-681.
- Bowen, V. T., K. M. Wong, and V. E. Moshkin. 1971. "Plutonium-239 in and Over the Atlantic Ocean." Journal Marine Research. 29:1-10.
- Bovard, P., A. Grauby, and A. Saas. 1968. "Chelating Effect of Organic Matter and Its Influence on the Migration of Fission Products." In: Isotopes and Radiation in Soil Organic-Matter Studies. CONF-680725, pp. 471-95 (in French).
- Boyd, G. E. 1959. "Technetium and Promethium." J. Chem. Educ. 36:3-14.
- Boyd, G. E. and Q. V. Larson. 1956. "Report on the Occurrence of Technetium on the Earth's Crust." J. Phys. Chem. 60:707-715.
- Boyle, R. W. 1965. Geology, Geochemistry, and Origin of the Lead-Zinc-Silver Deposits of the Keno Hill-Galena Hill Area, Yukon Territory. Geol. Surv. Canada Bulletin III.
- Breger, I. A., M. Deul, and S. Rubinstein. 1955. "Geochemistry and Mineralogy of a Uraniferous Lignite." Econ. Geol. 50:206-226.
- Brehler, B. and R. Fuge. 1974. "Iodine." In: Handbook of Geochemistry, Vol. II/3, Springer-Verlag, New York. p. 53-1.

- Brisbin, I. L., Jr., R. J. Beyers, R. W. Dapson, R. A. Geiger, J. B. Gentry, J. W. Gibbons, M. H. Smith, and S. K. Woods. 1974. "Patterns of Radio-cesium in the Sediments of a Stream Channel Contaminated by Production Reactor Effluents." Health Physics. 27:19-27.
- Brown, D. J. 1967. Migration Characteristics of Radionuclides Through Sediments Underlying the Hanford Reservation. ISO-SA-32.
- Brown, R. E., R. E. Franklin, and R. H. Miller. 1969. "Reactions of Cerium-144 in Solution and Suspensions of Soil Humic Acid and Bentonite." Soil Science Society of America, Proceedings. 33:677-681.
- Brown, D. J. and W. A. Haney. 1964. Chemical Effluents Technology Waste Disposal Investigations July-December, 1973 - The Movements of Contaminated Ground Water from the 200 Areas to the Columbia River. HW-80909.
- Brown, J. H. and M. D. Keller. 1952. "Uranium in the Clay of a Black Radioactive Shale." Science. 115:632-633.
- Brungs, W. A. 1974. Distribution of Cobalt 60, Zinc 65, Strontium 85, and Cesium 137 in a Freshwater Pond. U.S. Dept. HEW. Public Health Service. Environmental Health Series, Radiological Health.
- Brungs, W. A. 1963. The Relative Distribution of Multiple Radionuclides in a Freshwater Pond. Thesis. Ohio State University, Columbus, OH.
- Burkov, V. V. and Ye. K. Podporina. 1966. "First Data on Rare Earths in Kimberlite." Dokl. Acad. Sci. USSR. Earth Science Section. 171:215-219.
- Burney, G. A. and R. M. Harbour. 1974. Radiochemistry of Neptunium. NAS-NRC Nuclear Sci. Ser. NAS-NS-3060.
- Busey, R. H. and Q. V. Larson. 1958. Chemistry Division Annual Progress Report for Period Ending June 20, 1958. ORNL-2584.
- Butler, J. M. 1964. Ionic Equilibrium. Addison-Wesley, Reading, MA. pp. 180-183.
- Calvo, M. M. 1974. "The Role of Humic Natural Organic Matter in Uranium Concentration." IAEA-SM-183/33. In: Formation of Uranium Ore Deposits.
- Cameron, D. R. and A. Klute. 1977. Convective-Dispersive Solute Transport with a Combined Equilibrium and Kinetic Adsorption Model. Water Resources Research, Vol. 13, No. 1.
- Carye, A. G., Jr. and M. H. Cutshall. 1973. "Zinc-65 Specific Activities from Oregon and Washington Continental Shelf Sediments and Benthic Invertebrate Fauna." In: Radioactive Contamination of the Marine Environment. IAEA, Vienna, pp. 287-305.

- Carrigan, Jr., P. H. 1968. Radioactive Waste Dilution in the Clinch River Eastern Tennessee. U.S. Geol. Survey Prof. Paper 433-G, pp. 61-69.
- Carrigan, Jr., P. H. 1969. Inventory of Radionuclides in Bottom Sediment of the Clinch River Eastern Tennessee. USGS-Professional Paper 433-I, 18 p.
- Carrigan, P. H., R. J. Pickering, T. Tamura, and R. Forbes. 1967. Radioactive Materials in Bottom Sediment of Clinch River: Part A, Investigations of Radionuclides in Upper Portion of Sediment. ORNL-3721 (Suppl. 2A).
- Carritt, D. E. and S. Goodgal. 1954. "Sorption Reactions and Some Ecological Implications." Deep-Sea Research. 1:224-243.
- Cerrai, E., M. G. Mezzadri, B. Schreiber, and C. Triulzi. 1970. "Some Radioactivity Measurements of Sediment Samples Collected in the North Adriatic Sea." Energia Nucleare. 17:(3)176-181.
- Cerrai, E., M. G. Mezzadri and C. Triulzi. 1969. "Sorption Experiments of Strontium, Cesium, Promethium, and Europium on Marine Sediment Samples." Energia Nucleare. 16(6)378-385.
- Cerrai, E., M. G. Mezzadri, B. Schreiber, and C. Triulzi. 1970. "Some Radioactivity Measurements of Sediment Samples Collected in the North Adriatic Sea." Energia Nucleare. 17:176-181.
- Cerrai, E., B. Schreiber, and C. Triulzi. 1965. "⁹⁰Sr in Upper Layers of Coastal Sediments of the Ligurian Sea and Contribution of Some Radionuclides to their Radioactivity." Energia Nucleare. 12:549-52.
- Cerrai, E., B. Schreiber, C. Triulzi. 1967. "Vertical Distribution of ⁹⁰Sr, ¹⁴⁴Ce, ¹⁴⁷Pm, and ¹⁵⁵Eu in Coastal Marine Sediments." Energia Nuclear. 14:586-92.
- Champlin, J. B. F. and G. G. Eichholz. 1976. "Fixation and Remobilization of Trace Contaminants in Simulated Subsurface Aquifers." Health Physics. 30:215-219.
- Champlin, J. B. 1970. Transport of Radioisotopes by Fine Particulate Matter in Aquifers. Thesis, Georgia Inst. of Tech., Atlanta, GA.
- Champlin, J. B. F. 1969. Transport of Radioisotopes by Fine Particulate Matter in Aquifers. PB-232179.
- Charlot, G. 1957. Qualitative Analysis and Solution Reactions. Fourth Edition. Masson, Paris.
- Chase, M. W., J. L. Curnutt, H. Prophet, R. A. McDonald and A. N. Syverud. 1975. "JANAF Thermochemical Tables, 1975 Supplement." Journ. Phys. and Chem. Ref. Data 1974. (1)4.

- Cheng, H. and H. Hamaguchi. 1968. "Studies on the Adsorption of Radioisotopes on Marine Sediments. I. Role of Exchangeable Cations on the Adsorption of Cesium and Exchange Equilibria." Health Phys. 14:1353-63.
- Cherdyntsev, V. V., V. L. Zverev, V. M. Kuptsov, and G. T. Kislitsina. 1968. "Plutonium-239 in Nature." Geochemistry International. 5:355-361.
- Christenson, C. W., M. B. Ettinger, G. G. Robuck, E. R. Hermann, K. C. Kohr, and F. F. Newell. 1951. "Removal of Plutonium from Laboratory Wastes." Ind. at Eng. Chem. 43:7:1509-15.
- Christenson, C. W., E. B. Fowler, G. L. Johnson, E. H. Rex, and F. A. Virgil. 1958. "Soil Adsorption of Radioactive Wastes at Los Alamos." Sewage and Industrial Waste. 30:1478-1489.
- Christenson, C. W. and P. G. Thomas. 1962. Movement of Plutonium Through Los Alamos Tuff. TID-7628, Part of Second Ground Disposal of Radioactive Wastes Conference Atomic Energy of Canada Limited Chalk River, Canada, September 26-29, 1961. p. 248-281.
- T. M. Church, editor. ACS Symposium Series 18.
- Clanton, U. S. 1968. Sorption and Release of ^{89}Sr and ^{137}Cs by Recent Sediments of the Guadalupe River of Texas. Thesis, University of Texas, Austin, TX.
- Clark, S. P., J. E. Peterman and K. S. Heier. 1966. "Abundances of Uranium, Thorium, and Potassium." In: Handbook of Physical Constants. S. P. Clark (ed.). Geol. Soc. Am. Mem. 97.
- Clayton, R. M., I. Friedman, D. L. Graaf, T. K. Mayeda, W. F. Meents and N. F. Shimp. 1966. "The Origin of Saline Formation Waters. I. Isotopic Composition." J. Geophys. Res., 71, 3869-3882.
- Cleveland, J. M. 1970. The Chemistry of Plutonium. Gordon and Breach Science Publishers.
- Cline, J. F. 1968. Uptake of ^{241}Am and ^{239}Pu by Plants. BNWL-714, pp. 8.24-8.25.
- Coleman, J. C. 1963. "The Kinetics of the Disproportionation of Americium (V)." Inorg. Chem. 2:53.
- Coleman, N. T., R. J. Lewis, and D. Craig. 1963. "Sorption of Cesium by Soils and Its Displacement by Salt Solutions." Soil Sci. Soc. Am. Proc.
- Collet, M., R. Maushart and P. Spaander. 1968. "Accumulation of Radioactive Materials by River Silt." In: Radiation Protection. Pt-2, W. S. Snyder et al. (eds.), pp. 1343-9.

- Collins, A. G., J. H. Bennett, and O. K. Manuel. 1971. "Iodine and Algae in Sedimentary Rocks Associated with Iodine-Rich Brines." Bull. Geol. Soc. Am. 82:2607.
- Connick, R. E. and W. H. McVey. 1949. "The Aqueous Chemistry of Zirconium." J. Am. Chem. Soc. 71:3182-3192.
- Corey, J. C. and A. L. Boni. 1975. Removal of Plutonium from Drinking Water by Community Water Treatment Facilities. IAEA-SN-199/81.
- Corey, J. C. and J. W. Fenimore. 1968. "Tracing Groundwater with Chloride Ions and Tritium Through Acid Kaolinitic Soil." Int. J. Appl. Rad. Isotopes. 19:741-746.
- Corey, J. C. and J. H. Horton. 1968. "Movement of Water Tagged with ^2H , ^3H and ^{18}O Through Acidic Kaolinitic Soil." Soil Sci. Soc. Am., Proc. 32:471-475.
- Cotton, F. A. and G. Wilkinson. 1962. Advanced Inorganic Chemistry. Interscience Publishers.
- Cowser, K. E. 1962. Movement of Ruthenium in the ORNL Waste-Pit System. TID-7628, p. 513-31.
- Cowser, K. E. and F. L. Parker. 1958. "Soil Disposal of Radioactive Wastes at ORNL: Criteria and Techniques of Site Selection and Monitoring." Health Phys. 1:152-63.
- Cushing, C. E. and D. G. Watson. 1974. Aquatic Studies of Gable Mountain Pond. BNML-1884, Pacific Northwest Laboratory, Richland, WA.
- Cutshall, M. H. 1967. " ^{51}Cr in the Columbia River and Adjacent Pacific Ocean." RLO-1750-22 (Vol. 4), Paper 3.
- Dall'Aglia, M. 1971. "Study of the Circulation of Uranium in the Supergene Environment in the Italian Alpine Range." Geochim. et Cosmochim. Acta. 35:47-59.
- Dall'Aglia, M. and E. Casentini. 1970. "Distribution of Uranium Between Precipitates and Brines in the Solar Salt Plant of Margherita Di Savoia. Geochemical and Geological Considerations." Boll. Soc. Geol. Ital. 89:475-84.
- Dames and Moore. 1976. Development of Monitoring Programs for ERDA-Owned Radioactive Low-Level Waste Burial Sites. White Plains, NY.
- Dames and Moore. 1978. Migration of Radionuclides at Low-Level Waste Burial Grounds. Draft manuscript prepared for Atomic Industrial Forum, Inc.

- D'Ans, J. and E. Lax. 1967. Taschenbuch fur Chemiker and Physiker. 3 Aufl., Bd. I. Springer.
- Davis, G. L. 1947. "Radium Content of Ultramafic Igneous Rocks. I. Laboratory Investigation." Am. J. Sci. 245:677.
- Davydov, Yu. P. 1972. "Sorption of Hydrolyzed Forms of Pu(IV) by Silica Gel." Sov. Radiochem. 14(2):220-224.
- Davydov, Yu. P. and I. G. Bogatyreva. 1972. "Sorption Pu(IV) by Ion Exchange Resins in the Region of Hydrolysis of Plutonium (IV)." Sov. Radiochem. 14(2):209-214.
- Dawson, R. and E. K. Duursma. 1974. "Distribution of Radioisotopes Between Phytoplankton, Sediment, and Sea Water in a Dialysis Compartment System." Neth. J. Sea Res. 8:339-353.
- De, S. K., S. S. Rao, C. M. Tripathi, and C. Rai. 1971. "Retention of Iodide by Soil Clays." Indian Journal of Agricultural Chemistry. 4:43-49.
- DeBortoh, and P. Gaglione. 1970. "Study of the Dispersion of Radioactive Effluents into a Lake. I. Contamination of the Bottom Sediments." Minerva Fisiconucl. 14:190-6.
- Delaplane, W. H., W. O. Forster, and W. C. Renfro. 1969. Distribution of ^{65}Zn and ^{60}Co in Fractionated Sediment of the Columbia River Estuary. RLO-1750-54, pp. 92-5.
- Dement'yev, V. S. and M. G. Syromyatnikov. 1965. "Mode of Occurrence of Thorium Isotopes in Ground Waters." Geokhimiya. No. 2:211-218.
- Dement'yev, V. S. and M. G. Syromyatnikov. 1968. "Conditions of Formation of a Sorption Barrier to the Migration of Uranium in an Oxidizing Environment." Geochemistry International. 5:394-400.
- Desai, M. V. M. and A. K. Ganguly. 1970. Interaction of Trace Elements with Organic Constituents in the Marine Environment. BARC-488, p. 102.
- Dey, M. N. and K. C. Pillai. 1971. "Radium in Aquatic Environment of Trombay." In: Proc. of the National Symposium on Radiation Physics. Bombay; Bhabha Atomic Res. Center, pp. 541-53.
- Dorta, C. C. and E. Rona. 1971. "Geochemistry of Uranium in the Cariaco Trench." Bull. Mar. Sci. 21:754-765.
- Doshi, G. R., T. M. Krishnamorthy, V. M. Sastry, and T. P. Sarma. 1973. "Sorption Behavior of Trace Nuclides in Sea Water on Manganese Dioxide." Indian Journal of Chemistry. 11:158-151.

- Duguid, J. O. 1977. "Hydrologic Transport of Radionuclides from Low-Level Waste Burial Grounds." CONF-770512-7, presented at Symposium on the Management of Low Level Radioactive Waste at the Georgia Inst. of Technology, Atlanta, GA, May 23-27, 1977.
- Duguid, J. O. 1975. Status Report on Radioactivity Movement from Burial Ground in Melton and Bethel Valleys. ORNL-5017.
- Duguid, J. O. 1976. Annual Progress Report of Burial Ground Studies at Oak Ridge National Laboratory: Period Ending September 30, 1975. ORNL-5141.
- Duguid, J. O. 1974a. Groundwater Transport of Radionuclides from Buried Waste: A Case Study at Oak Ridge National Laboratory. CONF-740406-5.
- Duguid, J. O. 1974b. "Groundwater Transport of Radionuclides from Buried Waste: A Case Study at Oak Ridge National Laboratory." In: Proc. of the 2nd AEC Environmental Protection Conference. WASH-1332-74-V-1, pp. 511-529.
- Dunigan, E. P. and C. W. Francis. 1972. "Adsorption and Desorption of Cobalt 60, Strontium 85, and Cesium 137 on Soil Humic Acid." Soil Science. 114:494-496.
- DuPont. 1965. Sorption of Sr and Cs by Stream Beds. TID-26519.
- Dutt, G. R., M. S. Shaffer and W. J. Moore. 1972. Computer Simulation Model of Bio-physic-chemical Processes in Soils. University of Arizona. Agr. Exp. Sta. Tech. Bul. 196.
- Duursma, E. K. 1973. "Concentration Effects of ^{137}Cs , ^{65}Zn , ^{60}Co , and ^{106}Ru Sorption by Marine Sediments with Geochemical Implications." Neth. J. Res. 6:225-240.
- Duursma, E. K. 1973. Specific Activity of Radionuclides Sorbed by Marine Sediments in Relation to the Stable Element Composition. IAEA-SM-158/4, pp. 57-71.
- Duursma, E. K. 1972. "Geochemical Aspects and Applications of Radionuclides in the Sea." Oceanogr. Mar. Biol. Ann. Rev. 10:137-223.
- Duursma, E. K. and C. J. Bosch. 1970. "Theoretical, Experimental, and Field Studies Concerning Diffusion of Radioisotopes in Sediments and Suspended Particles of the Sea. Part B: Methods and Experiments." Netherlands Journal of Sea Research. 4:395-469.
- Duursma, E. K. and D. Eisma. 1973. "Theoretical, Experimental and Field Studies Concerning Reactions of Radioisotopes with Sediments and Suspended Particles of the Sea. Part C: Applications to Field Studies." Netherlands Journal of Sea Research. 6:265-324.

- Duursma, E. K., and M. G. Gross. 1971. "Marine Sediments and Radioactivity. In: Radioactivity in the Marine Environment. National Academy of Sciences, Washington, DC, pp. 147-160.
- Duursma, E. K. and P. Parsi. 1974. "Distribution Coefficients of Plutonium Between Sediment and Seawater." In: Activities of the International Laboratory of Marine Radioactivity. IAEA-163, pp. 94-96.
- Duursma, E. K., P. Parsi, and G. Statham. 1974. Fixation of Radionuclides with Time by Marine Sediments. IAEA-163. pp. 107-108.
- Edgington, D. N., J. J. Alberts, M. A. Wahlgren, J. L. Karttunen and C. A. Reeve. 1975. Plutonium and Americium in Lake Michigan Sediments. IAEA-SM-199/47.
- Edgington, D. N., C. W. Kennedy, G. E. Bartelt, and C. M. Bobula. 1977. Plutonium in the Great Miami River, Ohio - Summary of an Experiment Conducted in October 1976. ANL-77-5 Part III, pp. 83-84.
- Ehnhalt, D. H. 1973. "On the Uptake of Tritium by Soil Water and Ground Water." Water Resources Research. 9:1073-1074.
- Eichholz, G. G., T. F. Craft, and A. N. Galli. 1967. "Trace Element Fractionation by Suspended Matter in Water." Geochim. et Cosmochim. Acta. 31:737-745.
- Eliason, J. R. 1966. "Montmorillonite Exchange Equilibria with Strontium-Sodium-Cesium." Am. Mineral. 51:324-335.
- El Nadi, A. F. and M. Ammar. 1960. "Thorium Content in Nile Water." Proc. Math. Phys. Soc. (U.A.R.). No. 24:11-16.
- Emery, R. M. and D. C. Klopfer. 1975. "The Distributions of Transuranic Elements in a Freshwater Pond Ecosystem." Prepared for Eighth Rochester International Conference on Environmental Toxicology: Radioisotopes in the Aquatic Environment, Models and Mechanisms.
- Emery, R. M., D. C. Klopfer, T. R. Garland, and W. C. Weimer. 1975. "Ecological Behavior of Plutonium and Americium in a Freshwater Pond." BNWL-SA-5346, Pacific Northwest Laboratory, Richland, WA.
- Emery, R. M., D. C. Klopfer and M. C. McShane. 1977. The Ecological Export of Plutonium from a Reprocessing Waste Pond.
- Emery, R. M., D. C. Klopfer, and W. C. Weimer. 1974a. Ecological Behavior of Plutonium and Americium in a Freshwater Ecosystem. Phase I. Limnological Characterization and Isotopic Distribution. BNWL-1867.

- Emery, R. M. and T. R. Garland. 1974b. The Ecological Behavior of Plutonium and Americium in a Freshwater Ecosystem: Phase II. Implications of Differences in Transuranic Isotopic Ratios. BNL-1879, Pacific Northwest Laboratory, Richland, WA.
- Enfield, C. G. and B. E. Bledsoe. 1975. Kinetic Model for Orthophosphate Reactions in Mineral Soils. EPA-660/2-75-022.
- Ermolaev, M. P., A. P. Zhidikora, and V. A. Zarinski. 1965. "On the Silicate Form of Uranium Transport in Aqueous Solutions." Geokhimiya. No. 7:813-826 (in Russian).
- Essington, E. H. and H. Nishita. 1966. "Effect of Chelates on the Movement of Fission Products Through Soil Columns." Plant and Soil. 24:1-23.
- Essington, E. H. and W. E. Nork. 1969. Radionuclide Contamination Evaluation-Milrow Event. NVO-1229-117.
- Essington, E. H., H. Nishita and A. J. Steen. 1965. "Release and Movement of Radionuclides in Soils Contaminated with Fallout Material from an Underground Thermonuclear Detonation." Health Physics. 11:689-698.
- Evans, E. J. 1956. Plutonium Retention in Chalk River Soil. CRHP-660.
- Evans, D. W. 1973. Effects of Ocean Water on the Soluble-Suspended Distribution of Columbia River Radionuclides. Thesis, Oregon State University, Corvallis, OR, 56 pp.
- Evans, D. W. and N. H. Cutshall. 1973. Effects of Ocean Water on the Soluble - Suspended Distribution of Columbia River Radionuclides. IAEA-SM-158/8.
- Evans, R. D. and C. Goodman. 1941. "Radioactivity of Rocks." Bull. Geol. Soc. Am. 52:459.
- Evans, R. D., C. Goodman, and N. B. Keevil. 1942. "Radioactivity: The Earth's Heat and Geological Age Measurements." In: Handbook of Physical Constants. Geol. Soc. Am. Special Papers 36, Sec. 18, p. 267.
- Eyman, L. D. and N. R. Kevern. 1975. "Cesium-137 and Stable Cesium in a Hypereutrophic Lake." Health Physics. 28:549-555.
- Fairbridge, R. W. (ed.). 1972. The Encyclopedia of Geochemistry and Environmental Sciences. Van Nostrand Reinhold Company.
- Faure, J., P. Viallef, A. Grauby, and P. Picat. 1972. "Complexing of the Organic Matter of a Sediment and Certain Radioisotopes. Distribution of these Radioisotopes as a Function of the Molecular Weight of the Organic Substances." Compt. Rend. Hebd. Seances Acad. Agr. Fr. 58:377-383 (in French).

- Feldman, I. 1976. "The Colloidal Nature of Radionuclides in Seawater." In: Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms. Edited by M. W. Miller and J. N. Stannard, Ann Arbor Science Pub., Ann Arbor, MI.
- Feldman, M. H. 1961. Summary Report, 1959-1961. Winchester Laboratory, Winchester, Massachusetts and Grand Junction, Colorado. WIN-125.
- Fitzgerald, G. P. 1970. "Aerobic Lake Muds for the Removal of Phosphorus from Lake Waters." Limn. and Ocean. Vol. 15, pp. 550-555.
- Fleischer, M. 1966. "Index of New Mineral Names, Discredited Minerals and Changes of Mineralogical Nomenclature in Vols. 1-50 of the American Mineralogist." Am. Mineral. 51:1248.
- Folsom, T. R. and V. F. Hodge. 1975. "Experiments Suggesting Some First Steps in the Dispersal and Disposal of Plutonium and Other Alpha Emitters in the Ocean." Marine Science Communications. 1:213-247.
- Forster, W. O. and P. J. Hanson. 1969. Particulate ^{65}Zn and ^{51}Cr in Columbia River Estuary. RLO-1750-54. pp. 55-7.
- Foster, R. F. 1963a. Radiological Status of the Hanford Environs for June 1963. HW-76525-6.
- Foster, R. F. 1963b. Radiological Status of the Hanford Environs for August 1963. HW-76525-8.
- Foster, R. F. 1964. Radiological Status of the Hanford Environs for August 1964. HW-80892-8.
- Fowler, E. B. and E. H. Essington. 1974. "Soils Element Activities October 1972 - September 1973." In: The Dynamics of Plutonium in Desert Environments. P. B. Dunnaway and M. G. White (eds.). NVO-142, pp. 7-16.
- Frey, F. A., M. A. Haskin, J. A. Poetz, and L. A. Haskin. 1968. "Rare Earth Abundances in Some Basic Rocks." J. Geophys. Res. 73:6085-6098.
- Fried, S., A. M. Friedman, J. Hines, G. Schmitz, and M. Wheeler. 1977. "Distribution of Plutonium and Americium at an Old Los Alamos Waste Disposal Site." In: Proc. Sym. on Dynamics of Transuranics in Terrestrial and Aquatic Environment. Gatlinburg, TN, October 1976.
- Fried, S., A. M. Friedman, and L. A. Quarterman. 1974a. Annual Report on Project ANO115A, Fiscal Year 1974. ANL-8115.
- Fried, S., A. M. Friedman, and R. Weeber. 1974b. Studies of the Behavior of Plutonium and Americium in the Lithosphere. ANL-8096, pp. 10-11.

- Friend, A. G. 1963. "The Aqueous Behavior of ^{85}Sr , ^{137}Cs , ^{65}Zn , and ^{60}Co as Determined by Laboratory Type Studies." In: Transport of Radionuclides in Fresh Water Systems. TID-7664.
- Frissel, M. J. and P. Reiniger. 1974. Simulation of Accumulation and Leaching in Soils. Wageningen Centre for Agricultural Publishing and Documentation.
- Fryssinger, G. R. 1962. "Cesium-Sodium Ion Exchange on Clinoptilolite." Nature. 194:351.
- Fukai, R. and H. N. Lang. 1968. Studies on the Chemical Behavior of Radionuclides in Seawater. I. General Considerations, and Study of Precipitation of Trace Amounts of Chromium, Manganese, Iron, Cobalt, Zinc and Cerium. IAEA. Radioactivity in the Sea, Publication No. 22.
- Fukai, R. and C. N. Murray. 1973. "Environmental Behavior of Radiocobalt and Radiosilver Released from Nuclear Power Stations into Aquatic Systems." In: Environmental Behavior of Radionuclides Released in the Nuclear Industry. IAEA, Vienna. pp. 217-242.
- Fukai, R. and C. N. Murray. 1974. "Adsorption and Desorption of Plutonium and Americium in Freshwater - Sediment and Seawater - Sediment Systems." In: Activities of the International Laboratory of Marine Radioactivity. IAEA-163, pp. 96-103.
- Fukai, R., C. N. Murray, G. Statham, and K. Asari. 1974. "Radionuclide Measurements of Water, Sediments, and Biota, Collected from the Ligurian Sea: Pu-239, 240, Sr-90, and Cs-137." In: Activities of the International Laboratory of Marine Radioactivity. IAEA-163:134-318.
- Gabelman, J. W. 1971. "Sedimentology and Uranium Prospecting." Sediment. Geol. 6:145-186.
- Gaines, G. L. and H. C. Thomas. 1953. "Adsorption Studies on Clay Minerals. II. A Formulation of the Thermodynamics of Exchange Adsorption." J. Chem. Phys. 21:714-718.
- Gardner, K. and O. Skulberg. 1964. "Sorption Phenomena of Radionuclides to Clay Particles in River Water." Intern. J. Air Water Pollution. 8:229-41.
- Garrels, R. M. and C. L. Christ. 1965. Solutions, Minerals and Equilibria. Harper and Row. New York, pp. 213-216.
- Garrels, R. M. and M. E. Thompson. 1962. American J. of Science. Vol. 260, p. 57.
- Gast, R. G. 1975. The Behavior of Technetium-99 in Soils and Plants. Progress Report. COO-2447-1.

- Giacoletto, C. and C. Triulzi. 1970. Radiochemical Studies for Radioactivity Determinations on Marine Sediment Samples: Cs-137, Sb-125, and Co-60. CISE-N-118.
- Ginzburg, S. I., N. A. Ezerskaya, I. V. Prokof'eva, N. V. Fedorenko, V. I. Shlenskaya, and N. K. Bel'skii. 1975. Analytical Chemistry of Platinum Metals. Translated by N. Kaner, Israel Program for Scientific Translations.
- Glenn, J. L. 1971. Relations Among Radionuclide Content and Physical, Chemical, and Mineral Characteristics of Columbia River Sediments. TID-25786.
- Glover, P. A., F. J. Miner, and W. L. Polzer. 1977. Plutonium and Americium Behavior in the Soil/Water Environment. I. Sorption of Plutonium and Americium by Soils. BNWL-2117, Pacific Northwest Laboratory, Richland, WA, pp. 235-246.
- Gloyna, E. F., S. K. Bhagat, Y. Yousef, and C. Shih. 1966. Transport of Radionuclides in a Model River. STI-PUB-126, pp. 11-32.
- Gloyna, E. F., Yousef, Y. A. and T. J. Padden. 1971. Radioactivity Transport in Water: Continuous Release of Radionuclides in a Small Scale Ecosystem. Technical Report ORO-490-21.
- Goldberg, E. D., Mikoide, R. A. Schmitt and R. H. Smith. 1963. Rare Earth Distributions in the Marine Environment.
- Goldberg, E. D. 1975. Marine Geochemistry Research. Progress Report. UCSD-34P84X9.
- Goldberg, M. C., V. J. Janzer, C. G. Angelo, and W. A. Beetem. 1962. The Effect of Sodium Ion Concentration on Distribution Coefficients for Tuffs from NTS. U.S.G.S. Technical Letter NTS-16.
- Goldschmidt, V. M., T. Barth. G. Lunde, and U. W. Zachariasen. 1926. Geochemische Verteilungsgesetze der Elemente. VII. Skrifter Norske Videnskaps Akad. Oslo, I. Mat-Naturv. K1., No. 2.
- Goldsztaub, S. and R. Wey. 1955. "Adsorption of Uranyl Ions by Clays." Bull. Soc. Franc. Mineral. Crist. 78:242.
- Goldsztein, M. and J. Ros. 1963. "On the Uranium Content of Sediments of the Western Basin of the Mediterranean." Bull. Inst. Oceanog. (in French).
- Gonzalez, G. F. and A. M. Gomez. 1961. "Geochemistry of Cobalt in Soils of Western Andalusia. IV. Cobalt Clays and Correlation Between Cobalt and Iron, Clay and Manganese Contents." An. Edafol. Agrobiol. 23:563-572.

- Grandstaff, D. E. 1976. "A Kinetic Study of the Dissolution of Uraninite." Econ. Geol. 71(8):1493-1506.
- Granger, H. C. 1963. Radium Migration and Its Effect on the Apparent Age of Uranium Deposits at Ambrosia Lake, New Mexico. U.S. Geol. Survey Prof. Paper 475-B, pp. B-60-B-63.
- Granger, H. C., E. S. Santos, B. G. Dean and F. B. Moore. 1961. "Sandstone-Type Uranium Deposits at Ambrosia Lake, New Mexico - an Interim Report." Econ. Geol. 56(7):1179-1209.
- Grebenshchikova, V. I., M. B. Chernyavskaya, and N. R. Andreeva. 1972. "Sorption of Tetravalent Elements by Mordenite II. Sorption of Pu(IV)." Radiokhimiya. 15(6):761-766.
- Grebenshchikova, V. I., V. N. Nikonov, A. S. Pershin, and N. R. Andreeva. 1975. "Some Properties of Hydroxo Complexes of Plutonium (IV)." Soviet Radiochem. 17(3):384-387.
- Grebenshchikova, V. I. and Y. P. Davydov. 1961. "A Study of the State of Pu(IV) in Dilute Solutions of Nitric Acid." Radiokhimiya. 3:155-164.
- Grebenshchikova, V. I. and Y. P. Davydov. 1965. "State of Pu(IV) in the Region of pH 1.0-12.0 at a Plutonium Concentration of $2.0 \times 10^{-5}M$." Radiokhimiya. 7:191-195.
- Grebenshchikova, V. I., Y. P. Davydov, and A. S. Pershin. 1971. "The Adsorption of Plutonium (+4) on a Precipitate of Barium Sulfate." Soviet Radiochemistry. 13:457-459.
- Green, D. B., T. J. Logan and M. E. Smeck. 1978. "Phosphate Adsorption-Desorption Characteristics of Suspended Sediments in the Maumee River Basin of Ohio." J. of Environ. Qual. 7(2):208-212.
- Gromiec, M. J. and E. F. Gloyna. 1973. Radioactivity Transport in Water: Final Report. Technical Report No. 22. ORO-23.
- Gromov, V. V. 1975. Investigation of the Behavior of Trace Elements in Ocean Water by the Desorption Method. BNL-tr-611.
- Gromov, V. V. and V. I. Spitsyn. 1974. "Influence of Phytoplankton on the Physicochemical State of ^{239}Pu , ^{106}Ru , ^{99}Tc and ^{60}Co in Sea Water." Transl. Dokl. Akad. Nauk SSSR. 215(2):451-453.
- Gromov, V. V., V. V. Surikov, and Yu. A. Bogdanov. 1972. "Adsorption of Yttrium-90, Niobium-95, and Cerium-141 by Suspension and Bottom Deposits of the Indian Ocean." Sov. Radiochem. 14:834-8.
- Gromov, V. V. and V. I. Spitsyn. 1974. "Sorption of ^{239}Pu , ^{106}Ru , and ^{99}Tc by Bottom Sediments of the Pacific Ocean." Sov. Radiochem. 16:157-162.

- Gross, M. G. 1972. "Sediment-Associated Radionuclides from the Columbia River." In: Columbia River Estuary and Adjacent Ocean Waters. A. T. Parter (ed.), University of Washington Press, pp. 736-54.
- Gross, M. G. 1967. Distribution and Movement of Radioactive Continental Shelf Sediment, Northwestern United States. RLO-1725-73.
- Gross, M. G. 1966. "Distribution of Radioactive Marine Sediment Derived from the Columbia River." Journal of Geophysical Research. 71:2017-2021.
- Gross, M. G., D. A. McManus, and J. S. Creager. 1963. Preliminary Report on the Sediments and Radioactivity in the Vicinity of the Columbia River Effluent. Brown Bear Cruise, 291 (July 29 - August 12, 1961), 311 (July 23 - August 14, 1962). Tech. Report No. 84. TID-20200.
- Habashi, F. 1962. "Correlation Between the Uranium Content of Marine Phosphates and Other Rock Constituents." Econ. Geol. 57:1081-1084.
- Hacquaert, A. L. 1925. "Pink Calcite from Tantara (Katanga)." Natuurw. Tijds. Antwerp. Vol. 7, p. 102.
- Haglund, D. S. 1968. The Distribution of Uranium in Recent Carbonate Sediments and Skeletons of Organisms and the Effect of Diagenesis on Uranium Redistribution. Thesis, Rensselaer Polytechnic Institute, Troy, NY.
- Haglund, D. S., G. M. Friedman, and D. S. Miller. 1969. "The Effect of Freshwater on the Redistribution of Uranium in Carbonate Sediments." J. Sediment. Petrol. 39:1283-1296.
- Hajek, B. F. 1966. Plutonium and Americium Mobility in Soils. BNWL-CC-925, Pacific Northwest Laboratory, Richland, WA.
- Hajek, B. F. and K. C. Knoll. 1966. Disposal Characteristics of Plutonium and Americium in a High Salt Acid Waste. BNWL-CC-649, Pacific Northwest Laboratory, Richland, WA.
- Hakonson, T. E. and F. W. Whicker. 1975. "Cesium Kinetics in a Montane Lake Ecosystem." Health Physics. 28:699-706.
- Hakonson, T. E. 1972. Cesium Kinetics in a Montane Lake Ecosystem. Thesis. Colorado State University, Fort Collins, CO.
- Hakonson, T. E. and L. J. Johnson. 1973. "Distribution of Environmental Plutonium in the Trinity Site Ecosystem After 27 Years." Proceedings of the Third International Congress of the International Radiation Protection Association, pp. 242-247.

- Hakonson, T. E., L. J. Johnson and W. D. Purtyum. 1973. "The Distribution of Plutonium in Liquid Waste Disposal Areas at Los Alamos." In: Proceedings of the Third International Congress of the International Radiation Protection Association, September 9-14, 1973, Washington, DC, pp. 248-253, CONF-730907-P1.
- Hakonson, T. E., J. W. Nyhan and W. D. Purtyum. 1975. Accumulation and Transport of Soil Plutonium in Liquid Waste Discharge Areas at Los Alamos. IAEA-SM-199/99.
- Hale, V. O. and A. Wallace. 1970. "Effect of Chelates on Uptake of Some Heavy Metal Radionuclides from Soil by Bush Beans." Soil Sci. 109:262-263.
- Halevy, E. 1965. "The Exchangeability of Hydroxyl Groups in Kaolinite." Geochim. et Cosmochim. Acta. 28:1139-1145.
- Hamaguchi, H. 1941. "Chemical Investigations of Deep-Sea Deposits. VIII. Radium Content of Deep-Sea Deposits." J. of the Chem. Soc. of Japan. 62:836-42.
- Hamid, A. and B. P. Warkentin. 1967. "Retention of ^{131}I Used as Tracer in Water Movement Studies." Soil Sci. 104:279-82.
- Haney, W. A. 1963. Fission Product Tritium in Fuel Reprocessing Wastes. HW-SA-3303.
- Haney, W. A. 1964. "Consequences of Activity Release." Nuclear Safety. 5:399-403.
- Haney, W. A. 1967. Final Report on the Effects of Ben Franklin Dam. BNWL-412, Pacific Northwest Laboratory, Richland, WA.
- Haney, W. A., D. J. Brown, and A. E. Reisenauer. 1962. Fission Product Tritium in Separations Wastes and in the Ground-Water. HW-74536.
- Haney, W. A. and C. E. Linderoth. 1959. Exploratory Field Study of a Ground Waste Disposal Facility. HW-60115.
- Hansen, R. O. and G. L. Huntington. 1969. "Thorium Movements in Morainal Soils of the High Sierra, California." Soil Science. 108:257-265.
- Hanson, P. J. 1967. Vertical Distribution of Radioactivity in the Columbia River Estuary. RLO-1750-22 (vol. 2), Paper 2.
- Harrison, F. L. 1969. Radioactive Debris from Underground Nuclear Explosions: 1. Physical and Chemical Characteristics, 2. Biological Availability of the Radionuclides to Aquatic Animals. UCRL-50596.

- Harter, R. D. 1968. "Adsorption of Phosphorus by Lake Sediment." Soil Sci. Soc. Amer. Proc. 32:514-518.
- Haskin, L. A., et al. 1966. "Meteoric, Solar, and Terrestrial Rare Earth Distributions." In: Physics and Chemistry of the Earth. L. H. Ahrens et al. (eds.), Vol. 7, Oxford, Pergamon Press.
- Haskin, L. A. and R. A. Schmitt. 1967. "Rare-Earth Distributions." In: Researches in Geochemistry. Vol. 2. P. H. Abelson (ed.), John Wiley & Sons, Inc., pp. 234-259.
- Haury, G. and W. Schikorski. 1977. "Radioactive Inputs into the Environment, Comparison of Natural and Man-Made Inventories." In: Global Chemical Cycles and Their Alterations by Man. Edited by W. Strumm, pp. 165-188, Berlin.
- Haushild, W. L., G. R. Dempster, Jr., and H. H. Stevens, Jr. 1973a. Distribution of Radionuclides in the Columbia River Streambed from the Nuclear Reactors, Hanford Reservation to Longiver, Washington. TID-26531.
- Haushild, W. L., H. H. Stevens, Jr., J. L. Nelson and G. R. Dempster, Jr. 1973b. Radionuclides in Transport in the Columbia River from Pasco to Vancouver, Washington. USGS Professional Paper 433-N, pp. NI-N43.
- Haushild, W. L., H. H. Stevens Jr., J. L. Nelson, G. R. Dempster, Jr. 1971. Radionuclides in Transport in the Columbia River from Pasco to Vancouver Washington. USGS. TID-25894, 77 p.
- Havlik, B. 1970. "Radioactive Pollution of Rivers in Czechoslovakia." Health Physics. 19:617-625.
- Havlik, B., J. Grafova, and B. Nycova. 1968a. "Radium-226 Liberation from Uranium Ore Processing Mill Waste Solids and Uranium Rocks into Surface Streams - I." Health Physics. 14:417-422.
- Havlik, B., B. Nycova, and J. Grafova. 1968b. "Radium-226 Liberation from Uranium Ore Processing Mill Waste Solids and Uranium Rocks into Surface Streams - II." Health Physics. 14:423-430.
- Hawkes, H. E. 1954. Geochemical Prospecting Investigations in the Nyeba Lead-Zinc District, Nigeria. USGS Bulletin 1000-B.
- Hawkins, D. B. and H. L. Short. 1965. Equations for the Sorption of Cesium and Strontium on Soil and Clinoptilolite. 100-12046.
- Hawkins, R. H. 1975. "Migration of Tritium from a Nuclear Waste Burial Site." In: Proc. Third Environmental Protection Conference. ERDA-92. 2:622-637.

Hayes, D. W. 1976. Tritium in the Savannah River Estuary and Adjacent Marine Waters. DP-MS-75-122.

Hayes, D. W., J. H. LeRoy and F. A. Cross. 1975. Plutonium in Atlantic Coastal Estuaries in the Southeastern United States. IAEA-SM-199/84.

Heier, K. S. and J. A. S. Adams. 1964. "The Geochemistry of the Alkali Metals." Phys. Chem. Earth. 5:235-380.

Heier, K. S. and J. L. Carter. 1964. "Uranium, Thorium, and Potassium Contents in Basic Rocks and Their Bearing on the Nature of the Upper Mantle." In: The Natural Radiation Environment. p. 75, J. A. S. Adams and W. M. Lowder (eds.).

Heier, K. S. and J. J. W. Rogers. 1963. "Radiometric Determination of Thorium, Uranium, and Potassium in Basalts and in Two Magmatic Differentiation Series." Geochim. et. Cosmochim. Acta. 27:137.

Helgeson, H. C. 1968. "Evaluation of Irreversible Reactions in Geochemical Processes Involving Minerals and Aqueous Solution--I, Thermodynamic Relations." Geochim. et Cosmochim. Acta. Vol. 32, p. 853.

Helgeson, H. C., T. H. Brown, A. Nigrini, and T. A. Jones. 1970. "Calculations of Mass Transfer in Geochemical Processes Involving Aqueous Solutions." Geochim. et Cosmochim. Acta. Vol. 34, p. 569.

Helgeson, H. C. 1969. "Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures." Am. J. Sci. 267:729-804.

Hem, J. D. 1970. Study and Interpretation of the Chemical Characteristics of Natural Water. Geological Survey Water Supply Paper 1473.

Hetherington, J. A. 1975. "Chapter 5. The Behavior of Plutonium Nuclides in the Irish Sea." In: Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms. Rochester International Conference on Environmental Toxicity, 8th, 1975.

Hetherington, J. A., D. F. Jefferies, N. J. Mitchell, R. J. Pentreath and D. S. Woodhead. 1975. Environmental and Public Health Consequences of the Controlled Disposal of Transuranic Elements to the Marine Environment. IAEA-SM-199/11.

Higgins, G. H. 1959. "Evaluation of the Ground-Water Contamination Hazard from Underground Nuclear Explosions." J. Geophys. Res. 64:1509-1520.

Hirano, S., T. Koyanagi, and M. Saiki. 1973. The Physico-Chemical Behavior of Radioactive Cerium in Seawater. IAEA-SM-158/3, pp. 47-55.

- Hirst, D. M. 1962. "The Geochemistry of Modern Sediments from the Gulf of Paria. II. The Location and Distribution of Trace Elements." Geochim. et Cosmochim. Acta. 26:1147-1188
- Holland, H. D. and J. L. Kulp. 1954. "The Mechanism of Removal of Thorium and Radium from the Oceans." Geochim. et Cosmochim. Acta. 5:214-224.
- Horrath, E. 1960. "Investigations of Uranium Adsorption to Peat in Natural Waters Containing U-Traces." Magyar Tudományos Akad. Atommag Kutató Intézete, Közlemények. 2:177-183 (in Hungarian).
- Horstman, E. L. 1957. "The Distribution of Lithium, Rubidium, and Caesium in Igneous and Sedimentary Rocks." Geochim. et Cosmochim. Acta. 12:1-28.
- Horton, J. H. and D. I. Ross. 1960. "Use of Tritium from Spent Uranium Fuel Elements as a Ground-Water Tracer." Soil Science. 90:267-271.
- Howery, D. G. and H. C. Thomas. 1965. "Ion Exchange on the Mineral Clinoptilolite." J. Phys. Chem. 69:531-537.
- Hubbard, J. E. 1968. ¹³⁷Cs in an Alpine Watershed. Thesis, Colorado State University, Fort Collins, CO.
- Hubbard, J. E. and W. D. Striffler. 1973. "Cesium-137 in a Mountain Stream Channel." Water Resour. Res. 9:1440-1442.
- Hubbell, D. W. and J. L. Glenn. 1973. Distribution of Radionuclides in Bottom Sediments of the Columbia River Estuary. Geological Survey Professional Paper 433-L, 63 pp.
- IAEA. 1975. "The Oklo Phenomenon." Proc. Sym., International Atomic Energy Agency, Libreville, 23-27, June 1975.
- Imahashi, M. 1970. "Uranium and Thorium in Hydrothermally Altered Rocks Under Acid Conditions. As Exemplified by Silicified Rocks from Tateyama Jigokudani, Toyama." Nippon Kagaku Zasshi. 91:668-9 (in Japanese).
- Iskra, A. A., N. V. Kulikov, and U. G. Bakhurov. 1969. "Behavior of Natural Radioactive Elements in Non-Running Freshwater Basin." A. Energ. (U.S.S.R.). 27:134-7 (in Russian).
- Izrael, U. A., V. N. Petrov, A. A. Pressman, F. A. Rovinsky, E. D. Stukin, and A. A. Ter-Saakov. 1969. Radioactive Contamination of the Environment by Underground Nuclear Explosions and Methods of Forecasting It.
- Izrael, Yu. A. and F. Ya. Rovinskii. 1970. Hydrological Uses of Isotopes Produced in Underground Nuclear Explosions for Peaceful Purposes. UCRL-Trans-10458.

- Jackson, D. D. 1976. Radiochemical Studies for the Nuclear Chemical Mining of Copper. UCRL-52025.
- Jacobs, D. C. 1974. Impacts in Groundwater of Effluents Arising in the Nuclear Industry. NP-20456, pp. vp., Paper 16.
- Jacobs, D. G., Y. E. Kim, and O. M. Sealand. 1966. Application of Mineral Exchange to Reactor Technology. ORNL-4007, pp. 27-33.
- James, R. O. and T. W. Healy. 1972. "Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface." J. Colloid Interfac. Sci. 40:65-81.
- Jenne, E. A. and J. S. Wahlberg. 1968. Role of Certain Stream-Sediment Components in Radioion Sorption. U.S.G.S. Professional Paper 433-F.
- Jenne, E. A., ed. 1979. "Chemical Modeling in Aqueous Systems." ACS Symposium Series 93, American Chemical Society, Washington, DC.
- Jennings, A. R. and M. C. Schroeder. 1968. "Evaluation of Selected Isotopes as Ground Water Tracers." Water Resour. Res. 4:829-836.
- Johnson, V., M. H. Cutshall and C. Osterberg. 1967. "Retention of ^{65}Zn by Columbia River Sediment Water Resources Research." 3(1):99-102.
- Jones, A. D. and G. R. Choppin. 1969. "Complexes of Actinide Ions in Aqueous Solutions." Actinide Reviews. 1:311-336.
- Jordan, C. F., J. R. Kline, and D. S. Sasscer. 1971. "Tritium Movement in an Old-Field Ecosystem Determined Experimentally." In: Radionuclides in Ecosystems. CONF-710501-P1, pp. 199-203.
- Joseph, A. B., P. F. Gustafson, I. R. Russel, E. A. Schuert, H. L. Volchok, A. Tamplin. 1971. "Sources of Radioactivity and Their Characteristics." In: Radiochemistry in the Marine Environment. National Academy of Sciences.
- Joshi, L. U. and A. K. Ganguly. 1970. "Disequilibrium Studies in $^{232}\text{Th}/^{228}\text{Th}$ Activity Ratio in Some Sediment Samples of India." Proceedings of the Chemistry Symposium, Bombay. Dept. of Atomic Energy, II:137-48.
- Juguet, B., M. Donner, L. Coin, and C. Burg. 1966. Importance of Mud and Suspended Matter in the Transport and Elimination of Radionuclides Contained in Surface Waters. IAEA-SM-72/7 (in French).
- Kampbell, D. H. 1964. Cerium, Iron, and Manganese Sorption by Soil Colloid and Uptake by Plants. Thesis, Univ. of Missouri, Columbia, MO.
- Karttunen, J. O. and D. N. Edgington. 1974. "Distribution of Plutonium in Lake Michigan Sediments." In: Radiological and Environmental Research Division Annual Report, January - December 1974. Ecology. ANL-75-3 (Pt. 3), pp. 113-127.

- Katcoff, S. 1958. "Fission-Product Yield from U, Th, and Pu." Nucleonics. 16:78-86.
- Katsurayama, K. 1968. "Accumulation of Radioactivity in Rice Fields." Annu. Rep. Res. Reactor Inst. Kyoto University. 1:293-97.
- Kaufman, W. J. and P. C. Klingerman. 19--. Nature and Disposition of Sediment Sorbed Radionuclides Entering San Francisco Bay, pp. 149-159.
- Kaufmann, R. F., G. G. Eadie and C. R. Russell. 1975. Summary of Ground Water Quality Impacts of Uranium Mining and Milling in the Grants Mineral Belt, New Mexico. U.S.E.P.A., Off. Rad. Prog.-Las Vegas Facility. Tech. Note ORP/LV-75-4.71 p.
- Kaufmann, R. F., G. G. Eadie and C. R. Russell. 1976. "Effects of Uranium Mining and Milling on Ground Water in the Grants Mineral Belt, New Mexico." Ground Water. 14(5):296-308.
- Kaufman, S. and W. F. Libby. 1954. "The Natural Distribution of Tritium." Phys. Rev. 93:1337.
- Kaufman, W. J. and G. T. Orlob. 1955. "Measuring Ground Water Movement with Radioactive and Chemical Tracers." Paper presented at the Annual Meeting of the California Section of ANMA, Sacramento.
- Kawabata, T. 1967. "Studies on the Sorption and Release of Radionuclides by River Sediments." J. Radiation. Res. 8:20-31.
- Keller, C. 1971. The Chemistry of the Transuranium Elements. Vol. 3. Kernchemie in Einzeldarstellungen. Verlag Chemie/GmbH.
- Kennedy, C. W., G. E. Bartelt, and K. A. Orlandini. 1977. Uranium in Water and Suspended Sediments of the Great Miami River, Ohio. ANL-77-5 Part III, pp. 86-88.
- Kepak, F. 1974. "Separation of Radionuclides in Colloidal Form from Aqueous Solutions." Journal of Radioanalytical Chemistry. 20:159-166.
- Kepak, F. 1966. "Sorption of the Radioisotopes ^{35}S , ^{131}I and ^{106}Ru on Hydrated Oxides in Laboratory Columns." Collection Czechoslov. Chem. Commun. 31:3500-3511.
- Kester, D. R. and R. M. Pytkowicz. 1967. "Determination of the Apparent Dissociation Constants of Phosphoric Acid in Seawater." Limn. and Ocean. 12:243-252.

- Khalid, R. A., W. H. Patrick, Jr. and R. P. Gambrell. 1978. "Effect of Dissolved Oxygen on Chemical Transformations of Heavy Metals, Phosphorus, and Nitrogen in an Estuarine Sediment." Estuarine and Coastal Marine Science. (6):21-35.
- Kimura, Y., H. Morishima, T. Koga, H. Kawai and Y. Honda. 1968. "Studies on the Behavior and Distribution of Radioactive Substances in Coastal and Estuarine Waters." Kinki Daigaku Genshiryaku Kenkyusho Nonpo. 7:21-31 (in Japanese).
- Klechkovsky, V. M. 1956. On the Behavior of Radioactive Fission Products in Soil. Their Absorption by Plants and Their Accumulation in Crops. AEC-TR-2867.
- Kline, J. R. and C. F. Jordan. 1968. "Tritium Movement in Soil of Tropical Rain Forest." Science. 160:550-551.
- Klingeman, P. C. 1965. Transport of Radionuclides in Surface and Estuarine Waters. Thesis, University of California, Berkeley, CA.
- Klingeman, P. C. and W. J. Kaufman. 1965. Transport of Radionuclides with Suspended Sediment in Estuarine Systems. TID-24140.
- Knaelmann, M. 1970. "Effect of Concentration on the Iodide Sorption by Various Soils." Atomkernenergie. 16:247-52 (in German).
- Knoll, K. C. 1965. Reaction of High Salt Aqueous Plus Organic Waste with Soil. BNWL-CC-313, Pacific Northwest Laboratory, Richland, WA.
- Knoll, K. C. 1969. Reactions of Organic Wastes in Soil. BNWL-860, Pacific Northwest Laboratory, Richland, WA.
- Koczy, F. F. 1949. "Thorium in Sea Water and Marine Sediments." Geol. Foren. i Stockholm Forh. 71:238-42.
- Koczy, F. F., E. Tomic, and F. Hecht. 1957. "Geochemistry of Uranium in the Baltic Sea Basin." Geochim. et Cosmochim. Acta. 11:86-102 (in German).
- Kokotov, Yu. A., R. F. Popova, I. Tsing-Chih, and M. Shih-tsi. 1962. "Sorption of Long Lived Fission Products by Soils and Argillaceous Minerals. II. Sorption of Cerium-144 by Soils." Radiokhimiya. 4:227-228.
- Koliadin, L. B., D. S. Nikolaev, S. M. Grashchenko, Y. V. Kuznetsov, and K. F. Lazarev. 1960. "States of Uranium Detected in Black Sea Waters." Doklady Akad. Nauk S.S.S.R. 132:915-17 (in Russian).
- Kolodny, Y. 1969. Studies in Geochemistry of Uranium and Phosphorites. University of California. Thesis.
- Kolodny, Y. and I. R. Kaplan. 1970. Deposition of Uranium in the Sediment and Interstitial Water of an Anoxic Fjord. CONF-700965-1.

- Koranda, J. J. 1965. "Preliminary Studies of the Persistence of Tritium and ^{14}C in the Pacific Proving Ground." Health Phys. 11:1445-1457.
- Korotkin, Yu. S. 1972. Study of Transplutonium Element Hydrolysis. II. Hydrolysis of Americium (III) in the Presence of Ions with Positive and Negative Hydration Energy. JIWR-P-6403.
- Kotegov, K. V., O. N. Pavlov and V. P. Shvedov. 1968. "Technetium." In: Advances in Inorganic Chemistry and Radiochemistry. 11:1-90, Academic Press, NY.
- Kovalevskii, A. L. 1967. "Dependence of the Content of Some Trace Elements on the Clayiness of Soils." Mikroelem. Biosfere Ikh Primer. Sci. Khoz. Med. Sib. Dal'nego Vostoka, Dokl. Sib. Knof., 2nd. 1964. O. V. Makew. Buryat. Khizhn. Izd. Ulan-Ude, USSR.
- Krylov, A. Y. and M. M. Shats. 1958. Some Regularities of Uranium Migration in Waters of Northwestern Districts of USSR. AEC-tr-4474:319-32.
- Kubose, D. A., M. G. Lai, H. A. Goya, and H. I. Cordova. 1968. Radioactivity Release from Radionuclide Power Sources. VIIa. Dissolution Studies of Plutonium Dioxide in the Ocean, 5 Months' Exposure. USNRDL-TR-68-74.
- Kudo, A. 1969. Radioactivity Transport in Water. Interaction Between Flowing Water and Bed Sediment. Thesis, University of Texas, Austin, Texas.
- Kudo, A. and E. F. Gloyna. 1971. "Transport of ^{137}Cs , II Interaction with Bed Sediments." Water Research. Vol. 5, pp. 71-79.
- Kulikov, N. V. 1968. "Influence of Certain Complexons on Radioisotope Sorption by Soil." Tr. Inst. Ekol. Rast. Zknivotn. 61:21-5 (in Russian).
- Kulikov, N. V. and I. V. Molchanova. 1972. Radioisotopes in the Soil - Solution System. INIS-MF-887-3-, pp. 2-13 (in Russian).
- Kuo, S. and E. G. Lotse. 1974. "Kinetics of Phosphate Adsorption and Desorption by Lake Sediments." Soil Sci. Soc. Amer. Proc. 38:50-54.
- Kurokawa, Y. 1971. "Data of Natural Radioactivity in Japan." Hoken Butsuri. 6:192-3 (in Japanese).
- Kuznetsov, Y. V. 1969. "On Occurrence Forms of Ionium (^{230}Th) and Thorium (^{232}Th) in the Ocean." Geokhimiya. No. 2:177-84 (in Russian).
- Kuznetsov, Y. V., V. K. Legin, A. P. Lisitsyn, and Z. H. Simonyak. 1964. Radioactive Ocean Suspensions. I. Isotopes of Thorium in Ocean Suspensions. Radiokhimiya. 6:242-54 (in Russian).

- Kuznetsov, Y. V., V. K. Legin, A. P. Lisitsyn, and Z. N. Simonyak. 1967. "Radioactivity of Oceanic Suspensions. II. Uranium in Oceanic Suspensions." Radiokhimiya. 9:489-97 (in Russian).
- Kuznetsov, Y. V., E. V. Komarov, A. N. Elizarova, Z. N. Simonyak and A. A. Bochkov. 1973. "Simulation of the Forms of Thorium-230 in Seawater to Study its Sedimentation Mechanism." Sov. Radiochem, pp. 715-720.
- Kuznetsov, Y. V. and V. N. Schebetkovskii. 1971. "Distribution of Radioactive Isotopes Between Sea Waters and Sediments." Geokhimiya. No. 12:1466-72 (in Russian).
- Kuznetsov, Y. V., Z. N. Simonyak, A. P. Lisitsyn, and M. S. Frenkikh. 1968. Thorium Isotopes (^{230}Th , ^{232}Th) in the Surface Layer of the Indian Ocean Sediments." Geochem. Int. 5:169-177.
- Labeyrie, L. D., H. D. Livingston and V. T. Bowen. 1975. Comparison of the Distributions in Marine Sediments of the Fallout Derived Nuclides ^{55}Fe and $^{239,240}\text{Pu}$: A New Approach to the Chemistry of Environmental Radionuclides. IAEA-SM-199/115.
- Lambert, M. S. and D. S. Nikolaev. 1962. "The Mode of Uranium Occurrence in the Waters of the Azov Sea and in a Number of Estuaries and Rivers of the Azov-Black Sea Basin." Doklady Akad. Nauk S.S.S.R. 142:681-2 (in Russian).
- Lammers, W. T. 1968. The Distribution of ^{60}Co , ^{106}Ru , and ^{137}Cs Among Suspended and Dissolved Particles in White Oak Lake. K-1758.
- L'Annunziata, M. F. and W. H. Fuller. 1968. "The Chelation and Movement of ^{89}Sr - ^{90}Sr (^{90}Y) in a Calcareous Soil." Soil Sci. 105:311-19.
- Latimer, W. M. 1952. The Oxidation States of the Elements and Their Potentials in Aqueous Solutions. Second Edition. Prentice-Hall, Inc., Englewood Cliffs, NJ.
- Lauderdale, R. A. 1951. "Treatment of Radioactive Water by Phosphate Precipitation." Industrial and Engineering Chemistry. 43:1538-1540.
- Lavrukhina, A. K. and A. A. Pozdnyakov. 1970. Analytical Chemistry of Technetium, Promethium, Astatine and Francium. Translated by R. Kondor. Ann Arbor - Humphrey Science Publishers.
- Lazarev, K. F., D. S. Nikolaev, and S. M. Grashchenko. 1961. "Concentration of Thorium Isotopes in Sea Water." Radiokhimiya. 3:623-35 (in Russian).
- Lean, D. R. S. and M. N. Charlton. 1976. A Study of Phosphorous Kinetics in a Lake Ecosystem in Environmental Biogeochemistry. Edited by J. O. Nriagu, Ann Arbor Science Publishers, Inc., Michigan.

- Legin, V. K., Y. V. Kuznetsov and K. F. Lazarev. 1966. "Uranium Occurrence in Marine Sediments." Geokhimiya. 5:606-608 (in Russian).
- Lerman, A. 1971. Transport of Radionuclides in Sediments. CONF-710, 5v1-P2, pp. 936-944.
- Lerman, A. and T. A. Lietzke. 1975. "Uptake and Migration of Tracers in Lake Sediments." Limnol. Oceanogr. 20:497-510.
- Lerman, A. and H. Taniguchi. 1971. Strontium-90 and Cesium-137 in Water and Deep Sediments of the Great Lakes. CONF-710501-P1, pp. 460-464.
- Lerman, A. and H. Taniguchi. 1972. "⁹⁰Sr: Diffusions Transport in Sediments of the Great Lakes." J. Geophys. Res. 77:474-81.
- Lester, D. H., G. Jansen and H. C. Burkholder. 1975. "Migration of Radionuclide Chains Through an Adsorbing Medium." In: Adsorption and Ion Exchange, AIChE Symposium Series, 152(71):202-214.
- Lewis, R. J. and H. C. Thomas. 1963. "Adsorption Studies on Clay Minerals. VIII. A Consistency Test of Exchange Sorption in the Systems Sodium - Cesium - Barium Montmorillonite." J. Chem. Phys. 67:1781-1783.
- Li, W. C., D. E. Armstrong, J. P. H. Williams, R. F. Harris and J. K. Syers. 1972. "Rate and Extent of Inorganic Phosphate Exchange in Lake Sediments." Soil Sci. Soc. Amer. Proc. 36:279-285.
- Liebscher, K., F. Habashi, and T. Schonfeld. 1961. "Observations on the Behavior of Fission Product in Surface Waters." Atompraxis. 7:94-100 (in German).
- Lindenbaum, A. and W. Westfall. 1965. "Colloidal Properties of Plutonium in Dilute Aqueous Solution." Inter. J. App. Radiation and Isotopes. 16:545-553.
- Lindsay, W. L. 1972. "Inorganic Phase Equilibria of Micronutrients in Soils." In: Micronutrients in Agriculture, pp. 41-57. Soil Sci. Soc. Amer. Inc., Madison WI.
- Lisitsyn, A. P. and M. S. Frenkikh. 1968. "Uranium and Radium in the Surface Layer of Oceanic Sediments." Geokhimiya. No. 3:323-33 (in Russian).
- Lister, B. and L. McDonald. 1951. Some Aspects of the Solution Chemistry of Zirconium. AERE-C/R-801.
- Lomenick, T. F. 1963. "Movement of Ruthenium in the Bed of White Oak Lake." Health Phys. 9:835-45.

- Lomenick, T. F. and T. Tamura. 1965. "Naturally Occurring Fixation of ^{137}Cs on Sediments of Lacustrine Origin." Soil Sci. Soc. Amer., Proc. 29:383-7.
- Magno, P., T. Reavey, and J. Apidianakis. 1970. Liquid Waste Effluents from a Nuclear Fuel Reprocessing Plant. BRH-NERHL-70-2.
- Mahmoud, K. A., Y. A. Yousef, N. I. Abdel-Kerim, and W. E. Y. Abdel-Malik. 1968. "Affinity of Ismailia Canal Bottom Sediments for Certain Radionuclides." Isotope Radiat. Res. 1:9-18.
- Mahmoud, K. A., Y. A. Yousef, M. M. Ishak, W. E. Y. Abdel-Malik, S. R. Khalil, A. Shafik, and R. M. K. El-Shinawy. 1973. "Transfer Mechanism and Concentrating Processes of Certain Radionuclides in the Aquatic Ecology of the Ismailia Canal." In: Environmental Behavior of Radionuclides Released in the Nuclear Industry. IAEA, Vienna. pp. 205-215.
- Manskaya, S. M., G. V. Drozdora, and M. P. Yemel'yanova. 1956. "Fixation of Uranium by Humic Acids and Melanoidins." Geokhimiya. No. 4.
- Marshall, J. S., D. N. Edgington and M. A. Wahlgren. 1973. Great Lakes Radioecology Program: Introduction. ANL-8060, Part 3, pp. 1-5.
- Marter, W. L. 1974. Radioactivity from SRP Operations in a Downstream Savannah River Swamp. DP-1370.
- Martin, J. M., J. Jednacak and V. Pravdic. 1971. "The Physico-Chemical Aspects of Trace Element Behavior in Estuarine Environments." Thalassia, Ugoslavica. 7(2):619-637.
- Masuda, K. and T. Yamamoto. 1971. "Studies on Environmental Contamination by Uranium. II. Adsorption of Uranium on Soil and Its Desorption." J. Radiat. Res. 12:94-99.
- Means, J. L., D. A. Crerar, and J. O. Duguid. 1976. Chemical Mechanisms of ^{60}Co Transport in Ground Water from Intermediate - Level Liquid Waste Trench 7: Progress Report for Period Ending June 30, 1975. ORNL/TM-5348.
- Meeusen, M. A., G. J. Willems and C. J. DeRanter. 1975. "Sorption Capacity Studies of Scheldt Sediments for ^{60}Co , ^{85}Sr , and ^{137}Cs ." J. Pharm. Belg. 30(1):82-90.
- Menzel, R. G. 1968. "Uranium, Radium, and Thorium Content in Phosphate Rocks and Their Possible Radiation Hazard." J. Agr. Food Chem. 16:231-34.
- Mercer, B. W. 1966. Adsorption of Trace Ions from Intermediate Level Radioactive Wastes by Ion Exchange. BNWL-180, Pacific Northwest Laboratory, Richland, WA.

- Mercer, B. W. 1967. "Ion Exchange Equilibria of Trace Cesium-137 and Strontium-85 in Multicomponent Systems." BNWL-SA-1173, Pacific Northwest Laboratory, Richland, WA.
- Merriam, C. N., Jr. and H. C. Thomas. 1956. "Absorption Studies on Clay Minerals. IV. Alkali Ions on Attapulgite." J. Chem. Phys. 24:993.
- Meyer, G. L. 1975. Preliminary Data on the Occurrence of Transuranium Nuclides in the Environment at the Radioactive Waste Burial Site. Maxey Flats, KY.
- Mihalik, P. 1968. Uranium Compounds in the Dominion Peefs, and Their Association with Phosphorus Compounds. NIM-415.
- Miner, F. J., P. A. Glover, and H. W. Miller. 1973. Plutonium Behavior in the Soil/Water Environment. RFP-2004-A, pp. 1-3.
- Miner, F. J., P. A. Glover, and W. L. Polzer. "Plutonium Behavior in the Soil/Water Environment. I. Sorption of Plutonium by Soils." Agronomy Abstracts, p. 35.
- Miyake, Y. and Y. Sugimura. 1975. The Plutonium Content in the Pacific Ocean Waters. IAEA-SM-199/22.
- Mizuno, A. and T. Mochizuki. 1970. "Distribution of Uranium in the Sediments from San'in Off-Shore, Southwestern Japan." Chishitsu Chosasho Geppo. 21:287-292 (in Japanese).
- Mo, T. and F. G. Lowman. 1975. Laboratory Experiments on the Transfer Dynamics of Plutonium from Marine Sediments to Seawater and to Marine Organisms. CONF-750503-5, 35 p.
- Mo, T., A. D. Suttle, and W. M. Sackett. 1973. "Uranium Concentrations in Marine Sediments." Geochim. et Cosmochim. Acta. 37:35-51.
- Molchanova, I. V. 1968. "Behavior of Cerium-144, in Various Types of Soil." Tr. Inst. Ekol. Rast. Zhivotn. 61:4-11.
- Montgomery, D. M., H. E. Kolde, and R. L. Blanchard. 1977. Radiological Measurements at the Maxey Flats Radioactive Waste Burial Site 1974-75. EPA-520/5-76/020.
- Moore, L. R. 1964. "The Microbiology, Mineralogy and Genesis of a Tonstein." Prac. Yorkshire Geol. Soc. 34:235-292.
- Morel, F. and J. Morgan. 1972. "A Numerical Method for Computing Equilibria in Aqueous Chemical Systems." In: Environmental Science and Technology. 6(1):58.

- Mortensen, J. L. and E. C. Marcusiu. 1963. "Fission Product Soil Organic Matter Complexes. I. Strontium-90 (Yttrium-90) in Water Extracts and HCl Hydrolysis of Soil." Soil Sci. Soc. Am. Proc. 27:653-6.
- Mortensen, J. L., E. C. Marcusiu, and N. Holowaychuk. 1963. "Strontium Exchange Characteristics of Soils from the Ogctoruk Creek Watershed in Alaska." Ohio J. Sci. 63:225-31.
- Mortimer, C. H. 1941. "The Exchange of Dissolved Substances Between Mud and Water on Lakes." J. Ecology. 29:280-329.
- Moskin, A. I. 1969. "Complex Formation of the Actinides with Anions of Acids in Aqueous Solutions." Soviet Radiochemistry. 11:447.
- Mummer, C. N., D. L. Roukhust, and D. R. Kosiur. 1975. MIX2: A Computer Program for Modeling Chemical Reactions in Natural Waters. PB-251668, National Technical Information Service.
- Mun, A. I. and Z. A. Basilevich. 1964. "Some Characteristics of the Distribution of Iodine in Lake Muds." Geokhimiya. No. 5:468-476.
- Murray, E. G. and J. A. S. Adams. 1958. "Amount and Distribution of Thorium, Uranium, and Potassium in Sandstones." Geochim. et. Cosmochim. Acta. 13:260.
- Murray, C. N. and H. Kaursky. 1975. Plutonium and Americium Values in the North Sea and German Coastal Regions. IAEA-SM-199/26.
- Murray, C. N. and L. Murray. 1973. Adsorption-Desorption Equilibria of Some Radionuclides in Sediment-Fresh-Water and Sediment-Seawater Systems. IAEA-SM-158/7.
- Nagaya, Y. and M. Saiki. 1967. "Accumulation of Radionuclides in Coastal Sediment of Japan. I. Fallout Radionuclides in Some Coastal Sediments in 1954-1965." J. Radiat. Res. 8:37-43.
- Nakamura, K. and Y. Nagaya. 1975. "Accumulation of Radionuclides in Coastal Sediment of Japan, (2). Contents of Fission Products in Some Coastal Sediments Collected in 1966-1972." J. Radiat. Res. 16:184-192.
- Naumov, G. B. 1961. "Some Physico-Chemical Peculiarities of Uranium Behavior in Hydrothermal Solutions." Geokhimiya. No. 2:115-132 (in Russian).
- Nelson, D. J., R. L. Herman et al. 1961. Clinch River Studies. ORNL-3189, pp. 129-39.
- Nelson, D. M., and M. B. Lovett. 1977. The Oxidation State of Plutonium in the Irish Sea. ANL-77-5 Part III, p. 99.

- Nelson, J. L. and W. L. Haushild. 1970. "Accumulation of Radionuclides in Bed Sediments of the Columbia River Between Hanford Reactors and McNary Dam." Water Resour. Res. 6:130-7.
- Nelson, J. L., R. W. Perkins, J. M. Nielsen, and W. L. Haushild. 1966. Reactions of Radionuclides from the Hanford Reactors with Columbia River Sediments. IAEA-SM-72/8, pp. 139-61.
- Nevissi, A. and W. R. Shell. 1975. "Distribution of Plutonium and Americium in Bikini Atoll Lagoon." Health Physics. 28:539-547.
- Niggli, P. 1952. Rocks and Mineral Deposits. Volume 2.
- Nikolaev, D. S., V. M. Drozhzhin, K. F. Lazarev, and O. P. Korn. 1969. "The Geochemical Balance of Radioactive Elements in the Basin of the Black and Azov Seas. II. Reserves of Thorium Isotopes." Radiokhimiya. 11:688-98 (in Russian).
- Nikolskii, B. P., L. I. Krylov, B. B. Zakhvataev. 1974. "Sorption of Ions of Some Polyvalent Actinide and Rare-Earth Elements by a Cationite with a Ethalic Functional Group." Radiokhimiya. 16(2):162-166.
- Nishita, H. and E. H. Essington. 1967. "Effect of Chelating Agents on the Movement of Fission Products in Soils." Soil Science. 103(3):168-176.
- Nishita, H., M. Hamilton, and A. J. Steen. 1976. "Extractability of ^{238}Pu and ^{242}Cm from a Contaminated Soil as a Function of pH and Certain Soil Components." Presented at Meeting of Soil Science Society of America, November 28-December 3, Houston, Texas.
- Nishita, H., M. Hamilton and A. J. Steen. 1976. "Extractability of ^{238}Pu and ^{242}Cm from a Contaminated Soil as a Function of pH and Certain Soil Components. HNO_3 - NaOH System." Presented at Annual Meeting of Soil Science Society of America, Houston, Texas.
- Nishita, H., B. W. Kowalewsky, A. J. Steen, and K. H. Larson. 1956. "Fixation and Extractability of Fission Products Contaminating Various Soils and Clays I. Strontium-90, Ruthenium-106, Cesium-137, and Cerium-144." Soil Science. 81:317-326.
- Nishiwaki, Y., Y. Honda, Y. Kimura, H. Morishima, T. Koga, Y. Miyaguchi, and H. Kawai. 1972. "Behavior and Distribution of Radioactive Substances in Coastal and Estuarine Waters." In: Radioactive Contamination of the Marine Environment. IAEA-SM-158/11, pp. 177-193.
- Noshkin, V. E. 1972. "Ecological Aspects of Plutonium Dissemination in Aquatic Environments." Health Physics. 22:537-549.

- Noshkin, V. E. and V. T. Bowen. 1973. "Concentrations and Distributions of Long-Lived Fallout Radionuclides in Open Ocean Sediments." In: Radioactive Contamination of the Marine Environment. IAEA-SM-158/45, 671-686.
- Noshkin, V. E., K. M. Wong, R. J. Eagle, and C. Gatrousis. 1971. Transuranics at Pacific Atolls. I. Concentrations in the Waters at Enewetak and Bikini. UCRL-51612.
- Noshkin, V. E., K. M. Wong, K. Marsh, R. Eagle, G. Holladay, and R. W. Buddemeier. 1975. Plutonium Radionuclides in the Ground Waters at Enewetak Atoll. IAEA-SM-199/33.
- Ojima, T., H. Toratani, and H. Fujimoto. 1965. "Behavior of Radioactive Strontium, Cesium, and Cobalt in Marine Water." Ann. Rep. Radiat. Center Osaka Prefect. 6:93-7.
- ORNL. 1970. Siting of Fuel Reprocessing Plants and Waste Management Facilities. ORNL-4451.
- Ophel, I. L. 1973. Environmental Capacity of Fresh-waters for Waste Radionuclides. Environmental Behavior of Radionuclides Released in the Nuclear Industry. IAEA, Vienna, pp. 613-624.
- Ophel, I. L. and C. D. Fraser. 1971. Fate of Cobalt-60 in a Natural Freshwater Ecosystem. CONF-710501-PI. pp. 323-327.
- Ophel, I. L., C. C. Fraser, and J. M. Judd. 1972. Strontium Concentration Factors in Biota and Bottom Sediments of a Freshwater Lake. EUR-4800 (Vols. 1 and 2), pp. 509-30.
- Orcutt, R. G., M. N. E. Rifai, G. Klein, and W. J. Kaufman. 1957. "Underground Movement of Radioactive Wastes." Presented at Nuclear Engineering and Science Congress, Philadelphia, Pennsylvania, March 11, 1957.
- Orlova, E. I. 1965. "Migration of ^{90}Sr in the Ground Waters of Various Salt Compositions." Gig. Sanit. No. 7:46-50 (in Russian).
- Osterberg, C., M. Cutshall, V. Johnson, J. Cronin, D. Jennings, and L. Frederick. 1966. "Some Non-Biological Aspects of Columbia River Radioactivity." In: Disposal of Radioactive Wastes into Seas, Oceans and Surface Waters. IAEA-SM-72/18A, pp. 321-335.
- Palei, P. N. (comp.). 1962. Analytical Chemistry of Uranium. Trans. by M. Kaner. 1963. Israel Program for Scientific Translations Ltd., 421 p.
- Parker, M. 1966. Studies on the Distribution of Cobalt in Lakes. C00-1281-5.
- Parker, V. B., D. D. Wagman, and W. H. Evans. 1971. Selected Values of Chemical Thermodynamic Properties. U.S. Department of Commerce. NBS Technical Note 270-6.

- Pashneva, G. E., T. P. Slavnina, and V. V. Serebrennikov. 1965. "Rare Earth and Thorium Content in Soils of Tomsk Region." Izv. Sibirsk. Otd. Akad. Nauk SSSR, No. 4 Ser. Biol.-Med. Nauk. No. 1:58-52 (in Russian).
- Patterson, J. H., G. M. Matlack and G. B. Nelson. 1974a. "The Interaction of $^{238}\text{PuO}_2$ Heat Sources with Simulated Terrestrial Environments." Am. Nuclear Society Transactions. 19:33-34.
- Patterson, J. H., G. B. Nelson and G. M. Matlack. 1974b. The Dissolution of ^{238}Pu in Environmental and Biological Systems. LA-5624.
- Peperstraete, H., J. Vos, S. Van Puymbroeck and O. Banderborcht. 1973. Physico-chemical Characteristics of Five Ruthenium Salts During Freshwater to Marine Transition. IAEA-SM-158/52.
- Perkins, R. W., J. L. Nelson, and W. L. Haushild. 1966. "Behavior and Transport of Radionuclides in the Columbia River Between Hanford and Vancouver, Washington." Limnol. Oceanog. 11:235-48.
- Pettersson, H. 1949. "Exploring the Bed of the Ocean." Nature. 164:468-70.
- Phillips, J. W., J. Gruhlke and G. A. Gaul. 1977. Summary of Radioactivity Released in Effluents from Nuclear Power Plants from 1972 through 1975. EPA-520/3-77-006.
- Pickering, R. J. 1969. Distribution of Radionuclides in Bottom Sediment of the Clinch River Eastern Tennessee. USGS Prof. Paper 433-H. pp. H1-H25.
- Pickering, R. J. 1970. Composition of Water in Clinch River, Tennessee River, and Whiteoak Creek as Related to Disposal of Low-Level Radioactive Liquid Wastes. USGS Professional Paper 433-0, 15 p.
- Pickering, R. J., P. H. Carrigan, Jr., and F. L. Parker. 1965. The Clinch River Study - An Investigation of the Fate of Radionuclides Released to a Surface Stream. Geological Survey Circular 497.
- Pickering, R. J., P. H. Carrigan, T. Tamura, H. H. Abee, J. W. Beverage, and R. W. Andrew. 1966. Radioactivity in Bottom Sediments of the Clinch-Tennessee Rivers. IAEA-SM-72/4.
- Pillai, K. C. and E. Mathew. 1975. Plutonium in Aquatic Environment -- Its Behavior, Distribution and Significance. IAEA-SM-199/27.
- Piro, A., M. Bernhard, M. Branica, and M. Verzi. 1975. Incomplete Exchange Reaction Between Radioactive Ionic Zinc and Stable Natural Zinc in Seawater. IAEA-SM-158/2, pp. 29-44.
- Pirs, M. 1974. "Sorption-Desorption of Radioactive Caesium, Strontium, and Cerium on Earth Components." In: Population Dose Evaluation and Standards for Man and His Environment. IAEA, Vienna, pp. 539-551.

- Piiler, R. 1956. The Distribution of Thorium and Uranium in Sedimentary Rocks and the Oxygen Content of the Precambrian Atmosphere. Thesis, Rice Institute, Houston, Texas.
- Polzer, W. L. 1971. Solubility of Plutonium in Soil/Water Environments. CONF-710401, pp. 411-430.
- Polzer, W. L. and F. J. Miner. 1974. "Plutonium Behavior in the Soil/Water Environment. II. Mechanisms of Plutonium Sorption by Soils." Agronomy Abstracts, p. 37.
- Polzer, W. L. and F. J. Miner. 1977. Plutonium and Americium Behavior in the Soil/Water Environment. II. The Effect of Selected Chemical and Physical Characteristics of Aqueous Plutonium and Americium on Their Sorption by Soils. BNWL-2117, Pacific Northwest Laboratory, Richland, WA. pp. 255-286.
- Pokidin, V. K., Y. V. Kuznetov, E. A. Prozorovich, and F. A. Asadullaeva. 1972. "Radioactivity and Rate of Sediment Formation in the Caspian Sea." Geokhimiya. No. 7:834-43 (in Russian).
- Pourbaix, M. 1966. Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, Oxford, England.
- Prout, W. E. 1958. "Adsorption of Radioactive Wastes by Savannah River Plant Soil." Soil Science. 86:13-17.
- Prout, W. E. 1959. Adsorption of Fission Products by Savannah River Plant Soil. DP-394.
- Purtymun, W. D. 1971. Plutonium in Stream Channel Alluvium in the Los Alamos Area, New Mexico. LA-4561.
- Purtymun, W. D. 1973. Underground Movement of Tritium from Solid-Waste Storage Shafts. LA-5286-MS.
- Purtymun, W. D. 1974. Storm Runoff and Transport of Radionuclides in DP Canyon, Los Alamos County, New Mexico. LA-5744, pp. 1-7.
- Purushothaman, K. 1968. Transport of ^{85}Sr and ^{137}Cs Under Induced Clay Suspensions. Thesis, University of Texas, Austin, Texas.
- Purushothaman, K. 1971. "Radionuclide Transport in an Aquatic Model System." In: Trace Substances in Environmental Health. IV. D. D. Hemphill (ed.), Columbia, MO, Univ. of MO, pp. 174-85.
- Purushothaman, K. and E. F. Gloyna. 1968. Radioactivity Transport in Water: Transport of ^{85}Sr and ^{137}Cs Under Induced Clay Suspensions. ORO-490-13.

- Puschmann, H. 1970. "Research on Sorption of the Radionuclides ^{85}Sr , ^{137}Cs , and ^{131}I by Unconsolidated Sediments. Sands from the Low-Terraces of the Rivers Weser, Donau, Elbe/Germany." Deut. Gewässerk. Mitt. 14:63-72 (in German).
- Pyalling, A. O. 1970. "Effect of Physiochemical Conditions of the Medium on the Leaching of Uranium from Natural Dahllite." Probl. Regional Geol. Petrogr. Sibiri Metedy Geokhim. Geofiz. Issled. No. 2:88-91 (in Russian).
- Rabinowitz, D. D. 1969. Forced Exchange of Tritiated Water with Natural Clay. Master's Thesis, N. Mex. Inst. of Min. and Tech., Socorro, NM.
- Rabinowitz, D. D., C. R. Holmes and G. W. Gross. 1973. "Forced Exchange of Tritiated Water with Clays." In: Tritium, Messenger Graphics Pub., Phoenix and Las Vegas, 471-485.
- Radosavljevic, R. and T. Tasovac. 1970. "Capture of ^{60}Co by Suspended Particles in the Canube." In: Symposium International de Radioecologie. Vol. I. Fontenay-aux-Roses, France, pp. 83-92.
- Rai, D. and W. T. Franklin. 1973. Program for Computing Equilibrium Solution Composition in CaCO_3 and CaSO_4 Systems from Irrigation Water Compositions. Colorado State University, Water Management Technical Report No. 29.
- Rai, Dhanpat and R. J. Serne. 1978. "Solid Phases and Solution Species of Different Elements in Geologic Environments." PNL-2651. Stumm, W. and J. J. Morgan, Aquatic Chemistry. Wiley-Interscience, New York.
- Rai, Dhanpat and R. J. Serne. 1973. "Plutonium Activities in Soil Solutions and the Stability and Formation of Selected Plutonium Metals." Journal Environmental Quality. 6:89-95.
- Rancon, D. 1973. "The Behavior in Underground Environments of Uranium and Thorium Discharged by the Nuclear Industry." In: Environmental Behavior of Radionuclides Released in the Nuclear Industry. IAEA-SM-172/55, pp. 333-346 (in French).
- Raymond, J. R. 1964. Investigation of the Disposition and Migration of Gross Gamma Emitters Beneath Liquid Waste Disposal Sites. HW-81746, pp. 4.32-4.36.
- Raymond, J. R. 1965. Cesium and Strontium Distribution Beneath Liquid Waste Disposal Sites. BNL-235.
- Renfro, W. C. 1971. Seasonal Radionuclide Inventories in Alder Slough, an Ecosystem in the Columbia River Estuary. CONF-710501, P. 2, pp. 738-746.
- Reynolds, T. D. 1963. Transport of Strontium and Cesium by Stream and Estuarine Sediments. Thesis, University of Texas, Austin, Texas.

- Reynolds, T. D. and E. F. Gloyna. 1963. Radioactivity Transport in Water-Transport of Strontium and Cesium by Stream and Estuarine Sediments. Tech. Rpt. No. 1. TID-19559.
- Rhodes, D. H. 1952. Preliminary Studies of Plutonium Adsorption Hanford Soil. HW-24548.
- Rhodes, D. W. 1957a. "The Adsorption of Plutonium by Soil." Soil Science. 84:465-471.
- Rhodes, D. W. 1957b. "The Effect of pH on the Uptake of Radioactive Isotopes from Solution by a Soil." Soil Science Society of America, Proceedings. 21:389-392.
- Rhodes, D. W. and J. L. Nelson. 1957. Disposal of Radioactive Liquid Wastes from the Uranium Recovery Plant. HW-54721.
- Richmond, C. R. and E. M. Sullivan. 1974. Annual Report of Biomedical and Environmental Research Program of the LASL Health Division, January-December 1973. LA-5633-PR.
- Riley, J. P. and P. Sinkaseni. 1958. J. Mar. Res. 17:466.
- Ritchie, J. C., P. H. Hawks, and J. R. McHenry. 1972. "Thorium, Uranium, and Potassium in Upper Cretaceous, Paleocene, and Eocene Sediments of the Little Tallahatchie River Watershed in Northern Mississippi." Southeast Geol. 14:221-231.
- Robertson, D. E. 1974. Physicochemical Characterization of N-Reactor Effluent Radionuclides in Soil and Water Systems. BNWL-1950, Pacific Northwest Laboratory, Richland, WA, Pt. 2, pp. 82-85.
- Robertson, D. E. and R. W. Perkins. 1974. "Radioisotope Ratios in Characterizing the Movement of Different Physical and Chemical Species Through Natural Soils." BNWL-SA-5024, Pacific Northwest Laboratory, Richland, WA.
- Robertson, D. E. and R. W. Perkins. 1975. "Radioisotope Ratios in Characterizing the Movement of Different Physical and Chemical Species Through Natural Soils." In: Isotope Ratios as Pollutant Source and Behavior Indicators. Vienna, IAEA, IAEA-SM-191/24, pp. 123-131.
- Robertson, D. E., W. B. Silker, J. C. Langford, M. R. Petersen and R. W. Perkins. 1973. "Transport and Depletion of Radionuclides in the Columbia River." In: Radioactive Contamination of the Marine Environment. IAEA-SM-158/9, pp. 141-158.
- Robie, R. A., and D. R. Waldbaum. 1968. "Thermodynamic Properties of Minerals and Related Substances at 298.15°K (25°C) and One Atmosphere (1.013 bars) Pressure and at Higher Temperatures." Geol. Surv. Bull. 1259.

- Rogers, J. J. W. 1964. "Statistical Test of the Homogeneity of the Radioactive Components of Granite Rocks." In: The Natural Radiation Environment, J. A. S. Adams and W. M. Lowder (eds.), p. 51.
- Rogers, J. J. W. and J. A. S. Adams. 1974. "Thorium Solubilities in Water." Handbook of Geochemistry, K. H. Wedepohl, ed., Vol. II-4, p. 90-H-1, Springer-Verlag, New York.
- Ronov, A. B., Yu. A. Balashov, and A. A. Migdisov. 1967. "Geochemistry of the Rare Earths in the Sedimentary Cycle." Geochemistry International. 4:1-17.
- Rosenqvist, I. T. 1963. "Studies in Position and Mobility of the H Atoms in Hydrous Micas." In: Clays and Clay Minerals. Monograph No. 13, pp. 11-135, Macmillan Co., NY.
- Routson, R. C., G. Jansen, and A. V. Robinson. 1975. Sorption of ^{99}Tc , ^{237}Np , and ^{241}Am on Two Subsoils from Differing Weathering Intensity Areas. BNML-1889, Pacific Northwest Laboratory, Richland, WA.
- Routson, R. C., G. Jansen, and A. V. Robinson. 1976a. ^{99}Tc , ^{237}Np , and ^{241}Am Sorption on Two Subsoils from Differing Weathering Intensity Areas. BNML-2000, Pacific Northwest Laboratory, Richland, WA, Pt. 2, pp. 50-52.
- Routson, R. C., G. Jansen and A. V. Robinson. 1976b. ^{241}Am , ^{237}Np , and ^{99}Tc Sorption on Two United States Subsoils from Differing Weathering Intensity Areas. BNML-1889, Pacific Northwest Laboratory, Richland, WA.
- Routson, R. C. and R. J. Serne. 1972a. One Dimensional Model of the Movement of Trace Radioactive Solute Through Soil Columns: The PERCOL Model. BNML-1718, Pacific Northwest Laboratory, Richland, WA.
- Routson, R. C. and R. J. Serne. 1972b. Experimental Support Studies for the PERCOL and Transport Models. BNML-1719, Pacific Northwest Laboratory, Richland, WA.
- Rovinskii, F. Ya. 1967. "Migration of ^{90}Sr in Stagnant Waters." Radiokhimiya. 9:80-4 (in Russian).
- Rozhkova, Ye. V., Ye. G. Razumnaya, M. B. Serebryakova and O. V. Schebak. 1959. "Role of Sorption in Concentration of Uranium in Sedimentary Rocks." Tr. II. Mezhdunar. knof. po miro nmu ispol'z. atom. energii. 3.
- Rozzell, T. C. and J. B. Andelman. 1971. "Plutonium in the Water Environment. II. Sorption of Aqueous Plutonium on Silica Surfaces." Advances in Chemistry Series. 106:280-98.
- Rubtsov, D. M. 1966. "Distribution of Thorium in Various Soils." Pochvovedenie. No. 3:55-67 (in Russian).

- Rubtsov, D. M. 1972. "Thorium and Uranium Content in the Clay Fraction of Podzolic Mountain Soils of Thin Forests." Radioekol. Issled Priir. Biogeotsenozakh, pp. 53-66 (in Russian).
- Rubtsov, D. M. 1972. "Thorium and Radium Content in the Silt Fraction of the Podzolic Mountain Soils of Thin Forests. Radioekologicheskie Issledavaniya Prirodnkh Biogeotsenozakh." In: Izdatel'stov Nauka, Verkhovskaya (ed.), pp. 42-53.
- Ruf, M. 1968. "Contamination of Fresh Water with Radioactive Material with Special Attention to Sludge of River Dams." Wasserwirtschaft. 58:16-22 (in German).
- Ryabchikov, D. I. and E. K. Golbraikh. 1969. Analytical Chemistry of Thorium. Translated by A. Aladjem. Ann Arbor-Humphrey Science Publishers.
- Saas, A. and A. Grauby. 1973. "Mechanisms for the Transfer to Cultivated Soils of Radionuclides Discharged by Nuclear Power Stations into the System: River-Irrigated Soil--Ground Water." In: Environmental Behavior of Radionuclides Released in the Nuclear Industry. IAEA-SM-172/56, pp. 255-269.
- Safronova, N. G. 1974. "Kinetics of the Self-Purification of a Body of Water Containing Strontium-90 as a Result of Absorption of the Radionuclide by the Bottom Deposits." Sov. J. Ecol. 4:101-105.
- Sakanoue, M. 1960. "Geochemical Studies on the Radioactive Sediments. III. Uranium, Phosphorus, and Arsenic in the Sedimentary Bed at Ningyo Pass." Nippon Kagaku Zasshi. 81:898-902.
- Sakanoue, M. 1960. "Geochemical Studies on the Radioactive Sediments. II. Uranium Content of Natural Waters from the Ningyo-Pass Mining Area." Nippon Kagakii Zasshi. 81:896-898.
- Salo, A. and R. Saxen. 1974. Role of Humic Substances in the Transport of Radionuclides. SFL-A-20.
- Sanchez, A. L. 1977. Distribution Coefficients of Pu-237 and Am-241 in Aquatic Environments. Non-thesis Masters Research, Department of Oceanography.
- Sanchez, A. L. and W. R. Schell. 1977. Distribution Coefficients for Transuranic Elements in Aquatic Environments.
- Savin, A. M. 1967. Oxygen and Hydrogen Isotope Ratios in Sedimentary Rocks and Minerals. Ph.D. Dissertation, Calif. Inst. of Tech. Pasadena, CA.
- Sasscer, D. S., C. F. Jordan, and J. R. Kline. 1971. "Mathematical Model of Tritiated and Stable Water Movement in an Old-Field Ecosystem." In: Radionuclides in Ecosystems. CONF-710501-P1, pp. 915-923.

- Schebetkovskii, V. N. and Yu. V. Kuzketsov. 1971. "(W73-04324) Behavior of Cs-137 and Ce-144 in the Sorption System Sea Water-Sediment." Trans. from Radiokhimiya. 13(6):911-913.
- Schell, W. R. and R. L. Walters. 1975. "Plutonium in Aqueous Systems." Health Physics. 29:589-597.
- Schell, W. R., T. H. Sibley, A. Nevissi and A. Sanchez. 1979. Distribution Coefficients for Radionuclides in Aquatic Environments. II. Studies on Marine and Freshwater Sediment Systems Including the Radionuclides 106-Ru, 137-Cs and 241-Am. Second Annual Research Progress Report, NUREG/CR-0802.*
- Schell, W. R., T. H. Sibley, A. Sanchez and J. R. Clayton, Jr. 1980. Distribution Coefficients for Radionuclides in Aquatic Environments. III. Adsorption and Desorption Studies of 106Ru, 137Cs, 241Am, 89Sr and 237Pu in Marine Freshwater Systems. NUREG/CR-0803.*
- Schmalz, B. L. 1972. Radionuclide Distribution in Soil Mantle of the Lithosphere as a Consequence of Waste Disposal at the National Reactor Testing Station. 100-10049.
- Schneider, H. 1970. "To the Question of the Lording Capacity of the Rhine for Radioactive Nuclides. 6. Sorption of Radionuclides on Selected Minerals." Gas-Wasserfach, Wasser-Abwasser. 111:21-6 (in German).
- Schneider, H. and W. Block. 1968. "On the Question of the Capacity of the Rhine for Radioactive Nuclides. Sorption of Radionuclides by Sediments of the Rhine." Gas-Wasserfach. 109:1410-15 (in German).
- Schneider, K. J. and A. H. Platt (eds). 1974. High-Level Waste Management Alternatives. BNWL-1900, Pacific Northwest Laboratory, Richland, WA, Volume I, Appendix 2.D, pp. 2.D.7-2.D.8.
- Schubert, A. J., E. R. Russell, and L. S. Myers. 1950. "Dissociation Constants of Radium Inorganic Acid Complexes Measured by Ion Exchange." J. Biol. Chem. 185:387-398.
- Schultz, R. K. 1965. "Soil Chemistry of Radionuclides." Health Physics. 11:1317-1324.
- Schumm, R. H., D. D. Wagman, S. M. Bailey, W. H. Evans, and V. B. Parker. 1973. Selected Values of Chemical Thermodynamic Properties. Tables for the Lanthanide (Rare Earth) Elements (Elements 62 through 76) in the Standard Order of Arrangement. NBS Technical Note 270-7.
- Schwille, F., W. Lippok and D. Weisflog. 1967. Model Experiments on Fluid Flow in the Transition Zone from Unsaturated to Saturated Soil. IAEA-SM-93/11, pp. 151-159.

- Seaborg, G. T. and J. J. Katz (ed.). 1954. The Actinide Elements. McGraw Hill Book Company, Inc.
- Sedlet, J. and N. W. Golchert. 1977. "Environmental Monitoring for Some Transuranium Elements." Presented at 4th International Congress of the International Radiation Protection Association, Paris, France, April 24-30, 1977 (CONF 770409-5).
- Senftle, F. E. and M. B. Keevil. 1947. "Thorium-Uranium Ratios in the Theory of Genesis of Lead Ores." Trans. Am. Geophys. Union. 28:732.
- Serne, R. J. 1978. "Waste Isolation Safety Assessment Program Task 4 Contractor Information Meeting Proceedings." PNL-SA-6957, Pacific Northwest Laboratory, Richland, WA.
- Serne, R. J. and Dhanpat Rai. 1976. "Adsorption-Precipitation Behavior of Eu in Soils and Standard Clays." Agronomy Abstracts, p. 132.
- Serne, R. J., R. C. Routson and D. A. Cochran. 1974. Experimental Methods for Obtaining PERCOL Model Impact and Verification Data. BNWL-1721, Pacific Northwest Laboratory, Richland, WA.
- Seymour, A. H. 1977. 1976-77 Annual Progress Report Distribution Coefficients for Transuranic Elements in Aquatic Environments. Laboratory of Radiation Ecology College of Fisheries, University of Washington.
- Seymour, A. H., A. Nevissi, W. R. Schell and A. Sanchez. 1979. Distribution Coefficients for Radionuclides in Aquatic Environments. I. Development of Methods and Results for Plutonium and Americium in Fresh and Marine Water-Sediment Systems. First Annual Research Progress Report, NUREG/CR-0801.*
- Shade, J. W. 1974. Reaction of Hanford Sediments with Synthetic Waste, A Reconnaissance Study. ARH-CD-176.
- Shalinets, A. B. and A. V. Stepanov. 1972. "Investigation of Complex Formation of the Trivalent Actinide and Lanthanide Elements by the Method of Electromigration. XVII. Hydrolysis." Radiokhimiya. 14:280-282.
- Shannon, R. D. and C. T. Prewitt. 1969. "Effective Ionic Radii in Oxides and Fluorides." Acta. Cryst., B. 25:925.
- Shearer, S. D., Jr. 1962. The Leachability of Radium-226 from Uranium Mill Solids and River Sediments. Thesis, University of Wisconsin, Madison, WI.
- Shearer, S. D., Jr. and G. F. Lee. 1964. "Leachability of Radium-226 from Uranium Mill Solids and River Sediments." Health Physics. 10:217-227.

- Sheidina, L. D. and E. N. Kovarskaya. 1970. "Colloidal State of Pu(IV) in Aqueous Solutions." Sov. Radio. Chem. 12:229-233.
- Sheppard, J. C., J. A. Kittrick, and T. L. Hart. 1976. Determination of Distribution Ratios and Diffusion Coefficients of Neptunium, Americium and Curium in Soil-Aquatic Environments. RLO-2221-T-12-2.
- Shih, C. S. and E. F. Gloyna. 1968. Influence of Sediments on the Transport of Solutes. ORO-490-12a.
- Shukla, S. S., J. K. Syers, J. D. H. Williams, D. R. Armstrong and R. F. Harris. 1971. "Sorption of Inorganic Phosphate by Lake Sediments Soil." Sci. Soc. Amer. Proceed. Vol. 35, p. 244-245.
- Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17, Second Edition. The Chemical Society, London.
- Simpson, H. J., D. E. Hammond, B. L. Deck and S. C. Williams. 1975. Nutrient Budgets in the Hanford River Estuary in Marine Chemistry in the Coastal Environment.
- Simpson, H. J., R. M. Trier, C. R. Olsen, D. E. Hammond, A. Ege, L. Miller, J. M. Melack. 1980. "Fallout Plutonium in an Alkaline, Saline Lake." Science. 207:1071-73.
- Smith, W. T., J. W. Cobble, and G. E. Boyd. 1953. "Thermodynamic Properties of Technetium and Rhenium Compounds. I. Vapor Pressures of Technetium Heptoxide, Pertechnic Acid and Aqueous Solution of Pertechnic Acid." J. Am. Chem. Soc. 75:5773-5776.
- Somayajulu, B. L. K. and T. M. Church. 1973. "Radium, Thorium, and Uranium Isotopes in the Interstitial Water from the Pacific Ocean Sediment." J. Geophy. Res. 78:4529-31.
- Sorathesn, A., G. Bruscia, T. Tamura, and E. G. Struxness. 1960. Mineral and Sediment Affinity for Radionuclides. CF-60-6-93.
- Spitsyn, V. I., R. N. Bernovskaya, Yu. A. Bogdanov, V. V. Gromov, and V. N. Tikhomirov. 1969. "The State of Microquantities of Niobium-95 and Technetium-99 in Sea Water." Radiokhimiya. 11:607-709.
- Spitsyn, V. I., R. N. Bernovskaya, V. V. Gromov, and Yu. A. Bogdanov. 1973. "Trapping of Cerium-144 and Yttrium-91 by Ocean Sediments." Oceanology. 12(4):586-589.
- Spitsyn, V. I., V. D. Balukova, A. F. Naumova, V. V. Gromov, F. M. Spiridonov, E. M. Vetrov, and G. I. Gravfov. 1958. "A Study of the Migration of Radioelements in Soils." In: Proc. Second Annual U.N. Conf. Peaceful Uses of Atomic Energy. 18:439-448.

- Sprugel, D. G., R. N. Muller, G. E. Bartelt, C. W. Wayman and C. M. Bobula. 1975. Dispersal of Plutonium from an Effluent Pulse in the Great Miami River. ANL-75-60 Part III, pp. 28-31.
- Sreekumaran, C., K. C. Pillai, and T. R. Folsom. 1968. "The Concentrations of Lithium, Potassium, Rubidium and Cesium in Some Western American Rivers and Marine Sediments." Geochim. et Cosmochim. Acta. 32:1229-1234.
- Starik, I. E., N. I. Ampelogova, F. L. Ginzburg, M. S. Lambert, I. A. Skulskii, and V. N. Shchebetkovskii. 1959. "On the Molecular State of Ultra-Small Quantities of Radioelements in Solutions." Radiokhimiya. 1:370-378 (in Russian).
- Starik, I. E., Y. V. Kuznetsov, E. P. Petryaev and V. K. Legin. 1963. "Geochemistry of Radioactive Elements." Khim. Zemnoi Kory, Akad. Nauk SSSR Tr. Geokhim. Knof. 1:375-89.
- Starik, I. E. and M. S. Lambert. 1958. "State of Microquantities of Promethium in Aqueous Solutions." ZhNKh. 3:136.
- Starik, I. E. and K. F. Lazarev. 1960. "Effect of Crushing of Minerals on the Extraction of Radioactive Elements." Radiokhimiya. 11:749-752.
- Starik, I. E., D. S. Nikolaev, Y. V. Kuznetsov and V. K. Legin. 1961. "Radioactivity of Black Sea Deposits." Doklady Akad. Nauk. SSSR. 139:1456-9 (in Russian).
- Starik, I. E. and M. I. Poleyaya. 1958. The Leachability of ThX and Rd Th from Minerals. AEC-tr-4208, p. 108.
- Starik, I. Ye., F. Ye Starik and A. N. Apollonova. 1958. "Adsorption of Traces of Uranium on Iron Hydroxide and Its Desorption by the Carbonate Method." Zh. Neorgan. Khimii. 3(1).
- Stead, F. W. 1963. "Tritium Distribution in Ground Water Around Large Underground Fusion Explosions." Science. 142:1163-1165.
- Stead, F. W. 1964. "Distribution in Groundwater of Radionuclides from Underground Nuclear Explosions." In: Proc. Third Plowshare Symp. Engineering with Nuclear Explosives. April 21-23, 1964. TID-7695, pp. 127-138.
- Stewart, G. L. 1967. "Fractionation of Tritium and Deuterium in Soil Water. In: Isotope Techniques in the Hydrologic Cycle, Geophys. Monograph No. 11, 159-168.
- Stumm, W. and J. J. Morgan. 1970. Aquatic Chemistry. Wiley-Interscience, New York, pp. 407-412.
- Sugimura, Y. 1964. "Natural Radioactive Elements in the Ocean." Kahaku No Ryoiki. 18:89-101 (in Japanese).

- Szabova, T. 1976. "Effect of pH Value of Applied Solution on Radiiodine Sorption by Soils." Poľnohospodárstvo. 22:196-201.
- Szalay, A. 1957. "The Role of Humus in the Geochemical Enrichment of U in Coal and Other Bioliths." Acta Phys. Acad. Sci. Hungary. 8:25-35.
- Szalay, A. 1954. "The Enrichment of Uranium in Some Brown Coals in Hungary." Acta Geol. Acad. Sci. Hungary. 2:299-311.
- Szalay, S. and M. Szilagyi. 1964. "Retention of Fission Products by the Humic Acids of Peat - A New Method for the Treatment of Effluents." Fiz. Szemle. 15:388-91 (in Hungarian).
- Tamers, M. A. and H. C. Thomas. 1960. "Ion-Exchange Properties of Kaolinite Slurries." J. Chem. Phys. 64:29-32.
- Tamura, T. 1972. "Sorption Phenomena Significant in Radioactive - Waste Disposal. In: Underground Waste Management and Environmental Implications, T. D. Cook (ed.), Am. Assoc. Petrol. Geol., pp. 318-330.
- Tanji, K. K., G. R. Dutt, J. L. Paul and L. D. Doneen. 1967a. "Quality of Percolating Waters. II. A Computer Method for Predicting Salt Concentrations in Soils at Variable Moisture Contents." Hilgardia. 38(9).
- Tanji, K. K., L. D. Doneen and J. L. Paul. 1967b. "Quality of Percolating Waters. III. The Quality of Waters Percolating Through Stratified Substrata, as Predicted by Computer Analyses." Hilgardia. 38(9).
- Tanji, K. K. and L. D. Doneen. 1966. "A Computer Technique for Prediction of CaCO_3 Precipitation in HCO_3 Salt Solution." Soil Sci. Soc. Amer. Proc. 30:53-55.
- Tarutani, T. and S. Misumi. 1962. "Adsorption of Cerium Ion by Various Solid Substances in Aqueous Solution." Mem. Fac. Sci. Kyushu Univ., Ser. C. 5:21-6.
- Taylor, S. R. 1964. "Abundance of Chemical Elements in the Continental Crust: A New Table." Geochim. et Cosmochim. Acta. 28:1273-1285.
- Taylor, S. R. 1964. "Trace Element Abundances and the Chondritic Earth Model." Geochim. et Cosmochim. Acta. 28:1989-1998.
- Taylor, S. R. and A. J. R. White. 1966. "Trace Element Abundances in Andesites." Bull. Volcanol. 29:177-194.
- Teller, E., W. K. Talley and G. H. Higgins. 1968. The Constructive Uses of Nuclear Explosives. McGraw-Hill, New York.
- Templeton, W. L. and A. Preston. 1966. "Disposal of Radioactive Waters into Seas, Oceans and Surface Waters." In: IAEA Publication, pp. 267-289.

- Tewari, P. H., A. B. Campbell, and W. Lee. 1972. "Adsorption of Cobalt (+2) by Oxides from Aqueous Solution." Can. J. Chem. 50:1642-1648.
- Texas University. 1968. Radioactivity Transport in Water. Interaction Between Flowing Water and Bed Sediments. ORO-49-17.
- Thomas, H. C. 1967. The Thermodynamics of Ion Exchange on Colloidal Materials with Applications to Silicate Minerals. Thesis, University of North Carolina, Chapel Hill, NC.
- Thomas, W. A. and D. G. Jacobs. 1969. "Curium Behavior in Plants and Soil." Soil Science. 108:305-307.
- Thorburn, R. C. 1950. Absorption on Hanford Soil and Related Soil Properties. HW-15655.
- Tiller, K. G., J. F. Hodgson, and M. Peech. 1963. "Specific Sorption of Cobalt by Soil Clays." Soil Science. 95:392-399.
- Titaeva, N. A. 1967. "On the Character of Radium and Uranium Bond in Peat." Geokhimiya. No. 12:1493-99.
- Titaeva, N. A. and T. I. Veksler. 1969. "Uranium and Thorium During Weathering of Yakutia Rocks." Geokhimiya. No. 6:740-4 (in Russian).
- Travis, C. C. 1978. Mathematical Descriptions of Adsorption and Transport of Reactive Solutes in Soil: A Review of Selected Literature. ORNL-5403.
- Tritrennel, Ch., G. Knollmayer, E. Wanderer, H. G. Heintschel, and P. Stipanits. 1966. Behavior of Radioisotopes Released to a Stream. STI-PUB-126, pp. 89-105.
- Trotman-Dickinson, A. F. (Executive Ed.). 1973. Comprehensive Inorganic Chemistry. Pergamon Press, New York.
- Turekian, K. K. and K. H. Wedepohl. 1961. "Distribution of the Elements in Some Major Units of the Earth's Crust." Bull. Geol. Soc. America. 72:175.
- Tyuryukanova, E. B. and V. A. Kalugnia. 1971. "The Behavior of Thorium in Soils." Soviet Journal of Ecology. 2:467-469.
- Udal'tsova, N. I. 1963. "General Information on Uranium." In: Analytical Chemistry of Uranium, Israel Program for Scientific Translations, pp. 3-7.
- United States Environmental Protection Agency. 1973. Environmental Analysis of Uranium Fuel Cycle. Part III. Nuclear Fuel Reprocessing. EPA-520/9-73-0030.

- United States Nuclear Regulatory Commission. 1976. Proceedings of Nuclear Regulatory Commission Workshop on the Management of Radioactive Waste: Waste Partitioning as an Alternative, NR-COMF-001, p. 445.
- Van Dalen, A., F. DeWitte, and J. Wiskstra. 1975. "Distribution Coefficients for Some Radionuclides Between Saline Water and Clays, Sandstones and Other Samples from the Dutch Subsoil." Reactor Centrum Nederland, pp. 75-109.
- Van Genuchten, M. Th. and P. J. Wierenga. 1974. Simulation of One-Dimensional Solute Transfer in Porous Media.
- Vdovenko, V. M. and Yu. V. Dubasov. 1973. Analytical Chemistry of Radium. Israel Program for Scientific Translations.
- Veeh, H. H. 1967. "Deposition of Uranium from the Ocean." Earth Planet. Sci. Lett. 3:145-50.
- Vickery, R. C. 1953. Chemistry of the Lanthanons. Butterworths Sci. Publ. London.
- Vinogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultants Bureau, Inc.
- Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, R. H. Schumm, and K. L. Churney. 1971. Selected Values of Chemical Thermodynamic Properties. Tables for Elements 54 through 61 in the Standard Order of Arrangement. NBS Technical Note 270-5.
- Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm. 1969. Selected Values of Chemical Thermodynamic Properties. Tables for Elements 35 through 53 in the Standard Order of Arrangement. Nat. Bur. Stds. Technical Note 270-4.
- Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm. 1958. Selected Volumes of Chemical Thermodynamic Properties. U.S. Department of Commerce.
- Wahlberg, J. S. and M. J. Fishman. 1962. Adsorption of Cs on Clay Minerals. USGS Bulletin 1140-A.
- Wahlberg, J. S., J. H. Baker, R. W. Vernon, and R. S. Dewar. 1965. Exchange Adsorption of Strontium on Clay Minerals. USGS Bulletin 1140-C.
- Wahlberg, J. S. and R. S. Dewar. 1965. Comparison of Distribution Coefficients for Strontium Exchange from Solutions Containing One and Two Competing Cations. USGS Bulletin 1140-D.
- Wahlgren, M. A. and D. M. Nelson. 1972. "Plutonium in Lake Michigan Water." In: Radiological and Environmental Research Division Annual Report. Ecology, January - December 1972, ANL-7960, Part III, pp. 7-14.

- Wahlgren, M. A. and D. M. Nelson. 1973a. Evidence of an Annual Plutonium Cycle in the Near-Surface Waters of Lake Michigan. ANL-8060 (Pt. 3), pp. 90-92.
- Wahlgren, M. A. and D. M. Nelson. 1973b. Residence Times for ^{239}Pu and ^{137}Cs in Lake Michigan Water. ANL-8060 (Pt. 3) pp. 85-89.
- Wahlgren, M. A. and D. W. Nelson. 1973c. Plutonium in the Five Great Lakes: Comparison of Surface Waters. ANL-8060 (Pt. 3), pp. 93-98.
- Wahlgren, M. A. and J. S. Marshall. 1974. "Distribution Studies of Plutonium in the Great Lakes." In: Proc. Second International Conference on Nuclear Methods in Environmental Research. CONF-740701, pp. 267-275.
- Wahlgren, M. A. and D. M. Nelson. 1974. "Studies of Plutonium Cycling and Sedimentation in Lake Michigan." In: Proc. Seventeenth Conference on Great Lakes Research. CONF-740813-P1, pp. 212-218.
- Wahlgren, M. A., J. J. Alberts, D. M. Nelson, K. A. Orlandini. 1976. Study of the Behavior of Transuranics and Possible Chemical Homologues in Lake Michigan Water and Biota. IAEA-SM-199/44, pp. 9-24.
- Wahlgren, M. A., and D. M. Nelson. 1976. A Comparison of the Distribution Coefficients of Plutonium and Other Radionuclides in Lake Michigan to Those in Other Systems. ANL-76-88 Part III, pp. 56-60.
- Wahlgren, M. A., D. M. Nelson and E. T. Kucera. 1977a. Seasonal Cycling of Plutonium in the Water Column of Lake Michigan: 1975-1977. ANL-77-5 Part III, pp. 89-91.
- Wahlgren, M. A., J. J. Alberts, K. A. Orlandini and E. T. Kucera. 1977b. A Comparison of the Concentrations of Fallout-Derived Plutonium in a Series of Freshwater Lakes. ANL-77-5 Part III, pp. 92-94.
- Wahlgren, M. A., J. J. Alberts, D. M. Nelson, and K. A. Orlandini. 1977c. Study of the Occurrence of Multiple Oxidation of Plutonium in Natural Waters. ANL-77-5 Part III, pp. 95-98.
- Walker, J. B., and G. R. Choppin. 1967. Thermodynamic Parameters of Fluoride Complexes of the Lanthanides. Advances in Chemistry Series No. 71, The American Chemical Society, Washington DC, pp. 127-140.
- Wallace, A. 1969. Behavior of Certain Synthetic Chelating Agents in Soil and Biological Systems. UCLA-34-P-51-26, 92 pp.
- Ward, F. M. and H. W. Lakin. 1954. "Determination of Traces of Antimony in Soils and Rocks." Analytical Chemistry. 26:1168-1173.
- Weast, R. C. 1976. Handbook of Chemistry and Physics. The Chemical Rubber Co.

- Medepohl, K. H. 1969. Handbook of Geochemistry. Springer-Verlag Publishers, New York.
- Wheeler, M. L. and J. L. Warren. 1975. "Tritium Containment After Burial of Contaminated Solid Waste." Trans. Am. Nucl. Soc. 22:741.
- Wheelwright, E. J. 1973. Promethium Technology. Am. Nucl. Soc. Publications.
- Whitman, A. and E. S. Porter. 1958. Chemical Stream Pollution from Uranium Mills. WIN-99.
- Wildeman, T. R. and L. Haskin. 1965. "Rare-Earth Elements in Ocean Sediments." Jour. Geophys. Res. 70:2905-2910.
- Wilding, M. W. and D. W. Rhodes. 1963. Removal of Radioisotopes from Solution by Earth Materials from Eastern Idaho. IDO-14624.
- Wildung, R. E. R. C. Routson, R. J. Serne, and T. R. Garland. 1975. Pertechnetate, Iodide and Methyl Iodide Retention by Surface Soils. BNL-1950, Pt. 2, pp. 37-40.
- Williams, J. D. H., J. R. Syers, D. E. Armstrong and R. F. Harris. 1971. "Characteristics of Inorganic Phosphate in Noncalcerous Lake Sediments." Soil Sci. Soc. Amer. Proc. Vol. 35, pp. 556-561.
- Wilson, C. B. and T. H. Essig. 1970. Environmental Status of the Hanford Reservation for January-June, 1969. BNL-CC-2478.
- Wong, K. M., V. E. Noshkin, L. Surprenant and V. T. Bowen. 1970. Plutonium-239 in Some Marine Organisms and Sediments. HASL-227, pp. 1-25 through I-33.
- Wrenn, M. E. and S. J. Jinks. 1976. "The Dosimetric Implications of Release to the Aquatic Environment from Nuclear Power Industry." In: Environmental Toxicity of Aquatic Radionuclides Models and Mechanisms, M. W. Hitter and I. N. Stannard, eds., Ann Arbor Science Publishers, Ann Arbor, MI.
- Wrenn, M. E., S. M. Jinks, N. Cohen, and L. H. Hairr. 1974. ¹³⁷Cs and ¹³⁴Cs Distribution in Sediment, Water, and Biota of the Lower Hudson River and Their Dosimetric Implications for Man. CONF-730907, pp. 279-284.
- Wrenn, M. E., J. W. Lentsch, M. Eisenbud, G. J. Lauer, and G. P. Howells. 1971. Radiocesium Distribution in Water, Sediment, and Biota in Hudson River Estuary from 1964 through 1970. CONF-71050L-P1, pp. 334-343.
- Wruble, D. T., S. D. Shearer, D. E. Rushing and C. E. Sponagle. 1964. "Radioactivity in Waters and Sediments of the Colorado River Basin, 1950-1963." Rad. Health Data. 5(11):557-567.

- Yabuki, H. and M. Shima. 1973. "Uranium and Other Heavy Elements in Deep-Sea Sediments Coexisting with Manganese Nodules." Sci. Pap. Inst. Phys. Chem. Res. 67:155-6 (in Japanese).
- Yakobenchuk, V. G. 1968. "Radioactivity and Chemical Properties of Sod-Podzolic Soils in the Ukrainian Western Polesie." Visn. Sil's' Kogosped. Nauki. 11:45-50 (in Ukrainian).
- Yamamoto, T., E. Yunoki, M. Yamakawa, and M. Shimizu. 1973. "Studies on Environmental Contamination by Uranium. 3. Effects of Carbonate Ion on Uranium Adsorption to and Desorption from Soils." J. Radiat. Res. 14:219-224.
- Young, R. S. 1957. "The Geochemistry of Cobalt." Geochim. et. Cosmochim. Acta. 13:28-41.
- Yousef, Y. A., A. Kudo, and E. F. Gloyna. 1970. Radioactivity Transport in Water: Summary Report. ORO-490-20.
- Zirino, A. and S. Yamamoto. 1972. "A pH-Dependent Model for the Chemical Speciation of Copper, Zinc, Cadmium and Lead in Seawater." Limn. and Ocean. 17(5):661-671.
- Zirino, A. and M. L. Healy. 1970. "Inorganic Zinc Complexes in Seawater." Limn. and Ocean. 15(6):956-958.

*Available for purchase from the NRC/GPO Sales Program, U.S. Nuclear Regulatory Commission, Washington, DC 20555, and the National Technical Information Service, Springfield, VA 22161.

DATE

FILMED

5/16/94

END