38
87
7-8-82
SC

(1)

DOE/DP/04515-1

REDOX REACTIONS INVOLVING CHROMIUM,
PLUTONIUM, AND MANGANESE IN SOILS

FINAL REPORT
FOR THE PERIOD

MASTER

1 JULY 1978 TO 30 SEPTEMBER 1981

MICHAEL C. AMACHER AND DALE E. BAKER

JUNE 1982

WORK PERFORMED UNDER CONTRACT

DE-AS08-77DP04515

(FORMERLY DE-AC02-77DO-4515.A006)

**INSTITUTE FOR RESEARCH
ON LAND & WATER RESOURCES**

**THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA**

DISCLAIMER

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, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A08
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts, (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication, NTIS-PR-360 available from (NTIS) at the above address.

The Pennsylvania State University, in compliance with federal and state laws and regulations governing affirmative action and nondiscrimination, does not discriminate in the recruitment, admission, and employment of students, faculty, and staff in the operation of any of its educational programs and activities as defined by law. Accordingly, nothing in this publication should be viewed as directly or indirectly expressing any limitation, specification, or discrimination as to race, religion, color, or national origin; or to handicap, age, sex, or status as a disabled or Vietnam-era veteran, except as provided by law. Inquiries concerning this policy may be directed to the Affirmative Action Officer.

DOE/DP/04515--2

DE82 021130

DOE/DP/04515-2

REDOX REACTIONS INVOLVING CHROMIUM,
PLUTONIUM, AND MANGANESE IN SOILS*

FINAL REPORT
FOR THE PERIOD

1 JULY 1978 TO 30 SEPTEMBER 1981

MICHAEL C. AMACHER AND DALE E. BAKER

JUNE 1982

THE PENNSYLVANIA STATE UNIVERSITY
INSTITUTE FOR RESEARCH ON LAND AND WATER RESOURCES
UNIVERSITY PARK, PA 16802

PREPARED FOR THE

U.S. DEPARTMENT OF ENERGY
DIVISION OF ENERGY TECHNOLOGY
UNDER CONTRACT DE-AS08-77DP04515
(FORMERLY DE-AC02-77DP04515.A006)

**This publication was submitted to the Graduate School, The Pennsylvania State University, by M. C. Amacher as a thesis in Soil Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1981.*

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ABSTRACT

As a result of atmospheric testing of nuclear devices at the Nevada Test Site in southern Nevada, the soil and vegetation of several areas on the test site are contaminated with transuranic elements, particularly Pu and Am. Although particulate movement through wind and water erosion is the most important mechanism of dispersion of Pu at the test site, dispersion of water-soluble species may also be occurring. Under the direction of the Nevada Applied Ecology Group of the U.S. Department of Energy, a program is being developed to monitor the dispersion and bioavailability of transuranics, especially plutonium, in the environment.

However, because Pu is toxic, usually insoluble, not uniformly distributed in the soil, and can exist in four oxidation states in the environment, it is very difficult to study. Therefore, Cr reactions in soil were investigated as a possible general model for Pu reactions in soil, since it was postulated that the redox chemistries of the two elements should be similar. An evaluation of data from the literature indicated that the reduced forms of both elements are usually relatively immobile in soils while the oxidized forms are usually relatively mobile and hence more bioavailable. The redox chemistries appear to be controlled by organic matter, minerals containing Fe(II), and manganese oxides. Thermodynamic calculations revealed that both elements should be highly soluble in the presence of manganese oxides. In addition the solubility of Pu can be enhanced by radiolytic oxidation. Reduction of both elements by organic matter and oxidation of Cr by manganese oxides in soils have been demonstrated, and it was postulated that the conditions necessary for oxidation of Pu by manganese oxides exist in Nevada Test Site soils.

Chemical fractionation methods were used to determine the redox states of Pu in a Nevada Test Site soil and the amounts of Pu associated with various soil components in order to deduce possible reactions between the various Pu species and soil components so that weathering and dispersion by chemical mechanisms can be predicted. Chemical fractionation and kinetics experiments were performed to study reactions of Cr with soil, manganese oxides, and fulvic acids in order to provide information to eventually develop a qualitative, predictive model for Pu behavior in soil.

The fractionation of soil Pu revealed that only a few percent of the total soil Pu was associated with organic matter and/or iron oxides with the remainder probably existing as stable PuO_2 . Oxidized Pu was found in the soil, but the presence of oxidized Pu appeared to be due to Pu dissolved by the extracting solutions reacting with the soil manganese oxides. The amount of oxidized Pu found was a very small fraction of the total soil Pu, although carbonate-rich waters dissolving PuO_2 in the presence of manganese oxides could result in oxidized Pu leaching through the soil profile.

Chemical fractionation revealed that Cr from organic sources such as sewage sludge remained in soil in a reduced state associated with the organic matter or perhaps organo-Cr complexes sorbed to iron oxides and was not oxidized by manganese oxides. Inorganic sources of Cr (CrCl_3 , $\text{Cr}(\text{OH})_3$, and Cr_2O_3) were oxidized in soil, but only a few percent of the added Cr was oxidized while the remainder was sorbed by the various soil components (organic matter and iron oxides, etc.) and apparently was unavailable for oxidation. Although complete oxidation was predicted, not all the solution Cr(III) was oxidized because the Mn(IV) at the

surfaces of the manganese oxide minerals was "used up" and access of Cr(III) to Mn(IV) beneath the mineral surface was blocked by Mn(II) remaining sorbed to the mineral. The initial rate of oxidation was extremely rapid followed by a rapid fall-off in oxidation rate as surface Mn(IV) was used up. At low temperature and pH levels the oxidation reaction was sufficiently slowed down to follow zero-order kinetics. Reduction of Cr(VI) in soil and by fulvic acid was found to be slow and followed first-order kinetics. Reduction was rapid only at low pH levels. Therefore, immediate Cr availability is probably controlled through oxidation by manganese oxides while long-term control is probably exerted through reduction by organic matter.

Qualitatively, it appears that Cr reactions in soil could be used as a general model for Pu reactions in soil although important differences exist. Chief among these is the radioactivity of Pu which can affect the reactions of this element in soils.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.	iii
LIST OF TABLES.	viii
LIST OF FIGURES	x
ACKNOWLEDGMENTS	xiii
INTRODUCTION.	1
THEORETICAL CONSIDERATIONS.	10
Stability of Chromium and Plutonium Species in Aqueous Environments.	10
Radiolytic Oxidation and PuO ₂ Microsphere Dissolution Studies.	19
Thermodynamics of Chromium and Plutonium Oxidation by Manganese Oxide Minerals.	25
Additional Evidence for the Oxidation of Plutonium by Manganese Oxide Minerals in Soil Environments	34
Hypothesis and Objectives.	36
MATERIALS AND METHODS	38
Plutonium Experiments.	38
Soil Sample Collection.	38
Chemical Fractionation of Soil Pu and Am.	38
Oxidation of Carbonate-Soluble Pu	42
Pu Valence State Separation Methods	42
Chromium Experiments	45
Soil Sample Collection and Characterization	45
Preparation of MnO ₂ Minerals.	47
Extraction of Fulvic Acid from Leather Dust and Soil.	49
Chemical Fractionation of Soil Cr and Mn.	50
Fate of Cr from Sludge and Leather Dust Applied to Soil in Laboratory Incubation Experiments	53
Effect of Drying, Storage Time, and Organic Matter Removal on the Ability of Soil to Oxidize Cr	54
Cr Oxidizing Capacity of Soil	56
Effect of Cr Concentration on Cr Oxidation by Soil	56
Extractability of Cr(VI) with KH ₂ PO ₄	57
Oxidation of Cr from Different Sources at Selected Concentrations in Soil with Time	59
Kinetics of Cr Oxidation by Moist Hagerstown Silt Loam.	60

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Kinetics of Cr Oxidation by MnO_2 Minerals.	64
Kinetics of Cr Oxidation by δ - MnO_2 in the Presence of Fulvic Acid and the Kinetics of Cr and Mn Reduction by Fulvic Acid.	68
RESULTS AND DISCUSSION	71
Plutonium Experiments	71
Chemical Fractionation of Soil Pu.	71
Extraction of Soil Pu(V/VI).	76
Oxidation of Carbonate-Soluble Pu.	80
Extraction of Soil Am.	80
Chromium Experiments.	82
Chemical Fractionation of Soil Cr and Mn	82
Fate of Cr from Sludge and Leather Dust Applied to Soil in Laboratory Incubation Experiments	90
Effect of Drying, Storage Time, and Organic Matter Removal on the Ability of Soil to Oxidize Cr.	94
Effect of Cr Concentration on Cr Oxidation by Soil.	101
Cr Oxidizing Capacity of Soil.	105
Extractability of Soil Cr(VI) with KH_2PO_4	105
Oxidation of Cr from Different Sources at Selected Concentrations in Soil with Time.	114
Kinetics of Cr Oxidation and Sorption by Moist Hagerstown Silt Loam	121
Kinetics of Cr Oxidation by MnO_2 Minerals.	126
Kinetics of Cr Oxidation by δ - MnO_2 in the Presence of Fulvic Acid and the Kinetics of Cr and Mn Reduction by Fulvic Acid.	146
SUMMARY AND CONCLUSIONS.	156
LITERATURE CITED	163

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Reactions and equilibrium constants used to construct stability diagrams	13
2	Summary of $^{239}\text{PuO}_2$ dissolution studies	20
3	Oxidation or reduction half-reactions involving Cr, Mn, and Pu.	26
4	Radioactive contamination survey of fourteen soil samples collected from Areas 11A, 11B, 11C, and 11D of the NTS.	39
5	Properties of MnO_2 minerals	48
6	Conditions for experiments on the effect of soil/solution ratio on extraction of soil Cr(VI) by KH_2PO_4	58
7	Summary of reaction conditions for experiments on the kinetics of Cr oxidation by moist Hagerstown silt loam.	61
8	Summary of reaction conditions for experiments on the kinetics of Cr oxidation by manganese oxide minerals.	65
9	Summary of reaction conditions for experiments on the kinetics of Cr oxidation in the presence of fulvic acid and the kinetics of Cr and Mn reduction by fulvic acid.	69
10	Plutonium extracted from a soil sample from Area 11C (NTS) using various extracting reagents.	72
11	Plutonium extracted from a soil sample from Area 11C (NTS) using various extracting reagents.	77
12	Oxidation of Na_2CO_3 soluble Pu in a soil sample from Area 11C (NTS) using $\delta\text{-MnO}_2$	81
13	Effect of extraction time on Na_2CO_3 extractable Pu in a soil sample from Area 11C (NTS)	81
14	Americium extracted from a soil sample from Area 11C (NTS) using various extracting reagents.	83

LIST OF TABLES (Continued)

<u>Table</u>		<u>Page</u>
15	Water content (θ_{dw}), pH, and organic matter (O.M.) content of collected Hagerstown silt loam and Murrill silt loam samples.	83
16	Chromium in 0.5 M NaOH extractable organic matter from sludge and moist Hagerstown silt loam and Murrill silt loam amended with sludge.	84
17	Chemical fractionation of soil Cr	85
18	Chemical fractionation of soil Mn	88
19	Total and NaOCl extractable Cr in moist Hagerstown silt loam amended with sludge.	89
20	Total and NaOCl extractable Cr in air-dried Hagerstown silt loam amended with sludge.	89
21	Potassium phosphate extractable Cr(VI) in moist Hagerstown silt loam samples treated with sludge and leather dust in laboratory incubation studies	92
22	Sodium hypochlorite extractable Cr in moist Hagerstown silt loam samples treated with sludge and leather dust in laboratory incubation studies	93
23	Chromium oxidizing ability of Hagerstown, Murrill, and Chrome soils as affected by drying, storage time, and organic matter removal.	95
24	Effect of water removal by various treatments on the Cr oxidizing ability of Murrill silt loam	100
25	Chromium(VI) extracted from moist Hagerstown silt loam using various concentrations of KH_2PO_4 in solution.	108
26	Effect of soil/solution ratio on the KH_2PO_4 extraction of Cr(VI) from moist Hagerstown silt loam. Soil/solution ratio varied by holding soil amount constant while varying KH_2PO_4 solution volume	110
27	Effect of varying Cr(III) concentration on the oxidation of Cr in moist Murrill silt loam with time	115
28	Effect of Cr(III) source and amount on the oxidation of Cr in moist Hagerstown silt loam with time	118
29	Potassium phosphate extractable Cr(VI) in moist Hagerstown silt loam amended with Cr_2O_3	120

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Examples of normal Pu distributions in two NTS soil profiles.	3
2	Examples of abnormal Pu distributions in three NTS soil profiles.	4
3	Stability of PuO_2 in 10^{-12} M Pu at 25°C , $10^{-3.5}$ atm CO_2 , and 1 atm total pressure assuming radiolytic oxidation is not occurring	12
4	Stability of PuO_2 in 10^{-8} M Pu at 25°C , $10^{-3.5}$ atm, and 1 atm total pressure assuming radiolytic oxidation is occurring	16
5	Stability of $\text{Cr}(\text{OH})_3$ and Cr_2O_3 in 10^{-6} M Cr at 25°C and 1 atm total pressure.	18
6	Solubility of PuO_2 as controlled by $\delta\text{-MnO}_2$ in the absence of reducing agents at 25°C , $10^{-3.5}$ atm CO_2 , and 1 atm total pressure assuming radiolytic oxidation is not occurring	29
7	Solubility of PuO_2 as controlled by $\delta\text{-MnO}_2$ in the absence of reducing agents at 25°C , $10^{-3.5}$ atm CO_2 , and 1 atm total pressure assuming radiolytic oxidation is occurring	31
8	Solubility of $\text{Cr}(\text{OH})_3$ as controlled by $\delta\text{-MnO}_2$ in the absence of reducing agents at 25°C and 1 atm total pressure	33
9	Experimental apparatus for studying the kinetics of Cr oxidation by moist Hagerstown silt loam and manganese oxide suspensions.	63
10	Effect of varying Cr(III) concentrations on the fraction of added Cr that is sorbed or oxidized by moist Hagerstown silt loam.	102
11	Effect of varying Cr(III) concentrations on the amount of soil solution total Cr and Cr(VI), KH_2PO_4 extractable Cr(VI), and total Cr(VI) produced in moist Hagerstown silt loam.	104
12	Exhaustion of Cr oxidizing capacity of moist Hagerstown silt loam	106
13	Successive KH_2PO_4 extractions of Cr(VI) from moist Hagerstown silt loam treated with three levels of Cr(III).	109

LIST OF FIGURES (Continued)

<u>Figure</u>		<u>Page</u>
14	Effect of soil/solution ratio on KH_2PO_4 extraction of Cr(VI) from moist Hagerstown silt loam. Soil/solution ratio varied by holding KH_2PO_4 solution volume constant while varying soil amount.	112
15	KH_2PO_4 extraction of Cr(VI) from moist Hagerstown silt loam at constant soil/solution ratio	113
16	Kinetics of Cr oxidation in moist Murrill silt loam.	117
17	Kinetics of Cr sorption by moist Hagerstown silt loam.	122
18	Effect of temperature on the kinetics of Cr oxidation in moist Hagerstown silt loam.	123
19	Effect of organic matter removal on the kinetics of Cr oxidation in moist Hagerstown silt loam.	125
20	Effect of temperature on the kinetics of Cr oxidation by $\delta\text{-MnO}_2$ at pH 5.5.	127
21	Effect of pH on the kinetics of Cr oxidation by $\delta\text{-MnO}_2$	130
22	Effect of temperature on the kinetics of Cr oxidation by $\delta\text{-MnO}_2$ at pH 1.0.	132
23	Kinetics of $\text{Cr}(\text{OH})_3$ oxidation by $\delta\text{-MnO}_2$ at pH 10.	133
24	Effect of ionic strength on the kinetics of Cr oxidation by $\delta\text{-MnO}_2$	135
25	Effect of solution composition on the kinetics of Cr oxidation by $\delta\text{-MnO}_2$	136
26	Effect of varying amounts of $\delta\text{-MnO}_2$ on the kinetics of Cr oxidation by $\delta\text{-MnO}_2$	138
27	Kinetics of Cr oxidation by $\delta\text{-MnO}_2$ and Mn reduction by Cr(III) with excess Cr present.	139
28	Effect of temperature on the kinetics of Mn reduction by Cr(III) at pH 1.0 with excess Cr present	141

LIST OF FIGURES (Continued)

<u>Figure</u>		<u>Page</u>
29	Kinetics of Cr oxidation by various MnO_2 minerals under selected conditions	142
30	Effect of temperature on OH^- demand during Cr oxidation and sorption in moist Hagerstown silt loam	144
31	Effect of temperature on OH^- demand during Cr oxidation by $\delta\text{-MnO}_2$	145
32	Kinetics of Cr reduction in moist Hagerstown silt loam.	147
33	Effects of temperature and pH on the kinetics of Cr reduction by soil fulvic acid.	148
34	Effects of temperature and pH on the kinetics of Cr reduction by leather dust fulvic acid.	150
35	Kinetics of Cr oxidation by $\delta\text{-MnO}_2$ in the presence of leather dust fulvic acid over a short time period	152
36	Kinetics of Cr oxidation by $\delta\text{-MnO}_2$ in the presence of leather dust fulvic acid over a long time period	153
37	Kinetics of Mn reduction by leather dust fulvic acid	154
38	Idealized diagram of Pu reactions in soil.	158
39	Idealized diagram of Cr reactions in soil.	159

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. Dale E. Baker, thesis adviser, for his guidance, assistance, and evaluation throughout the program of study. Grateful appreciation is also extended to Dr. Arthur Rose and Dr. K. K. S. Pillay for their involvement in the NAEG project and their review of this thesis program.

Recognition is also extended to Dr. William Steele, Dr. Les Lanyon, and Dr. Robert Hamilton for their review of the thesis program.

Grateful appreciation is also extended to the Department of Agronomy and the Institute for Research on Land and Water Resources for providing the research facilities, and to Paul Dunaway and the Nevada Applied Ecology Group for providing financial support for the project.

A special note of thanks is due the following people: Ernest Bondietti at Oak Ridge National Laboratory for providing laboratory training to the author in the area of plutonium chemistry; Nancy Daugherty and Roger Granlund of Health Physics for providing α -counting instrumentation; Hollis Berry and Ed Eubanks of Reynolds Electrical and Engineering Co. for assisting in the collection of soil samples at the Nevada Test Site; and Elizabeth Douglass for assistance with the laboratory experiments on chromium.

INTRODUCTION

As a result of atmospheric nuclear and non-nuclear explosions, numerous areas of the Nevada Test Site (NTS) in southern Nevada are contaminated with plutonium (Pu) and other transuranic elements. The Nevada Applied Ecology Group (NAEG) was established by the Atomic Energy Commission to study the problems associated with the contamination of NTS soils by Pu and other transuranic elements. The objectives of the NAEG are to:

1. Delineate locations contaminated by transuranics;
2. Determine concentrations of transuranics in ecosystem components;
3. Quantify rates of movement of transuranics among ecosystem components;
4. Evaluate radiological hazards of Pu;
5. Identify areas which need to be cleaned up or treated; and
6. Develop techniques for cleanup or treatment.

To assist the NAEG in meeting objectives 2 and 3 a program to monitor the dispersion and bioavailability of transuranics, and especially Pu, in the NTS soils is needed.

There are several mechanisms of Pu dispersion in the desert environment of the NTS. The major mechanisms of dispersion which are active in moving PuO_2 particles are wind erosion, water erosion, PuO_2 particles sifting vertically through a soil profile due to gravity, and mass flow of water moving through a soil profile. Of these, wind erosion is considered by the NAEG to be the most important mechanism through which Pu is transported both on and off site. The minor mechanisms of dispersion which are active in moving soluble Pu species are mass flow of water

moving through a soil profile and diffusion through the soil water. In addition to these mechanisms the activities of microorganisms and burrowing animals can also disperse Pu.

Bioavailability in this text refers to root uptake of Pu species. Plutonium can be delivered to plant roots by three mechanisms: mass flow, diffusion, and root interception. These mechanisms were originally proposed by Barber (1962) to explain root uptake of essential elements, but are also applicable to Pu. Mass flow and diffusion are dispersion processes while root interception involves roots coming into contact with soil particles contaminated with Pu while growing through the soil profile. The Pu can be taken up by the roots when root exudates dissolve the contaminated particles. Any or all of these mechanisms may be operating within a given soil profile.

Most of the available data from NTS soil and plant studies indicate that Pu shows little dispersion and low bioavailability in NTS soils (White and Dunaway (eds.), 1975, 1976, 1977a, 1977b, 1978). The dispersion that does occur is mostly due to particle transport by wind and water with wind transport being the most important. However, there are some anomalous data suggesting the presence of a more mobile Pu species within certain soil profiles at the NTS. Essington et al. (1976) have described normal Pu distributions (see Figure 1) within several NTS soil profiles. Normal Pu distributions are those in which 95% or more of the soil's plutonium is in the top 5 cm of soil with the remainder decreasing curvilinearly with depth. In contrast with this are abnormal Pu distributions within the soil profile such as those illustrated in Figure 2, also taken from Essington et al. (1976).

Figure 1. Examples of normal Pu distributions in two NTS soil profiles.

Figure 2. Examples of abnormal Pu distributions in three NTS soil profiles.

Abnormal profiles are those in which the Pu concentration is quite variable with depth, movement is strongly inhibited, or generally less than 95% of the Pu appears in the top 5 cm. The data from Area 11D and Double Tracks indicate substantial Pu migration with depth. This migration could be due to the movement of colloidal Pu or due to movement of soluble Pu species. It is this last possibility that this thesis will consider.

Plutonium is capable of existing in four oxidation states in normal aqueous environments (Cleveland, 1970), but Francis et al. (1976, Agronomy Abstracts, p. 128) have demonstrated using soil thin-layer chromatography that Pu(V/VI) species are far more mobile than Pu(IV) species. This is not surprising since Jacobson and Overstreet (1948) originally showed that Pu in lower valence states is more strongly sorbed to calcium bentonite than Pu in higher valence states. This stronger retention of lower valence Pu by soil minerals has been confirmed by Rai et al. (1979, Agronomy Abstracts, p. 151). Therefore, it seems likely that any mobile Pu species in the soils of the NTS would be Pu(V/VI). Because the soils of the NTS are calcareous (pH 7 to 8.3) (Leavitt, 1970), the Pu(VI) species, $\text{PuO}_2\text{CO}_3\text{OH}^-$, has been proposed (Baker et al., 1978) as the soluble Pu species in NTS soils, since this species is thought to be stable under such conditions (Rai and Serne, 1977).

The dominant Pu solid phase in certain NTS soils is thought to be PuO_2 (Tamura, 1974), which means Pu is quadrivalent in this mineral. In order for $\text{PuO}_2\text{CO}_3\text{OH}^-$ to be produced, PuO_2 would have to be oxidized. Oxidation of Pu(IV) by O_2 is so slow that it can be ignored (Cleveland, 1970; Bondietti, personal communication). One way for $\text{PuO}_2\text{CO}_3\text{OH}^-$ to be

produced is through radiolytic oxidation of PuO_2 . Radiolytic oxidation of PuO_2 has been discussed by Rai, Serne, and Swanson (1980), Bondietti and Reynolds (1976), and Bondietti and Sweeton (1977). Radiolytic oxidation is important for larger PuO_2 particles ($> 150 \mu\text{m}$), but is probably not important for dispersed, submicron PuO_2 particles in the environment (Bondietti and Sweeton, 1977). In soils the most likely oxidizing agent is manganese oxide minerals (Baker et al., 1978).

Therefore, the following hypothesis was proposed: under high Eh conditions, high HCO_3^- levels, low organic matter levels and negligible Fe(II) levels, PuO_2 particles can be oxidized to the mobile $\text{PuO}_2\text{CO}_3\text{OH}^-$ species by the manganese oxide minerals in a soil profile. Low organic matter levels and negligible Fe(II) levels are necessary, since these are good reducing agents for oxidized Pu (Cleveland, 1970; Bondietti et al., 1975). The conditions necessary for this oxidation reaction to occur were postulated to exist within soil profiles at the NTS.

One of the main objectives of this thesis was to study the redox chemistry of Pu in selected soil samples from the NTS by demonstrating the existence of oxidized Pu species in these soils and by determining the amount of Pu associated with various soil components (organic matter and Fe and Mn oxides) by means of chemical fractionation methods.

However, the soil chemistry of Pu is difficult to study because of the toxicity, very low solubility, multiple oxidation states, and heterogeneous distribution of this element within the soil profile. Therefore, a possible course of action would be to study another element whose redox chemistry in soils is similar to Pu under similar conditions, but is easier to work with. The redox chemistry of this element could then be used as a general model for the redox chemistry of Pu. Chromium (Cr)

is an element whose redox chemistry in soils probably is sufficiently similar to that of Pu, so that it could be used as a general model for Pu.

Certain findings in the literature on Cr (Bartlett and Kimble, 1976a; Bartlett and James, 1979) and on Pu (Rai and Serne, 1977; Rai et al., 1979, Agronomy Abstracts, p. 151; Rai, Serne, and Swanson, 1980; Bondietti and Sweeton, 1977; Bondietti and Reynolds, 1976; Francis et al., 1976, Agronomy Abstracts, p. 128; Jacobson and Overstreet, 1948; Cleveland, 1970) led to the following conclusions by the author regarding the similarities between Cr and Pu behavior in aqueous environments:

1. Both elements can exist in multiple oxidation states in normal aqueous environments. Chromium can exist in trivalent and hexavalent states, while Pu can exist in trivalent, quadrivalent, pentavalent, and hexavalent states;
2. Both elements can exist as cationic or anionic species in normal aqueous environments. Trivalent Cr exists as the cation, Cr^{3+} , and its hydrolysis products, or as the anion, CrO_2^- , at very low concentrations. Hexavalent Cr exists as the dichromate, $\text{Cr}_2\text{O}_7^{2-}$, or chromate, HCrO_4^- or CrO_4^{2-} , anions depending upon the pH. Plutonium has cationic forms such as Pu^{3+} and PuO_2^+ and anionic forms such as $\text{PuO}_2\text{CO}_3\text{OH}^-$;
3. Trivalent Cr and Pu(III/IV) cations are usually relatively "immobile" in normal aqueous environments, since they are strongly sorbed to soil components and hence are not readily bioavailable. On the other hand, Cr(VI) and Pu(VI) anions are usually relatively "mobile" in normal aqueous environments, since they are not as strongly sorbed to soil components

and hence are more readily bioavailable;

4. Hexavalent chromium and Pu(V/VI) species are thermodynamically stable under approximately the same chemical environments in solution; and
5. Both elements can be oxidized by soil manganese oxides. The oxidation of Cr(III) to Cr(VI) by soil manganese oxides is thermodynamically possible in most soil environments and has actually been observed in soils. This reaction occurs despite the presence of organic matter that would tend to keep Cr in the trivalent state. Oxidized Pu species have been observed in natural waters, the oxidation of Pu(IV) by manganese oxide minerals is thermodynamically possible in many soil environments, and the oxidation of Pu(IV) by MnO_2 has been observed in the laboratory.

In pointing out the similarities between Cr and Pu behavior in aqueous environments, it must be remembered that there are also many differences between the two elements and analogies cannot be over-extended. Chief among these differences is the radioactivity of Pu that can lead to radiolytic effects which are absent with Cr. Nevertheless, the similarities led to the hypothesis that some aspects of Cr redox chemistry in soils could be used as a general model for Pu redox chemistry. Therefore, the other objective of this thesis was to study the redox chemistry of Cr in the soil environment in order to provide information for the development of a general model for the redox chemistry of Pu in the soil.

Redox reactions involving Cr in the soil are also important in their own right, since improper land disposal of chromium-containing

wastes such as wastes from the metal finishing industry might result in oxidation of Cr(III) by soil manganese oxides which are widely distributed and eventual contamination of water supplies with hexavalent chromium. Hexavalent chromium is toxic to aquatic life and is a suspected human carcinogen (EPA, 1980).

Eventually studies such as these may form the basis for developing programs to monitor the dispersion and bioavailability of any element that exists in different oxidation states in various soil environments.

THEORETIAL CONSIDERATIONS

Stability of Chromium and Plutonium Species in Aqueous Environments

All four oxidation states of Pu can coexist in solution under certain conditions (Cleveland, 1970). Because Pu does have four oxidation states, the behavior of trace quantities of Pu in natural waters and soils is difficult to study. Numerous authors (Bondietti and Sweeton, 1977; Rai and Serne, 1977; Rai, Serne, and Swanson, 1980) have studied the problem of Pu speciation and solubility in aqueous environments, and have presented solubility and stability field diagrams for Pu solid phases and soluble species in an attempt to predict the behavior of Pu in soils.

Generally, these authors agree that under acid-reducing conditions Pu^{3+} is the most stable species in solution. Under oxidizing conditions the situation is not as clear due to lack of reliable equilibrium constants for some reactions between various Pu species. Recently, Rai, Serne, and Swanson (1980) have shown by means of an Eh-pH diagram constructed using newly available thermodynamic data that PuO_2^+ is the most stable Pu species in solution in oxidizing environments. Instead of showing distinct boundary lines between stability fields on their Eh-pH diagram, Rai, Serne, and Swanson (1980) drew the boundaries as shaded regions to indicate the uncertainties in the equilibrium constants. They did not consider hydroxide or carbonate complexes of Pu because they felt the equilibrium constants for the formation of these species were too uncertain for inclusion in the diagram. However, the failure to include these hydroxide and carbonate Pu species in the diagram may be a serious error, since these species may be the most stable under

oxidizing conditions, regardless of the uncertainties in the thermodynamic data. Because one does not have reliable thermodynamic data for a species, that does not mean the species does not exist or is unimportant. In an earlier paper, Rai and Serne (1977) prepared solubility diagrams for various aqueous plutonium species and solid Pu phases. They showed that under oxidizing conditions $\text{PuO}_2\text{CO}_3\text{OH}^-$ is the most stable Pu species although the reliability of its formation constant is suspect and that PuO_2 is the most stable solid phase.

Keeping in mind the uncertainties in the equilibrium constants (they may vary by as much as a few orders of magnitude) a stability diagram for PuO_2 in 10^{-12} M Pu at 25°C , $10^{-3.5}$ atm CO_2 , and 1 atm total pressure is presented in Figure 3. For details on the construction of Eh-pH stability diagrams the reader is referred to Garrels and Christ (1965). The equilibrium constants used in the construction of this diagram were taken from Rai and Serne (1977) and are presented in Table 1. Plutonium oxide was chosen as the solid phase, since it is the most stable (Rai and Serne, 1977; Rai, Serne, and Moore, 1980), and is also thought to be the predominant Pu solid phase in the soils of the NTS. A solution Pu concentration of 10^{-12} M was chosen because this represents the upper limit of Pu concentrations found in solution in natural waters contaminated with Pu (Bondiotti and Sweeton, 1977). Concentrations between 10^{-12} and 10^{-17} M have been observed (Bondiotti and Sweeton, 1977). A temperature of 25°C was chosen since most stability diagrams are drawn at this temperature, although daytime temperatures in the summer at the NTS greatly exceed this. The CO_2 concentration of $10^{-3.5}$ atm represents the level commonly found in the atmosphere although levels of up to 10^{-1} atm have been observed in the soil atmosphere

Figure 3. Stability of PuO_2 in 10^{-12} M Pu at 25°C , $10^{-3.5}$ atm CO_2 , and 1 atm total pressure assuming radiolytic oxidation is not occurring.

Table 1. Reactions and equilibrium constants used to construct stability diagrams.

Constants calculated from data listed in Rai and Serne (1977).

<u>Reaction</u>	<u>log K_{250C}</u>
$\text{PuO}_2 + 4 \text{H}^+ + \text{e}^- = \text{Pu}^{3+} + 2 \text{H}_2\text{O}$	9.9
$\text{PuO}_2 + 3 \text{H}^+ + \text{e}^- = \text{PuOH}^{2+} + \text{H}_2\text{O}$	2.9
$\text{PuO}_2 = \text{PuO}_2^+ + \text{e}^-$	-26.0
$\text{PuO}_2 + \text{CO}_2 + 2 \text{H}_2\text{O} = \text{PuO}_2\text{CO}_3\text{OH}^- + 3 \text{H}^+ + 2 \text{e}^-$	-50.0
$\text{Pu}^{3+} + \text{H}_2\text{O} = \text{PuOH}^{2+} + \text{H}^+$	- 6.95
$\text{PuO}_2^+ + \text{CO}_2 + 2 \text{H}_2\text{O} = \text{PuO}_2\text{CO}_3\text{OH}^- + 3 \text{H}^+ + \text{e}^-$	-24.0

Constants calculated from data listed in Rai and Serne (1977); Rai, Serne, and Moore (1980); and Rai, Serne, and Swanson (1980).

<u>Reaction</u>	<u>log K_{250C}</u>
$\text{PuO}_2 + 4 \text{H}^+ + \text{e}^- = \text{Pu}^{3+} + 2 \text{H}_2\text{O}$	20.8
$\text{PuO}_2 + 3 \text{H}^+ + \text{e}^- = \text{PuOH}^{2+} + \text{H}_2\text{O}$	14.8
$\text{PuO}_2 = \text{PuO}_2^+ + \text{e}^-$	-14.8
$\text{PuO}_2 + \text{CO}_2 + 2 \text{H}_2\text{O} = \text{PuO}_2\text{CO}_3\text{OH}^- + 3 \text{H}^+ + 2 \text{e}^-$	-39.4
$\text{Pu}^{3+} + \text{H}_2\text{O} = \text{PuOH}^{2+} + \text{H}^+$	- 6.0
$\text{Pu}^{3+} + 2 \text{H}_2\text{O} = \text{PuO}_2^+ + 4 \text{H}^+ + 2 \text{e}^-$	-35.6
$\text{PuO}_2^+ + \text{CO}_2 + 2 \text{H}_2\text{O} = \text{PuO}_2\text{CO}_3\text{OH}^- + \text{e}^-$	-24.6

when a great deal of microbial activity is occurring.

The upper and lower lines on the diagram define the stability field for water. The stability field for PuO_2 predominates over a very wide range in Eh and pH. Soil solutions with Eh and pH values within the PuO_2 field will have PuO_2 as the most stable phase under the conditions defined on the diagram although other phases such as $\text{Pu}(\text{OH})_4$ may exist metastably to PuO_2 . Under reducing conditions Pu^{3+} and PuOH^{2+} are the most stable species as indicated by the diagram. The Pu^{4+} ion and its hydrolysis species are so insoluble that they do not appear on the diagram. Under highly oxidizing conditions and at low pH the most stable species is PuO_2^+ . The stability field for PuO_2^+ would occupy a much wider range of Eh and pH if the $\text{PuO}_2\text{CO}_3\text{OH}^-$ species did not exist, but as the diagram indicates, $\text{PuO}_2\text{CO}_3\text{OH}^-$ is the most stable species under oxidizing conditions over a wide range of pH.

Over a pH range of 7 to 8 (most of the NTS soils fall in this range) the boundary line between PuO_2 and $\text{PuO}_2\text{CO}_3\text{OH}^-$ ranges between 605 and 515 mV. These Eh levels are certainly achievable in moderately well oxidized soils. At equilibrium solution Pu concentrations of less than 10^{-12} M, the boundary between PuO_2 and $\text{PuO}_2\text{CO}_3\text{OH}^-$ is moved to lower Eh values. Also as the CO_2 level increases, the boundary is moved to lower Eh values. However, one must remember that the value of the equilibrium constant used to construct the boundary between the PuO_2 and $\text{PuO}_2\text{CO}_3\text{OH}^-$ fields is uncertain, so that the actual position of the boundary might vary considerably from that shown on the diagram. In fact, the uncertainties in the positions of the boundaries between stability fields due to uncertainties in the data are probably far greater than changes in boundary positions due to changes in reactions conditions (different

solution concentration, temperature, CO₂ pressure).

Recently, new thermodynamic data have become available which may indicate how great the uncertainties in the data can be (Rai, Serne, and Moore, 1980; Rai, Serne, and Swanson, 1980). A stability diagram for PuO₂ and solution Pu species was constructed using this new data and is shown in Figure 4. The reactions and constants used to prepare this diagram are listed in Table 1. The temperature and CO₂ pressure conditions are the same for Figures 3 and 4, but a soluble Pu concentration of 10⁻⁸ M was chosen for the construction of Figure 4. This level is four orders of magnitude greater than the level chosen for Figure 3, and the PuO₂ stability field in Figure 4 is still considerably smaller than the PuO₂ field in Figure 3 even at this higher solution concentration. It is clear that Figure 4 predicts that PuO₂ is much more soluble than does Figure 3. Figure 4 also predicts that PuO₂⁺ is much more important than does Figure 3.

The equilibrium constants from Rai and Serne (1977) and Rai, Serne, and Swanson (1980) for reactions between the various solution Pu species are in fairly good agreement. The reason the two diagrams do not agree is the difference in equilibrium constants for the dissolution of PuO₂. Rai, Serne, and Moore (1980) studied the dissolution of PuO₂ microspheres and arrived at an experimentally determined value of -14.8 for log K for the reaction:

Baes and Mesmer (1976) calculated a log K value of -6.5 for the reaction:

Figure 4. Stability of PuO_2 at 10^{-8} M Pu at 25°C , $10^{-3.5}$ atm CO_2 , and 1 atm total pressure assuming radiolytic oxidation is occurring.

based on other thermodynamic data. This value was used by Rai and Serne in their earlier paper (Rai and Serne, 1977). Adding this value to a log K of -19.5 for the reaction:

leads to a log K of -26.0 for the reaction:

This value is considerably different from the experimentally determined value of -14.8. Rai, Serne, and Moore (1980) concluded that the Baes and Mesmer (1976) value was in error. However, the solubility of PuO_2 microspheres as determined by Rai, Serne, and Moore (1980) does not agree with the solubility of PuO_2 as determined by others (Bondietti and Reynolds, 1976; Bondietti and Sweeton, 1977; Dahlman et al., 1976). Thus, we have a probable error in the Baes and Mesmer (1976) value of several orders of magnitude since it was estimated from other thermodynamic data, uncertainties in PuO_2 microsphere solubility of a few orders of magnitude, and a very large discrepancy between the Baes and Mesmer (1976) data and the PuO_2 microsphere solubility. Reasons for these discrepancies are discussed in the next section on PuO_2 dissolution studies.

Chromium has two oxidation states (III and VI) which can exist in normal aqueous environments. A stability diagram for Cr_2O_3 and $\text{Cr}(\text{OH})_3$ in 10^{-6} M Cr at 25°C and 1 atm total pressure is shown in Figure 5. The thermodynamic data used in the construction of the diagram were taken from Garrels and Christ (1965). Over a very wide range of Eh and pH the stable solid phase for Cr is Cr_2O_3 although $\text{Cr}(\text{OH})_3$ would probably form

Figure 5. Stability of Cr(OH)_3 and Cr_2O_3 in 10^{-6} M Cr at 25°C and 1 atm total pressure.

metastably to Cr_2O_3 . The size of the $\text{Cr}(\text{OH})_3$ stability field is less than the size of the Cr_2O_3 field under the same conditions indicating $\text{Cr}(\text{OH})_3$ is more soluble than Cr_2O_3 . A soluble Cr concentration of 10^{-6} M (52 $\mu\text{g}/\ell$ Cr) was chosen, since this level represents the maximum permissible concentration in drinking water (EPA, 1980). Usually, concentrations of one-tenth this level are found in natural waters (Wedepohl, 1970). At higher solution Cr concentrations the Cr_2O_3 field increases and at lower solution Cr concentrations the field decreases. At low pH levels Cr^{3+} is the most stable species over a wide range in Eh. At high Eh levels the hexavalent HCrO_4^- and CrO_4^{2-} species are stable over a wide pH range. Thus, in moderately well oxidized soils we would expect Cr(VI) to exist.

By comparing Figures 3, 4, and 5 it can be seen that there is considerable overlapping of the stability fields of the hexavalent species of both elements. Thus, under roughly the same conditions Cr(VI) and Pu(VI) are stable. The extent of overlapping will change as equilibrium conditions change and uncertainties in the extent of overlapping are largely due to uncertainties in the thermodynamic data, but it does seem reasonable to assume that in many soils where Cr(VI) is stable, then Pu(VI) may be stable.

Radiolytic Oxidation and PuO_2 Microsphere

Dissolution Studies

There have been a number of PuO_2 microsphere dissolution studies and some of these are summarized in Table 2. The most important thing to note is that the soluble Pu is virtually all oxidized. The group at Oak Ridge National Laboratory (Bondietti and Reynolds, 1976; Dahlman et al., 1976; Bondietti and Sweeton, 1977) used coprecipitation and

Table 2. Summary of $^{239}\text{PuO}_2$ dissolution studies.

Solubility	Valence	Amt. $^{239}\text{PuO}_2$ Used	Equilibrating Solution	pH	Equilibration Time	Reference
$\sim 10^{-10}$ M	Pu(V/VI) $\sim 95\%$	--	10^{-4} M NH_4HCO_3	7	3 wks	Bondietti and Reynolds (1976)
$\sim 10^{-9}$ M	Pu(V/VI) $\sim 95\%$	2.2-2.7 mg	20 ml 10^{-3} M NaHCO_3	7	9 wks _e	Dahlman <u>et al.</u> (1976)
$\sim 10^{-11}$ M	Pu(V/VI) $\sim 95\%$	1.77 mg	20 ml 10^{-3} M NaHCO_3	7	10 wks	Bondietti and Sweeton (1977)
$\sim 10^{-6}$ - 10^{-9} M	Pu(V)	8 mg	20 ml 0.0015 M CaCl_2	4-8	13-36 wks	Rai, Serne, and Moore (1980)

Microsphere properties:

Calcined at 1150°C

149-174 μm diameter

0.012 m^2/g specific surface

chelation-solvent extraction techniques to show that nearly all the solution Pu contacting PuO_2 microspheres is Pu(V) and/or Pu(VI). Their methods did not allow them to distinguish between Pu(V) and Pu(VI). Rai, Serne, and Swanson (1980) working at Battelle Northwest Laboratories showed indirectly that the solution species contacting PuO_2 microspheres is Pu(V). They demonstrated using chelation-solvent extraction that Pu(IV) was absent from the equilibrium solution and using spectrophotometry that Pu(VI) was absent.

If the solution species of Pu contacting PuO_2 microspheres is Pu(V) and/or Pu(VI), then oxidation must have occurred during dissolution of PuO_2 . Oxidation of Pu(IV) by O_2 is so slow it can be ignored (Cleveland, 1970; Bondietti, personal communication). Therefore, another oxidizing agent must be present. The most likely candidate is H_2O_2 produced from the radiolysis of H_2O by the α radiation from the PuO_2 . The proposed mechanism of PuO_2 microsphere dissolution is as follows (Bondietti and Sweeton, 1977): Alpha emission recoils with sufficient energy to break chemical bonds cause fragmentation of the oxide lattice producing colloidal PuO_2 particles. This is the aggregate recoil effect. When the PuO_2 microspheres are placed in solution the PuO_2 colloidal particles are released to solution. This accounts for the rapid appearance of "polymeric" Pu which can be removed with an ultracentrifuge and does not extract using a chelation-solvent extraction method. These colloidal particles are more susceptible to dissolution than the microsphere. Thus, soluble Pu concentrations increase with time. The α radiation also causes the radiolysis of water with H_2O_2 produced. Hydrogen peroxide reactions with Pu are complex, since H_2O_2 can act as both an oxidizing and a reducing agent, but at neutral to alkaline pH values

H_2O_2 will oxidize Pu(IV), thus resulting in Pu(V/VI) in solution. This mechanism would account for the oxidized Pu in solution in the Oak Ridge experiments since they were run at neutral pH, but what about the studies by Rai, Serne, and Moore (1980) where acid pH levels were also used and virtually all solution Pu was found to be Pu(V)? A possible explanation is as follows: At acid pH levels the solubility of PuO_2 is increased to the point where disproportionation of Pu(IV) is more likely. Disproportionation of Pu(IV) leads to Pu(III) and Pu(VI). The Pu(III) could then be oxidized by H_2O_2 while the Pu(VI) is reduced resulting in net Pu(V) production. Whatever the mechanism it seems clear that the oxidation is due to a radiolytic effect.

The studies by Rai, Serne, and Moore (1980) indicate a solubility of PuO_2 at pH 7 two orders of magnitude greater than the solubility determined by the Oak Ridge group, but the variation in solubility as determined by the PuO_2 microsphere dissolution studies is not as great as the difference between the experimentally determined solubility (Rai, Serne, and Moore, 1980) and the solubility calculated from the Baes and Mesmer (1976) thermodynamic data (Rai and Serne, 1977).

At this point it is necessary to discuss the various discrepancies. First, there is the variability among the PuO_2 dissolution studies. The group at Oak Ridge used several methods to try to carefully distinguish between solution and ultrafine colloidal Pu. The Battelle group on the other hand was not as careful. Even though the Battelle group centrifuged their PuO_2 suspensions for 40 min at 6000 g and filtered them through 0.015 μm membrane filters, ultrafine Pu(IV) polymer may have been depolymerized and extracted during the tri-n-butyl phosphate extraction they used. This depolymerized and extracted Pu(IV) would

have been counted as oxidized Pu when in fact it was not. This would lead to a higher Pu solubility than that determined by the Oak Ridge group. The true solution Pu concentration in the Battelle experiments may have been much lower than the values reported and the solution species may have been Pu(VI), but was below the spectrophotometric detection limit. A careful evaluation of the reliability of the tri-n-butyl phosphate extraction method for trace solution Pu levels by comparison with the Oak Ridge methods is needed.

Aside from the problem of the reliability of the Battelle group data, Rai, Serne, and Moore (1980) concluded that their system was in equilibrium and that their measured redox potential was a valid Eh measurement. The fact that solution concentrations do not change over a long period of time is by itself an insufficient test for equilibrium. In fact, the concept of equilibrium may not be entirely meaningful where radiolytic oxidation and radioactive decay are occurring. The measured redox potential was in fact a mixed potential reflecting the potentials of the Pu redox species and the water radiolysis products. Even if equilibrium had existed, the measured potential may not accurately have reflected the true equilibrium Eh. A more useful experiment would be to study the dissolution of PuO_2 in Eh buffers. This problem was recognized by Rai, Serne, and Moore (1980) and they are planning further experiments along this line. Until more data are available we must conclude that Rai, Serne, and Moore (1980) may be erroneous in assuming their data can be used to calculate an equilibrium constant for the dissolution of PuO_2 .

However, if the PuO_2 microsphere dissolution study measurements are correct, there is the very large discrepancy between the experimentally

determined solubility and the solubility calculated from the Baes and Mesmer (1976) thermodynamic data (Rai and Serne, 1977) to resolve. This difference can probably be attributed almost entirely to radiolytic effects. Radiolytic oxidation is favored by larger PuO_2 particles where the radiation density is higher, but is probably unimportant among dispersed, submicron environmental-type PuO_2 (Bondietti and Sweeton, 1977). Therefore, we conclude that the solubility calculated from the PuO_2 microsphere dissolution study measurements may be reliable for those cases when large PuO_2 particles ($>$ silt size) are present in the soil if the measurements actually reflect equilibrium conditions, but the thermodynamically calculated solubility is probably reliable for dispersed, submicron PuO_2 particles. Thus, both stability diagrams (Figures 3 and 4) may have their use. However, the Pu levels actually observed in contaminated waters are more in accord with the thermodynamically calculated values than the PuO_2 microsphere dissolution measurements.

At the NTS most of the Pu is associated with the coarse silt-sized particles (Tamura, 1975). However, this does not necessarily mean that the PuO_2 particles are coarse silt-sized, but rather smaller PuO_2 particles are associated with silt-sized minerals. Plutonium also has been found occluded in glass and metal at nuclear event sites. Therefore, it is expected that radiolytic oxidation is not important in these soils except where large PuO_2 particles exist. Instead of radiolytic oxidation, oxidation by manganese oxides is favored and this is examined in the next section.

Thermodynamics of Chromium and Plutonium Oxidation
by Manganese Oxide Minerals

In Table 3 are several oxidation and reduction half-reactions involving Cr, Pu, and manganese (Mn) together with the log K values for the reactions. The log K values for the Pu half-reactions were calculated from data taken from Rai and Serne (1977); Rai, Serne, and Moore (1980); and Rai, Serne, and Swanson (1980). The log K values for the Cr half-reactions were taken from Bartlett and James (1979) who calculated their log K values from the data given in Garrels and Christ (1965), while the log K values for the Mn half-reactions were taken from Lindsay (1979). The Cr oxidation reactions shown are for the oxidation of Cr_2O_3 , $\text{Cr}(\text{OH})_3$, and aqueous Cr(III) to aqueous Cr(VI). The Mn reduction reactions shown are for the reduction of four common tetravalent manganese oxide minerals to aqueous Mn(II). The Pu oxidation reactions listed are for the oxidation of PuO_2 to aqueous PuO_2^+ or $\text{PuO}_2\text{CO}_3\text{OH}^-$.

If one of the Cr or Pu half-reactions is combined with one of the manganese oxide half-reactions and the log K values for the two half-reactions are added, a net redox reaction and its equilibrium constant are obtained. By choosing appropriate reaction conditions it is possible to calculate the equilibrium concentration of soluble Cr or Pu as a function of soil solution pH and soluble Mn(II) concentration.

As an example, consider the oxidation of PuO_2 to $\text{PuO}_2\text{CO}_3\text{OH}^-$ by $\delta\text{-MnO}_2$ which is the reaction being proposed as the one occurring in the NTS soils. The mineral $\delta\text{-MnO}_2$ is a hydrated, amorphous form of manganese oxide probably found in soils as a coating over silicate mineral particles (Taylor and McKenzie, 1966; McKenzie, 1977). First, the two half-reactions and their log K values from Table 3 are added to obtain the

Table 3. Oxidation or reduction half-reactions involving Cr, Mn, and Pu.

<u>Reaction</u>	<u>log K_{25°C}</u>
$0.17 \text{ Cr}_2\text{O}_3 + 0.67 \text{ H}_2\text{O} = 0.17 \text{ Cr}_2\text{O}_7^{2-} + 1.33 \text{ H}^+ + \text{e}^-$	-19.7
$0.17 \text{ Cr}_2\text{O}_3 + 0.83 \text{ H}_2\text{O} = 0.33 \text{ HCrO}_4^- + 1.33 \text{ H}^+ + \text{e}^-$	-20.0
$0.17 \text{ Cr}_2\text{O}_3 + 0.83 \text{ H}_2\text{O} = 0.33 \text{ CrO}_4^{2-} + 1.67 \text{ H}^+ + \text{e}^-$	-22.2
$0.33 \text{ Cr(OH)}_3 + 0.17 \text{ H}_2\text{O} = 0.17 \text{ Cr}_2\text{O}_7^{2-} + 1.33 \text{ H}^+ + \text{e}^-$	-18.6
$0.33 \text{ Cr(OH)}_3 + 0.33 \text{ H}_2\text{O} = 0.33 \text{ HCrO}_4^- + 1.33 \text{ H}^+ + \text{e}^-$	-18.9
$0.33 \text{ Cr(OH)}_3 + 0.33 \text{ H}_2\text{O} = 0.33 \text{ CrO}_4^{2-} + 1.67 \text{ H}^+ + \text{e}^-$	-21.0
$0.33 \text{ Cr}^{3+} + 1.17 \text{ H}_2\text{O} = 0.17 \text{ Cr}_2\text{O}_7^{2-} + 2.33 \text{ H}^+ + \text{e}^-$	-22.5
$0.33 \text{ Cr}^{3+} + 1.33 \text{ H}_2\text{O} = 0.33 \text{ HCrO}_4^- + 2.33 \text{ H}^+ + \text{e}^-$	-22.8
$0.33 \text{ Cr}^{3+} + 1.33 \text{ H}_2\text{O} = 0.33 \text{ CrO}_4^{2-} + 2.67 \text{ H}^+ + \text{e}^-$	-25.0
$0.33 \text{ CrO}_2^- + 0.78 \text{ H}_2\text{O} = 0.33 \text{ CrO}_4^{2-} + 1.33 \text{ H}^+ + \text{e}^-$	-15.2
$0.5 \text{ Mn}_3\text{O}_4 + 4 \text{ H}^+ + \text{e}^- = 1.5 \text{ Mn}^{2+} + 2 \text{ H}_2\text{O}$	31.5
$\text{MnOOH} + 3 \text{ H}^+ + \text{e}^- = \text{Mn}^{2+} + 2 \text{ H}_2\text{O}$	25.3
$0.5 \text{ Mn}_2\text{O}_3 + 3 \text{ H}^+ + \text{e}^- = \text{Mn}^{2+} + 1.5 \text{ H}_2\text{O}$	25.7
$0.5 \text{ MnO}_2 + 2 \text{ H}^+ + \text{e}^- = 0.5 \text{ Mn}^{2+} + \text{H}_2\text{O}$	22.1

Table 3 (Continued).

Equilibrium constants calculated from data listed
in Rai and Serne (1977)

<u>Reaction</u>	<u>log K_{250C}</u>
$\text{PuO}_2 = \text{PuO}_2^+ + e^-$	-26.0
$0.5 \text{ PuO}_2 + 0.5 \text{ CO}_2 + \text{H}_2\text{O} = 0.5 \text{ PuO}_2\text{CO}_3\text{OH}^- + 1.5 \text{ H}^+ + e^-$	-25.0

Equilibrium constants calculated from data listed in
Rai and Serne (1977); Rai, Serne, and Moore (1980);
and Rai, Serne, and Swanson (1980)

<u>Reaction</u>	<u>log K_{250C}</u>
$\text{PuO}_2 = \text{PuO}_2^+ + e^-$	-14.8
$0.5 \text{ PuO}_2 + 0.5 \text{ CO}_2 + \text{H}_2\text{O} = 0.5 \text{ PuO}_2\text{CO}_3\text{OH}^- + 1.5 \text{ H}^+ + e^-$	-19.7

net redox reaction and its log K value:

The equilibrium constant expression for this reaction is given by:

$$pK = p\text{Mn}^{2+} + p\text{PuO}_2\text{CO}_3\text{OH}^- - p\text{CO}_2 - \text{pH} = 5.8$$

Solving for $p\text{PuO}_2\text{CO}_3\text{OH}^-$ leads to:

$$p\text{PuO}_2\text{CO}_3\text{OH}^- = \text{pH} + p\text{CO}_2 - p\text{Mn}^{2+} + 5.8$$

Thus, the solution concentration of $\text{PuO}_2\text{CO}_3\text{OH}^-$ can be calculated as a function of pH, CO_2 pressure, and Mn(II) concentration.

This has been done for four levels of Mn(II), a CO_2 pressure of $10^{-3.5}$ atm, and over an environmentally meaningful range of pH values and the results are presented in Figure 6. The CO_2 pressure chosen represents the atmospheric CO_2 level. Increasing solubility of PuO_2 is favored as the dissolved carbonate concentration increases or as $p\text{CO}_2$ increases. The four Mn(II) concentrations chosen represent a range of levels likely to occur in soil solution. Each line on the graph represents the equilibrium concentration of $\text{PuO}_2\text{CO}_3\text{OH}^-$ as a function of pH for a given level of dissolved Mn(II), and $p\text{PuO}_2\text{CO}_3\text{OH}^-$ and pH values below a line indicate that the solution is undersaturated with respect to PuO_2 , so the reaction is thermodynamically spontaneous in the direction of oxidized Pu. At the pH levels found in the NTS soils significant

Figure 6. Solubility of PuO_2 as controlled by $\delta\text{-MnO}_2$ in the absence of reducing agents at 25°C , $10^{-3.5}$ atm CO_2 , and 1 atm total pressure assuming radiolytic oxidation is not occurring.

levels of dissolved Pu are favored by very low dissolved Mn(II) concentrations if $\delta\text{-MnO}_2$ is controlling PuO_2 weathering.

Figure 6 was constructed from the thermodynamic data listed in Rai and Serne (1977), and so is applicable to dispersed, submicron PuO_2 particles where radiolytic oxidation is unimportant. For larger PuO_2 particles where radiolytic oxidation occurs, even greater solubility of PuO_2 can be observed when $\delta\text{-MnO}_2$ controls the solution Eh. This situation is observed in Figure 7. The data of Rai, Serne, and Moore (1980) indicate that PuO_2 has a solubility of 10^{-6} to 10^{-9} M in the pH range of 4 to 8 when radiolytic oxidation is occurring provided their data are reliable. The Eh of the solution is poised by the radiolytic oxidation of PuO_2 , since no other oxidizing agents are present other than the products of water radiolysis. When $\delta\text{-MnO}_2$ is added to the solution a higher solution Eh is set by the $\delta\text{-MnO}_2$ equilibrium and much higher levels of soluble Pu could be observed as Figure 7 indicates. However, Figure 7 is invalid if the equilibrium constant calculated from the Rai, Serne, and Moore (1980) data is erroneous due to non-equilibrium conditions. Thus, we conclude that PuO_2 is highly unstable in the presence of $\delta\text{-MnO}_2$ and is especially so at larger particle sizes where radiolytic oxidation and oxidation by $\delta\text{-MnO}_2$ combine to dissolve the PuO_2 .

The above analysis assumes that $\delta\text{-MnO}_2$ is in control of the soil solution Eh and in the microenvironment surrounding the MnO_2 mineral this is the case. Even though the overall redox status of a soil might be controlled by the most abundant redox components in the soil (iron species and organic matter), microregions or zones of oxidation and/or reduction can occur where the redox status is controlled by a soil component that dominates the localized region (Bartlett, 1981). This is

Figure 7. Solubility of PuO_2 as controlled by $\delta\text{-MnO}_2$ in the absence of reducing agents at 25°C , $10^{-3.5}$ atm CO_2 , and 1 atm total pressure assuming radiolytic oxidation is occurring.

why Cr can be oxidized in soil even though manganese oxide is usually much less abundant in soils (<0.2%) than is organic matter (0.5-4%). However, outside the MnO_2 microenvironment organic matter and minerals containing Fe^{2+} ions probably control the Pu redox chemistry. These soil components would keep Pu in a reduced state, thus severely restricting its mobility. Bondietti et al. (1975) showed that fulvic acid and root exudate components (polygalacturonic and alginic acids) readily reduce Pu. Recently, researchers at Oak Ridge National Laboratory have demonstrated that the Fe^{2+} ions in ferromagnesian minerals will reduce Pu (Tamura, personal communication). Because of the widespread occurrence of Fe^{2+} and organic matter in soils it would be expected that Pu would remain in a reduced state in most soil environments, and indeed this seems to be the case most of the time. However, most of the iron in NTS soils would be Fe(III) and these soils are likely low in organic matter so the above situation may not be applicable to NTS soils. Sorption reactions also restrict the amount of solution Pu available, so that predicted levels are probably never achieved which is a fortunate situation considering the toxicity of the element. Thus, the levels of soluble Pu actually found are dictated by the rates of reaction with the various soil components.

It is also possible to illustrate the control $\delta\text{-MnO}_2$ has over the solubility of a Cr compound and this has been done for $\text{Cr}(\text{OH})_3$ and is shown in Figure 8. This diagram illustrates that $\text{Cr}(\text{OH})_3$ is extremely unstable in the presence of $\delta\text{-MnO}_2$, since the equilibrium occurs at pH levels well above those of normal soils. The diagram predicts that quite high levels of soluble, oxidized Cr could be produced as a result of the action of soil manganese oxides on $\text{Cr}(\text{OH})_3$. However, the

Figure 8. Solubility of Cr(OH)_3 as controlled by $\delta\text{-MnO}_2$ in the absence of reducing agents at 25°C and 1 atm total pressure.

presence of reducing agents and soil components which sorb Cr will limit the element's mobility. Also, it must be remembered that the diagrams in this section all depend upon thermodynamic considerations which tell what is possible and not the rate of the reactions.

Additional Evidence for the Oxidation
of Plutonium by Manganese Oxide
Minerals in Soil Environments

Besides the thermodynamic evidence there is additional direct and indirect experimental evidence to support the possibility of Pu oxidation by manganese oxides under certain conditions.

Cleveland (1970) has summarized the important redox reactions involving Pu and reports that Pu(IV) is oxidized to Pu(VI) by MnO_2 in the laboratory. The reaction is 90% complete in one hour using a batch technique and complete in 15 minutes using a column. Thus, the reaction is very fast on a geological time scale of hundreds to thousands of years.

Bondietti and Reynolds (1976) found that seepage water from a radioactive solid waste burial site contained ^{238}Pu that was mostly Pu(V/VI). Although the original chemical form of Pu in the burial site is unknown, it was postulated that it could be Pu(IV) in which case oxidation would have occurred in order to produce Pu(V/VI) in the seepage water. Since the isotope was ^{238}Pu and ^{238}Pu has a higher radiation density than ^{239}Pu , radiolytic oxidation is favored more with ^{238}Pu than with ^{239}Pu (Bondietti and Sweeton, 1977). The specific activity, average α -decay energy, and energy release rate of ^{238}Pu are 17.4 $\mu\text{Ci/g}$, 5.49 MEV, and 2.1×10^{14} EV/min, respectively, compared to values of 0.06 $\mu\text{Ci/g}$, 5.10 MEV, and 6.9×10^{11} EV/min for ^{239}Pu . However,

it is also possible that manganese oxide coatings on soil particles at the burial site and on sediments in the seepage water could have caused the oxidation of the buried Pu. The important fact is that Pu(V/VI) has been observed in natural waters.

Bondietti and Reynolds (1976) also found that when the clay fraction of Miami silt loam was treated to remove organic matter and a ^{238}Pu solution with all of the Pu initially in the quadrivalent state was added to yield a Pu concentration of 0.6 ppm in the clay, a significant fraction of Pu remained in solution over a long period of time rather than being sorbed. After three weeks only 50% of the added Pu had been sorbed by the treated clay compared to 99.9% by untreated clay, after eighteen weeks 61.5% had been sorbed by the treated clay compared to 99.8% by the untreated clay, and after fifty-two weeks 99.8% of the added Pu had finally been sorbed by the treated clay compared to 99.9% by the untreated clay. Of the Pu remaining in solution in contact with the treated clay about half was Pu(V/VI). No oxidized Pu could be found in the solution in contact with the untreated clay.

It seems clear that the soil organic matter kept Pu in a reduced state and thus strongly sorbed to the clay, but when the organic matter was removed more soluble, oxidized Pu appeared. Bondietti and Reynolds (1976) ascribed the appearance of oxidized Pu to a disproportionation or auto-oxidation reaction, but it is possible that any manganese oxides in the soil clay could have oxidized the added Pu, especially since the experiment was carried out at pH 4 where oxidation is favored.

It is interesting to note that when the free iron oxides were also removed from the soil clay, 99.8% of the added Pu was sorbed by the clay minus organic matter and free iron oxides. The dithionite-citrate-

bicarbonate of Mehra and Jackson (1960) method used to remove free iron oxides, also removes manganese oxides as well. Thus, it is not surprising that Pu initially in the quadrivalent state remained in that state and was strongly sorbed to the clay with the iron and manganese oxide coatings removed, especially if any Fe(II) was present which was quite likely since the dithionite reduces iron and traces of Fe(II) could have remained in the soil.

Hypothesis and Objectives

Consideration of both the thermodynamic and experimental evidence for the oxidation of Pu by soil manganese oxides led to the following hypothesis: under high Eh conditions, high HCO_3^- levels, low organic matter levels, and negligible Fe(II) levels, PuO_2 particles can be oxidized to the mobile $\text{PuO}_2\text{CO}_3\text{OH}^-$ species by manganese oxide minerals in a soil profile. The conditions necessary for this oxidation reaction to occur were postulated to exist within soil profiles at the NTS.

Therefore, one of the main objectives of this thesis was to study the redox chemistry of Pu in selected soil samples from the NTS. The study was carried out in two parts which were:

- 1) To measure oxidized Pu in selected NTS soil samples or at least establish as fact that oxidized Pu could be readily produced in such soils; and
- 2) To determine the amount of Pu associated with various soil components that may control the redox chemistry of Pu.

This information may eventually be used to deduce the relationships between soil and solution Pu species in order to predict the dispersion and bioavailability of this element. In addition since americium (Am) is also found in NTS soils, some chemical fractionation of soil Am data

were also obtained for possible future use.

The other main hypothesis in this thesis was that the redox chemistry of Cr in soil is sufficiently similar to that of Pu so that Cr reactions in soil could be used as a model for Pu reactions in soil. Therefore, the other main objective of the thesis was to study Cr reactions in soils in order to provide information to develop a general model for Pu reactions in soils. The experimental studies included:

- 1) Fractionation of soil Cr by selective extraction techniques in order to determine the fate of Cr from organic sources applied to soil;
- 2) Determinations of the rate and amount of Cr oxidation in soils and by various manganese oxide minerals as affected by the amount and source of Cr added and the reaction conditions; and
- 3) Determinations of the rate of Cr reduction in soil and by fulvic acid from soil and leather dust.

It is not expected that these studies would provide enough information to satisfactorily test the hypothesis: Cr reactions in soil can be used as a model for Pu reactions in soil. The goal was to provide basic information about Cr reactions in soil that might be the foundation for future studies with soil Pu. The ultimate goal of studies such as these is a mathematical model that will accurately predict the dispersion of multiple oxidation state elements in the environment.

MATERIALS AND METHODS

Plutonium Experiments

Soil Sample Collection

Fourteen soil samples were collected from Areas 11A, 11B, 11C, and 11D of the NTS on January 30, 1980. Area 11 is where both nuclear and safety-shot events occurred. Safety shots were detonations of nuclear devices by conventional explosions in order to test the safety of the devices. These tests resulted in the dispersion of PuO_2 throughout the area. Area 11 is also where abnormal Pu distributions in the soil profile have been observed (Essington *et al.*, 1976).

In each area sampled, samples were taken from open areas free from vegetation known as desert pavement and from underneath bushes around the perimeters of the open areas. The soil underneath the bushes was mounded up due to wind erosion and the activity of burrowing animals. Therefore, such areas are called desert mounds. In each area sampled, sufficient soil was taken from the top 2 cm of soil profile to fill a one-liter, wide-mouth, plastic bottle. All the soil samples were moist at the time of collection due to recent rains in the area.

Chemical Fractionation of Soil Pu and Am

All fourteen samples collected were surveyed by Reynolds Electrical and Engineering Company for radioactive contamination by counting the gamma radiation from each sample using a Ge(Li) detector. The results of this survey are presented in Table 4. Only two of the fourteen samples collected had detectable levels of Pu which reflects the variable Pu distribution common to test site areas. One of these two samples (sample no. 60346 from Area 11C) was selected for further study. This

Table 4. Radioactive contamination survey of fourteen soil samples collected from Areas 11A, 11B, 11C, and 11D of the NTS.

Sample no.	Area Sampled	Sample Weight	^{239}Pu	^{241}Am	^{137}Cs
		g	-----nCi/g $\pm$ % error-----		
60339	11A desert pavement	721	ND*	ND	ND
60340	11A desert mound	527	ND	ND	ND
60341	11B desert pavement	651	ND	25.3 (± 6.5)	ND
60342	11B desert pavement	737	ND	57.6 (± 6.3)	0.00114 (± 67.2)
60343	11B desert mound	454	ND	6.26 (± 7.0)	ND
60344	11B desert mound	533	ND	0.76 (± 9.0)	ND
60345	11C desert pavement	923	ND	37.8 (± 6.3)	0.00382 (± 31.7)
60346	11C desert pavement	735	751 (± 19.1)	94.8 (± 6.2)	ND
60347	11C desert mound	592	ND	23.0 (± 6.5)	ND
60348	11C desert mound	623	ND	7.13 (± 7.0)	ND
60349	11D desert pavement	796	266 (± 36.4)	31.9 (± 6.4)	0.0418 (± 13.3)
60350	11D desert pavement	680	ND	5.28 (± 7.1)	0.0261 (± 14.0)
60351	11D desert mound	662	ND	43.6 (± 6.4)	0.0137 (± 16.7)
60352	11D desert mound	661	ND	ND	

*None detected

sample was extracted with 0.01 M KH_2PO_4 , 0.2 M Na_2CO_3 , 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$, 0.1 M $\text{Na}_2\text{CO}_3 + 0.05 \text{ M } \text{Na}_4\text{P}_2\text{O}_7$, 5.25% NaOCl , 10% H_2O_2 , 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$, and dithionate-citrate-bicarbonate (DCB). These reagents were designed to extract various fractions of the soil (readily soluble ions, organic matter, and Fe and Mn oxides), and therefore various forms of Pu in the soil as discussed in the next chapter.

The extractions with KH_2PO_4 , Na_2CO_3 , $\text{Na}_4\text{P}_2\text{O}_7$, and $\text{Na}_2\text{CO}_3 + \text{Na}_4\text{P}_2\text{O}_7$ were carried out as follows. Duplicate 2.5-cm³ subsamples of moist soil from Area 11C were added to 15-ml plastic centrifuge tubes and 5.0 ml of extracting solution were added to each tube, followed by mixing on a vortex mixer. The samples were allowed to sit for one hour with periodic mixing. At the end of the one-hour period the samples were centrifuged for 5 min at 2852 g and the supernatants decanted for analysis. An additional Na_2CO_3 extraction was performed on a fresh sample using an extraction time of 5 min instead of one hour. To determine Pu(III) and Pu(IV) in the samples the TTA-xylene and PrF_3 -TTA-xylene methods as outlined below were used. To determine Pu(V) and Pu(VI) the $\text{Ca}(\text{NO}_3)_2$ -hexone and $\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene methods were used as outlined in a later section.

The NaOCl extraction which was a modified version of the method given by Anderson (1963) was run according to the following procedure. Duplicate 2.5-cm³ subsamples of moist soil were added to 15-ml plastic centrifuge tubes. Five ml of 5.25% NaOCl adjusted to pH 9.5 with 6 M HCl before use were added to the samples. The samples were mixed on a vortex mixer and placed in a sand bath at 100°C for 30 min. The samples were centrifuged for 2 min at 2852 g and decanted into 25-ml volumetric flasks. The extraction steps were repeated four more times and the

flasks were filled to volume with deionized water. The concentrations of the various Pu valence state species were determined using the methods outlined in a later section.

The H_2O_2 and $\text{NH}_2\text{OH}\cdot\text{HCl}$ extractions which were modifications of methods originally given by Taylor and McKenzie (1966) and Chao (1972) were carried out as outlined below. Duplicate 2.5-cm^3 subsamples of moist soil were added to 15-ml plastic centrifuge tubes and 5 ml of extracting solution were added followed by mixing on a vortex mixer. For the H_2O_2 extraction, 10% H_2O_2 was adjusted to pH 7 with 1 M NaOH before use and for the $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction, 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ was adjusted to pH 2 with 6 M HCl before use. The samples were allowed to stand overnight followed by centrifuging for 2 min at 2852 g and decanting the supernatants into 25-ml volumetric flasks. The extraction steps were repeated four more times and the flasks were filled to volume with deionized water. The concentrations of the various Pu valence state species were determined using the methods outlined in a later section.

The DCB extraction based on the method of Mehra and Jackson (1960) was carried out as follows. A citrate buffer was prepared by dissolving 226.0 g of sodium citrate, 25.0 g of sodium bicarbonate, and 210.0 g of sodium chloride in 2.5 l of deionized water. The pH of the solution was adjusted to 7.3 with 1 M NaOH and diluted to 3 l. Duplicate 2.5-cm^3 subsamples of moist soil were added to 15-ml plastic centrifuge tubes followed by 2.5 ml of deionized water and 2.5 ml of citrate buffer. The samples were mixed on a vortex mixer and placed in a sand bath at 80°C . After 10 min ~ 0.1 g of sodium dithionite was added to each tube, the tubes were mixed and returned to the sand bath for 15 min. The samples

were then centrifuged for 2 min at 2852 g and the supernatants were decanted into 25-ml volumetric flasks. The extraction steps were repeated twice more with the dithionite omitted for the last extraction. The flasks were filled to volume with deionized water and the concentrations of the various Pu species were determined using the methods outlined below.

Oxidation of Carbonate-Soluble Pu

To determine the amount of Pu in the soil dissolved by Na_2CO_3 and potentially oxidizable by excess $\delta\text{-MnO}_2$, the following experiment was run. Duplicate 2.5-cm^3 subsamples of soil were added to 15-ml plastic centrifuge tubes. One hundred milligrams of $\delta\text{-MnO}_2$ prepared as described in a later section were added to each tube followed by 1 ml of deionized water. The tubes were mixed on a vortex mixer and allowed to sit for three days. A 5.0 ml aliquot of 0.2 M Na_2CO_3 was added to each tube. The tubes were mixed on a vortex mixer and allowed to stand for one hour with periodic mixing. The tubes were then centrifuged for 5 min at 2852 g and the supernatants decanted for analysis. The Pu(III) and Pu(IV) species were extracted using the PrF_3 -TTA-xylene procedure as outlined below. The Pu(V) and Pu(VI) species were extracted using the $\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene procedure outlined below.

Pu Valence State Separation Methods

To separate Pu(III) and/or Pu(IV) from the various extracts, the TTA-xylene and/or PrF_3 -TTA-xylene methods were used (Bondietti and Reynolds, 1976). The TTA-xylene method was specific for Pu(IV) and depended on chelating the Pu(IV) with TTA (thenoyl trifluoroacetone) and extracting the Pu(IV)-TTA complex from the aqueous phase with xylene.

The PrF_3 -TTA-xylene method consisted of removing Pu(III) and Pu(IV) from solution by coprecipitation with PrF_3 and dissolving the precipitate and oxidizing the Pu(III) to Pu(IV) prior to the TTA-xylene extraction.

The TTA-xylene method consisted of the following steps. A 1.0 ml aliquot of sample was pipeted into a 1-dram vial. The sample was acidified to 1 M in HNO_3 by adding 60 μl of conc. HNO_3 . One ml of 0.5 M TTA in o-xylene was added to the sample followed by shaking for 10 min on a Thomas-Boerner oscillating shaker. After the phases separated, the xylene phase was withdrawn using a transfer pipet and added to another 1-dram vial. A 0.5 ml aliquot of 0.5 M TTA in xylene was added to the aqueous sample, followed by shaking for 5 min, withdrawing the organic phase, and combining it with the previously separated xylene phase. The combined xylene phases were then shaken for 10 min with 1.5 ml of 1 M HNO_3 . The xylene phase was withdrawn and evaporated on a stainless steel planchet which was then flamed before counting.

The procedure for the PrF_3 -TTA-xylene method for separating Pu(III) and Pu(IV) was as follows. A 1.0 ml aliquot of sample was pipeted into a 15-ml plastic centrifuge tube and diluted to 5 ml with deionized water. The sample was acidified to 1 M in HNO_3 and 0.5 M in H_2SO_4 by adding 350 μl of conc. HNO_3 and 150 μl of conc. H_2SO_4 . The sample was then made 0.02 M in $\text{Na}_2\text{Cr}_2\text{O}_7$ by adding 120 μl of 1 M $\text{Na}_2\text{Cr}_2\text{O}_7$. The dichromate was added to provide a holding oxidant environment in order to prevent any Pu(V/VI) in the sample from being reduced during the procedure and therefore counted as Pu(IV). A 100 μl aliquot of 6% praeaseodymium nitrate solution was added in order to total 2.0 mg of praeaseodymium in the sample. The sample was then made 2 M in HF by

adding 450 μl of conc. HF followed by mixing on a vortex mixer. After sitting for 5 min the PrF_3 precipitate was centrifuged out and the supernatant was transferred to another 15-ml centrifuge tube. The precipitate was washed in 1 M HNO_3 -1 M HF and then dissolved in 1.0 ml of 1 M HNO_3 saturated with boric acid. If Pu(III) was to be included in the analysis, then five drops of 3 M NaNO_3 were added to the dissolved precipitate followed by allowing the sample to sit for 10 min. The NaNO_3 oxidized the Pu(III) to Pu(IV). The sample was then taken through the TTA-xylene procedure.

To determine Pu(V) and/or Pu(VI) the $\text{Ca}(\text{NO}_3)_2$ -hexone and/or $\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene methods were used (Bondietti and Reynolds, 1976). The $\text{Ca}(\text{NO}_3)_2$ -hexone method was based on forming an aqueous Pu(V/VI) nitrate complex which was then extracted into the hexone phase. The $\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene method depended upon reducing the Pu(V/VI) to Pu(III/IV) prior to the PrF_3 coprecipitation and TTA-xylene extraction steps.

To determine Pu(V) and/or Pu(VI) by the $\text{Ca}(\text{NO}_3)_2$ -hexone method the aqueous phase remaining after the TTA-xylene extraction was made 3.5 to 4.0 M in $\text{Ca}(\text{NO}_3)_2$ by adding 0.9 g of $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ and 0.01 M in KBrO_3 by adding 100 μl of 0.1 M KBrO_3 . A 1-ml aliquot of pretreated hexone was then added and shaken for 3 min. After phase separation the hexone phase was withdrawn and evaporated on a stainless steel planchet. The extraction with hexone was repeated and the planchet was flamed before counting. To pretreat the hexone to destroy reducing agents and to equilibrate the hexone with acid, equal volumes of hexone and 0.01 M KBrO_3 -1 M HNO_3 were shaken together and the aqueous phase was discarded. The hexone was stored over 0.01 M KBrO_3 and 1 M HNO_3 .

To determine Pu(V) and/or Pu(VI) by the $\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene method the supernatant from the PrF_3 precipitation step outlined above was made 0.1 M in $\text{NH}_2\text{OH}\cdot\text{HCl}$ by adding 600 μl of 1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ to reduce any Pu(V) and/or Pu(VI) in the solution. Praeseodymium nitrate solution was then added to total 2.0 mg of praeseodymium in the sample. After 5 min the precipitate was centrifuged out and washed in 1 M HNO_3 -1 M HF. The precipitate was dissolved in 1 M HNO_3 saturated with boric acid and five drops of 3 M NaNO_3 were added followed by letting the sample sit for 10 min. The sample was then taken through the TTA-xylene method.

To extract all four oxidation states at one time, a 1.0-ml sample aliquot was made 0.1 M in $\text{NH}_2\text{OH}\cdot\text{HCl}$ followed by the PrF_3 -precipitation procedure and TTA-xylene procedure. The $\text{Na}_2\text{Cr}_2\text{O}_7$ was omitted from the PrF_3 procedure in this case.

The ^{239}Pu deposited on the planchets was determined by α -spectrometry using a Canberra model 2201 proportional counter and a Canberra multichannel analyzer with a Harshaw surface barrier detector. In addition the ^{241}Am content of some of the soil extracts was determined by γ -spectrometry using a NaI(Tl) detector.

Chromium Experiments

Soil Sample Collection and Characterization

Soil samples were collected in September 1979 from field plots established on Hagerstown silt loam (Typic Hapludalf; fine, mixed, mesic) amended with sewage sludge in 1974 and 1975. The sludge contained 660 μg of Cr per gram of dry sludge as determined by digestion in HNO_3 - HClO_4 and atomic absorption spectrophotometry (AAS) analysis (Doty *et al.*, 1977), and was applied at rates resulting in total sludge applications of 0, 11.2, 22.4, and 44.8 MT (metric tons)/ha for the two years combined.

This field experiment was a randomized complete block design with four replications. Details concerning other aspects of the experiment can be found in Baker et al. (1977, 1979).

For the purposes of this thesis two sets of soil samples were collected from these plots. One set was collected from the first block of sludge treatments, only. These samples were collected from the top 20 cm of soil, sieved through a 2-mm plastic screen while still moist, and stored in plastic bags while still moist. The other set was collected from all four blocks of sludge treatments. These samples were also collected from the top 20 cm of soil, but were air-dried before sieving and stored air-dried.

A soil sample was also collected in September 1979 from a field plot established on Murrill silt loam (Typic Hapludult; fine-loamy, mixed, mesic) that was amended with sewage sludge in 1972 through 1979 at the rate of 11.2 MT/ha/year. A soil sample was also collected from a Chrome gravelly silty clay loam (Typic Hapludalf; fine, mixed, mesic) in Chester County, Pennsylvania. This soil developed over serpentine parent material known to be high in chromium (Pearre and Heyl, 1960). The sample was collected from an area of known chromite mineralization with several old chromium prospects and mines nearby. These two samples were collected from the top 20 cm of soil and were sieved and stored while still moist.

The water content of the collected soil samples was determined gravimetrically by oven drying at 105°C (Gardner, 1965). Organic matter content was determined by dichromate-sulfuric acid oxidation (Allison, 1965). The pH of the soil samples was determined by adding 5 ml of deionized water to 5 g (dry weight basis) of moist soil, mixing the

suspension, waiting 30 min with periodic mixing, and measuring the pH with a combination pH-reference electrode calibrated with pH 4 and 7 buffers.

Preparation of MnO₂ Minerals

The minerals δ -MnO₂, Mn(II)-manganite, and α -MnO₂ were prepared according to methods described by Healy et al. (1965). The preparation of δ -MnO₂ and Mn(II)-manganite can be described by the reaction:

To prepare δ -MnO₂ a 0.2 M KMnO₄ solution was heated to boiling and conc. HCl was added to bring the solution to 0.6 M in HCl. This assured an excess of KMnO₄ which was needed to maintain the oxidizing conditions necessary to yield δ -MnO₂. The solution was allowed to sit overnight to complete the reaction and to cool. The suspension was filtered through a fritted glass funnel under suction and washed with deionized water and then with 0.05 M HClO₄ to remove unreacted KMnO₄ and HCl as well as KCl. The collected δ -MnO₂ was dried overnight at 60°C and ground with an agate mortar and pestle and stored until use. To prepare Mn(II)-manganite the same procedure was used except an excess of HCl was maintained in order to assure the reducing conditions needed to produce Mn(II)-manganite. To prepare α -MnO₂ some of the Mn(II)-manganite product was suspended in diluted KCl solution, heated to boiling, and refluxed for 10 hr. This converted the Mn(II)-manganite to α -MnO₂. The α -MnO₂ was washed and dried as described above. Reagent grade β -MnO₂ from Fisher Scientific Co. was washed with 0.05 M HClO₄ to remove impurities and dried overnight at 60°C. These minerals were characterized by Healy et al. (1965) and some of the properties are listed in Table 5.

Table 5. Properties of MnO_2 minerals.

Mineral	Chemical Properties	Structural Properties
$\delta\text{-MnO}_2$ (birnessite)	$\text{O:Mn} > 1.9$ $\text{ZPC} \sim 1.5$	Forms layered structure, crystals 2 to 3 atomic layers thick. BET surface area $300 \text{ m}^2/\text{g}$.
Mn(II)-manganite (manganous manganite) (10A manganite)	$\text{O:Mn} = 1.7\text{--}1.9$ $3\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ $\text{ZPC} \sim 1.8$	Double-layer structure. Main layers contain Mn^{4+} in sixfold coordination with O^{2-} and are separated by a 10A space containing Mn^{2+} coordinated with O^{2-} , OH^- , and H_2O . BET surface area = $30\text{--}50 \text{ m}^2/\text{g}$.
$\alpha\text{-MnO}_2$ (cryptomelane)	$\text{KMn}_8\text{O}_{16}$ Shows cation exchange properties $\text{ZPC} \sim 4.5$	Three-dimensional framework structure. Structure held open by K^+ .
$\beta\text{-MnO}_2$ (pyrolusite)	MnO_2 $\text{ZPC} \sim 7.3$	Tetragonal rutile structure.

To determine the Mn content of the four MnO_2 minerals, a weighed amount of each mineral was dissolved in a few milliliters of a dilute $\text{NH}_2\text{OH}\cdot\text{HCl}-\text{HNO}_3$ solution and diluted to 100 ml in a volumetric flask. The manganese concentration in each flask was measured by AAS and the % Mn content of each mineral calculated. The Mn content of the four minerals was found to be 45.5, 46.0, 52.0, and 60.8% for $\delta\text{-MnO}_2$, Mn(II)-manganite, $\alpha\text{-MnO}_2$, and $\beta\text{-MnO}_2$, respectively. This data was used to calculate the ratio of Mn(IV) to Cr(III) for the kinetic experiments described in a later section. To determine the capacity of $\delta\text{-MnO}_2$ to oxidize Cr(III), 20 mg of $\delta\text{-MnO}_2$ were added to 1000 ml of a 1000 $\mu\text{g/ml}$ Cr(III) solution. The solution was mixed, heated to 50°C for two hours, cooled to room temperature, and analyzed for Mn(II) by AAS and Cr(VI) by the s-diphenylcarbazide method developed by Bartlett and James (1979). The Mn(II) concentration was found to be 171 $\mu\text{moles/l}$. If all of this was assumed to be Mn(IV) initially, then according to the reaction stoichiometry 114 $\mu\text{moles/l}$ of Cr(VI) should be produced. Since 122 $\mu\text{moles/l}$ of Cr(VI) were actually found, one can conclude that essentially all of the $\delta\text{-MnO}_2$ is capable of oxidizing Cr(III).

Extraction of Fulvic Acid from

Leather Dust and Soil

Fulvic acid was extracted from leather dust and soil and partially purified according to the following procedure adapted from Stevenson (1965). Four 250-ml plastic centrifuge bottles were each filled with 200 ml of 0.5 M NaOH. Nitrogen was bubbled through the NaOH solution in each bottle to remove dissolved oxygen. A 40-g sample of Murrill silt loam was added to each of two of the four bottles while a 5-g sample of leather dust containing 2.6% Cr was added to each of the other two

bottles. The bottles were shaken for 18 hours at 120 osc/min and centrifuged for 20 min at 12,000 g. The supernatants were decanted into four new 250-ml plastic centrifuge bottles and the residues discarded. The supernatants were acidified to pH 1 using 6 M HCl and allowed to stand 1 hr. Following centrifugation for 20 min at 12,000 g the supernatants were decanted into four new centrifuge bottles and the residues discarded. The supernatants were adjusted to pH 7 using 5 M NaOH and allowed to stand 1 hr. Following centrifugation for 20 min at 12,000 g the supernatants were decanted and stored and the residues discarded.

The fulvic acid content of the purified NaOH extracts was determined gravimetrically by drying and combustion. A measured volume of each extract was added to an evaporating dish previously heated to 550°C and weighed. The dishes were heated in an oven at 105°C overnight, cooled in a dessicator, reweighed, heated in a muffle oven at 550°C for 20 min, cooled in a dessicator, and reweighed. The fulvic acid content was calculated as the weight of organic matter lost on combustion per volume of solution. The concentration of soil fulvic acid was found to be 944 mg/l while the concentration of leather dust fulvic acid was found to be 12.4 g/l.

Chemical Fractionation of Soil Cr and Mn

The collected soil samples were extracted with 0.01 M KH_2PO_4 to detect any Cr(VI) present in these soils using a modification of the method developed by Bartlett and James (1979). Duplicate 5-g samples (dry weight basis) of each moist soil were added to 50-ml plastic centrifuge tubes. Twenty ml of 0.01 M KH_2PO_4 were added to each sample, followed by mixing on a vortex mixer, shaking for 15 min at 240 osc/min,

centrifuging for 10 min at 630 g, filtering through 0.2 μ m membrane filters, and determining Cr(VI) in the extracts.

Chromium and Mn extractable with NaOH were determined on Hagerstown silt loam amended with 44 MT/ha sludge, Murrill silt loam, and the sludge used in the field experiments, using a modification of the Stevenson (1965) method. Duplicate 10-g samples (dry weight basis) of each moist soil were added to 100-ml plastic centrifuge tubes. Fifty ml of 0.5 M NaOH were added to each sample and the tubes were shaken for 12 hours at 120 osc/min. The samples were centrifuged for 10 min at 630 g and the supernatants were decanted into Erlenmeyer flasks. An additional 50 ml of 0.5 M NaOH were added to each sample followed by shaking for 1 hr, centrifuging, and decanting the supernatants into the Erlenmeyer flasks. Fifty ml of 1 M NaCl were added to each sample followed by mixing on a vortex mixer, centrifuging, and adding the supernatants to the Erlenmeyer flasks. The extracts were analyzed for total Cr and Mn by AAS.

Sodium pyrophosphate extractable Cr and Mn were also determined on the soil samples. Duplicate 5-g samples (dry weight basis) of each moist soil were shaken for 15 min at 240 osc/min with 25.0 ml of 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$. Following centrifugation of the samples for 10 min at 630 g the supernatants were acidified to pH 1 using 6 M HCl and recentrifuged. The extractions were repeated four more times on the Hagerstown and Murrill soils and twice more on the Chrome soil and the extracts were analyzed for total Cr and Mn.

All of the moist soil samples and the air-dried samples from the Hagerstown field plots were analyzed for pH 9.5, 5.25% NaOCl extractable Cr and Mn using a modification of the method from Anderson (1963).

Duplicate 5-g samples (dry weight basis) of each soil were added to 100-ml plastic centrifuge tubes and 10 ml of 5.25% NaOCl adjusted to pH 9.5 using 6 M HCl shortly before use were added to each sample. After mixing on a vortex mixer the tubes were placed in a boiling water bath for 15 min, centrifuged for 10 min at 630 g, and the supernatants decanted into 50-ml volumetric flasks. The extractions were repeated twice more adding the supernatants each time to the volumetric flasks. The flasks were diluted to volume with deionized water, mixed, and the solutions analyzed for total Cr and Mn.

Chromium and Mn extractable with H_2O_2 were also determined by a modification of the method of Taylor and McKenzie (1966). Duplicate 5-g samples (dry weight basis) of each moist soil were added to 100-ml plastic centrifuge tubes and 25.0 ml of 10% H_2O_2 adjusted to pH 3 with HNO_3 were added to each tube. After mixing on a vortex mixer the samples were allowed to sit overnight, centrifuged for 10 min at 630 g, and the supernatants analyzed for Cr and Mn. The extraction steps were repeated twice more. Another H_2O_2 extraction method was also used on the moist Hagerstown and Murrill samples. Duplicate 5-g samples (dry weight basis) of each soil were added to 500-ml Erlenmeyer flasks and 250 ml of 10% H_2O_2 adjusted to pH 2 with HNO_3 were added to each flask. After mixing and sitting overnight the suspensions were filtered and the filtrates were analyzed for total Cr and Mn.

Hydroxylamine hydrochloride extractable Cr and Mn were determined using modifications of the Chao (1972) method. Duplicate 5-g samples (dry weight basis) of each moist soil were added to 125-ml Erlenmeyer flasks and 25.0 ml of 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ adjusted to pH 2 using HCl were added. After mixing and sitting overnight the suspensions were filtered

and the filtrates analyzed for total Cr and Mn. Another $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction procedure was also used on the moist Hagerstown and Murrill samples. The procedure was identical to the previously described extraction using pH 2, 10% H_2O_2 except that pH 2, 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ was used in place of the H_2O_2 .

The moist soil samples were also analyzed for total Cr and Mn using the $\text{HF-HNO}_3\text{-H}_2\text{SO}_4\text{-HClO}_4$ digestion method described by Fiskell (1965) followed by AAS analysis. Teflon tubes and a block digester were used. A different method was used to determine total Cr in the air-dried samples collected from all four sets of field plots. This method used H_2O_2 , HNO_3 , and HCl and although it would not extract the total natural Cr content of the soil, it was deemed suitable for extracting Cr added with the sludge. A 1.000-g sample of each soil was added to a teflon tube and 2 ml of conc. HNO_3 and 2 ml of 10% H_2O_2 were then added. The tubes were heated in a block digester to dryness. The addition of HNO_3 and H_2O_2 and heating to dryness was repeated. Five ml of 6 M HCl were added, the tubes were warmed, and then the suspensions filtered into 100-ml volumetric flasks. The tubes and filter paper were rinsed with 0.1 M HCl , the rinsings added to the flasks, and the flasks filled to volume with deionized water. The flask contents were analyzed for Cr and Mn.

Fate of Cr from Sludge and Leather Dust Applied to Soil in Laboratory Incubation Experiments

Laboratory incubation experiments were run to determine if Cr in organic matter (leather dust or sludge) could be oxidized when mixed with soil. In one experiment duplicate 500-g samples (dry weight basis) of moist Hagerstown soil amended with 44.8 MT/ha sludge were each

amended with 50 g of leather dust with a 2.6% Cr content. The leather dust was mixed into each soil after which deionized water was added until a 50% water content (dry weight basis) was obtained in each sample. The samples were kept sealed in plastic bags for seven months at room temperature. The bags were able to prevent moisture loss, but gases (CO_2 and O_2) were able to diffuse in and out of the bags. At the end of this incubation time samples from each bag were analyzed for pH 9.5, 5.25% NaOCl extractable Cr. Periodically, throughout the incubation period samples were also analyzed for 0.01 M KH_2PO_4 extractable Cr(VI).

In another experiment duplicate 500-g samples (dry weight basis) of moist Hagerstown soil amended with 22.4 MT/ha sludge were each amended with 10 g of leather dust. The leather dust was mixed into each sample, no deionized water was added, and the samples were kept sealed in plastic bags for three months at room temperature. At the end of this time period samples from each bag were analyzed for pH 9.5, 5.25% extractable Cr and 0.01 M KH_2PO_4 extractable Cr(VI). This experiment was also done using 10 g of sludge (660 $\mu\text{g/g}$ Cr) per 500 g of soil.

Effect of Drying, Storage Time, and Organic Matter

Removal on the Ability of Soil to Oxidize Cr

To evaluate the Cr oxidizing ability of the collected soils and to study the effects of drying, storage time, and organic matter removal on the oxidizing ability, the following experiments were performed. A portion of each of the moist Hagerstown silt loam and Murrill silt loam was allowed to air-dry in open petri dishes while another fraction of each soil was oven-dried overnight at 105°C . A 5.0-g sample (dry weight basis) of each moist, air-dried, and oven-dried soil was subjected to a modification of the Cr oxidation test of Bartlett and James (1979).

The test consisted of adding 1.0 ml of 1000 $\mu\text{g/ml}$ Cr(III) to the sample in a 50-ml plastic centrifuge tube, mixing on a vortex mixer, adding 20.0 ml of 0.01 M KH_2PO_4 , mixing on a vortex mixer followed by shaking for 15 min at 240 osc/min, centrifuging for 10 min at 630 g, filtering through a 0.2 μm membrane filter, and analyzing the filtrate for Cr(VI) by the s-diphenylcarbazide method. To determine Mn reduced during the Cr oxidation test, each residual soil sample after the KH_2PO_4 extraction was shaken for 15 min at 240 osc/min with 20.0 ml of 0.5 M CaCl_2 , centrifuged, and the supernatants were analyzed for Mn(II) by AAS. To determine the original Mn(II) level in the soils plus the effect of drying on Mn reduction, a 5.0-g sample (dry weight basis) of each moist, air-dried, and oven-dried soil was extracted with 0.5 M CaCl_2 as just described. To determine the effect of time of air-drying and whether moist soil lost Cr oxidizing power over time, samples of air-dried and moist soils were periodically tested using the Cr oxidation test over the course of a year. To determine the effect of water removal by washing with organic solvents, 1.0 ml of 1000 $\mu\text{g/ml}$ Cr(III) was added to each of six 5.0-g samples (dry weight basis) of moist Murrill silt loam in 50-ml centrifuge tubes. Each sample was subjected to a different treatment. To the first sample, nothing was done, the second sample was dried for several hours at 105°C , the third sample was washed three times with ~ 20 ml of isopropyl alcohol, the fourth sample was washed with alcohol followed by oven-drying, the fifth sample was washed three times with ~ 20 ml of acetone, and the sixth sample was acetone washed and then oven-dried. Each sample was then extracted with 20.0 ml of 0.01 M KH_2PO_4 as with the Cr oxidation test and the extracts were analyzed for Cr(VI). To determine the effect of organic matter removal

on Cr oxidizing ability, duplicate 5.0-g samples (dry weight basis) of moist Hagerstown silt loam amended with 44.8 MT/ha sludge were washed three times with 2% Na_2CO_3 at pH 9.5, treated three times with pH 9.5, 5.25% NaOCl , and washed five times with pH 9.5, 2% Na_2CO_3 followed by the Cr oxidation test.

Cr Oxidizing Capacity of Soil

A 16-g sample (dry weight basis) of moist Hagerstown silt loam amended with 44.8 MT/ha sludge was added to a 50-ml plastic centrifuge tube. Twenty ml of 1000 $\mu\text{g/ml}$ Cr(III) solution were added followed by mixing and shaking for 15 min at 240 osc/min. After centrifuging for 10 min at 630 g the supernatant was filtered through a 0.2 μm membrane filter and analyzed for total Cr, Cr(VI), and Mn(II). This extraction procedure was repeated five more times in order to exhaust the soil's capacity to oxidize Cr.

Effect of Cr Concentration on Cr Oxidation by Soil

A 20-g sample (dry weight basis) of moist Hagerstown silt loam amended with 44.8 MT/ha sludge was added to each of eight 50-ml plastic centrifuge tubes. A set of eight Cr(III) solutions each with a different Cr(III) concentration (0, 1, 5, 10, 50, 100, 500, and 1000 $\mu\text{g/ml}$ Cr(III)) was prepared and 20.0 ml of each solution were added to the tubes, one Cr(III) level per soil sample. The samples were shaken for 15 min at 240 osc/min, centrifuged for 10 min at 630 g, and filtered through 0.2 μm membrane filters. The filtrates were analyzed for total Cr and Cr(VI). Following washing each sample three times with acetone, each sample was extracted with 20.0 ml of 0.01 M KH_2PO_4 for 15 min at

240 osc/min shaking speed. After centrifugation and filtration the extracts were analyzed for Cr(VI). The experiment was replicated.

Extractability of Cr(VI) with KH_2PO_4

Several experiments were conducted to study the suitability of using KH_2PO_4 as an extractant for Cr(VI) in soil. In the first, the extraction of soil Cr(VI) using varying concentrations of KH_2PO_4 was studied. A 20-g sample (dry weight basis) of moist Hagerstown silt loam amended with 44.8 MT/ha sludge was added to each of three 50-ml plastic centrifuge tubes. A 20.0 ml aliquot of 1000 $\mu\text{g/ml}$ Cr(III) solution was added to each sample followed by shaking for 15 min at 240 osc/min, centrifuging for 10 min at 630 g, and discarding the supernatants. To the first tube was added 20.0 ml of 0.1 M KH_2PO_4 , to the second, 20.0 ml of 0.01 M KH_2PO_4 , and to the third, 20.0 ml of 0.001 M KH_2PO_4 . Following shaking for 15 min at 240 osc/min, centrifuging for 10 min at 630 g, and filtering through 0.2 μm membrane filters, the extracts were analyzed for Cr(VI).

The successive extraction of soil Cr(VI) with 0.01 M KH_2PO_4 was also studied. In this experiment 20 g (dry weight basis) of moist Hagerstown silt loam amended with 44.8 MT/ha sludge was treated with 20.0 ml of 1000 $\mu\text{g/ml}$ Cr(III) solution as before. The sample was then successively extracted with 20.0 ml portions of 0.01 M KH_2PO_4 until negligible Cr(VI) level was found in the extract. The experiment was repeated using 10 and 100 $\mu\text{g/ml}$ Cr(III) solutions.

A series of experiments was also run to examine the effect of soil/solution ratio on Cr(VI) extraction by KH_2PO_4 . The conditions of these experiments are summarized in Table 6. In the first experiment the soil/solution ratio was changed by varying the amount of soil and

Table 6. Conditions for experiments on the effect of soil/solution ratio on extraction of soil Cr(VI) by KH_2PO_4 .

Soil Amount	Volume of 1000 $\mu\text{g/ml}$ Cr^{3+}	Volume of 0.01 M KH_2PO_4 Extracting Solution	Soil/Solution Ratio
g	-----ml-----		g/ml
<u>Experiment 1</u>			
5	5.0	20.0	1:4
10	10.0	20.0	1:2
15	15.0	20.0	1:1.33
20	20.0	20.0	1:1
<u>Experiment 2</u>			
5	5.0	5.0	1:1
5	5.0	10.0	1:2
5	5.0	15.0	1:3
5	5.0	20.0	1:4
<u>Experiment 3</u>			
5	5.0	5.0	1:1
10	10.0	10.0	1:1
15	15.0	15.0	1:1
20	20.0	20.0	1:1

holding the volume of KH_2PO_4 solution constant. In the second experiment the amount of soil was held constant while the solution volume was varied. In the third experiment both the soil amount and solution volume were varied, but the ratio was held constant. The extraction procedures were the same as already outlined. All of the experiments described above were replicated.

Oxidation of Cr from Different Sources at Selected Concentrations in Soil with Time

Various incubation experiments were done in order to study the oxidation of Cr from different sources at selected concentrations with time. In the first experiment four 100-g samples (dry weight basis) of moist Murrill silt loam in plastic bags were treated with 0, 1, 5, and 10 ml of a 1000 $\mu\text{g/ml}$ Cr(III) solution, one Cr treatment per sample, to yield levels of 0, 10, 50, and 100 $\mu\text{g/g}$ of soil Cr. Deionized water was added to each sample to bring the soils to a 50% water content by weight. The soils were mixed in the bags to insure even distribution of the Cr treatments. At periodic intervals samples of wet soil from each bag were extracted by an immiscible displacement-centrifugation method (Mubarak and Olsen, 1976). The extraction consisted of adding 15 g of wet soil from each bag to 50-ml centrifuge tubes, adding 10 ml of chloroform to each tube, and centrifuging for 1 hr at 48,300 g. The aqueous phases were withdrawn and analyzed for total Cr and Cr(VI). At periodic intervals 6-g samples of wet soil from each bag were extracted with 20.0 ml of 0.01 M KH_2PO_4 for 30 min at 180 osc/min, centrifuged for 10 min at 630 g, and filtered through 0.2 μm membrane filters. The filtrates were analyzed for Cr(VI).

In another experiment 300 g (dry weight basis) of moist Murrill silt loam were amended with 3.0 ml of a 1000 $\mu\text{g/ml}$ Cr^{3+} solution to provide soil Cr level of 10 $\mu\text{g/g}$. The soil was brought to a 100% water content with deionized water and mixed. At periodic intervals samples of the slurry were filtered through 0.2 μm membrane filters and the filtrates were analyzed for Cr(VI) and pH.

In another experiment 500 g (wet weight basis) of moist Hagerstown silt loam amended with 44.8 MT/ha sludge were amended with 50 g of Cr_2O_3 and 100 ml of deionized water. The soil was mixed and at periodic intervals 5-g samples (dry weight basis) were extracted with 0.01 M KH_2PO_4 as described above and the extracts were analyzed for Cr(VI).

In the final incubation experiment two 500-g samples (dry weight basis) of moist Hagerstown silt loam were amended with 5 and 50 ml of 1000 $\mu\text{g/ml}$ Cr(III) solution to provide soil Cr levels of 10 and 100 $\mu\text{g/g}$, respectively. Two additional 500-g samples were amended with 5 and 50 ml of a 1000 $\mu\text{g/ml}$ Cr(III) as $\text{Cr}(\text{OH})_3$ suspension to provide soil Cr levels of 10 and 100 $\mu\text{g/g}$. The $\text{Cr}(\text{OH})_3$ suspension was prepared by adjusting the pH of 1000 $\mu\text{g/ml}$ Cr(III) solution to 10 with NaOH. Freshly precipitated $\text{Cr}(\text{OH})_3$ was used. The samples were brought to a 50% water content by weight and mixed thoroughly. At periodic intervals the soil solution was extracted by the immiscible displacement-centrifugation method and analyzed for Cr(VI) and pH. Extractions with 0.01 M KH_2PO_4 were also run and Cr(VI) determined in the extracts.

Kinetics of Cr Oxidation by Moist

Hagerstown Silt Loam

A summary of the reaction conditions for experiments on the kinetics of Cr oxidation by moist Hagerstown silt loam is given in Table 7. The

Table 7. Summary of reaction conditions for experiments on the kinetics of Cr oxidation by moist Hagerstown silt loam.

Sample Amount	Solution Volume	Solution Composition	[Soil]	[Cr(III)] ₀	pH	Temp.
g	ml		g/l	μmole/l		°C
10	800	2.5 x 10 ⁻⁴ m KCl 10 x 10 ⁻⁴ m MgCl ₂ 50 x 10 ⁻⁴ m CaCl ₂	12.5	192	5.5	2
10	800	2.5 x 10 ⁻⁴ m KCl 10 x 10 ⁻⁴ m MgCl ₂ 50 x 10 ⁻⁴ m CaCl ₂	12.5	192	5.5	23
10	800	2.5 x 10 ⁻⁴ m KCl 10 x 10 ⁻⁴ m MgCl ₂ 50 x 10 ⁻⁴ m CaCl ₂	12.5	192	5.5	28
10	800	2.5 x 10 ⁻⁴ m KCl 10 x 10 ⁻⁴ m MgCl ₂ 50 x 10 ⁻⁴ m CaCl ₂	12.5	192	5.5	50
10	800	0.01 M CaCl ₂	12.5	192	5.5	27
10*	800	0.01 M CaCl ₂	12.5	192	5.5	27
10	800	2.5 x 10 ⁻⁴ m KCl 10 x 10 ⁻⁴ m MgCl ₂ 50 x 10 ⁻⁴ m CaCl ₂ 4 x 10 ⁻⁴ m DTPA	12.5	192	5.5	26

*Organic matter removed from soil using pH 9.5, 5.25% NaOCl.

experimental apparatus used in these experiments is shown in Figure 9. It included a gas diffuser for bubbling N_2 through the suspension to sweep dissolved CO_2 out, a port for the addition of Cr(III) solution, a syringe sampler, a stirrer, a combination pH-reference electrode for monitoring the suspension pH, and a delivery tube for 0.01 M NaOH to adjust the suspension pH. The pH electrode and NaOH delivery tube were connected to a Fisher auto-titrator set to hold a constant pH (pH stat).

A typical kinetic experiment was run as follows. A 10-g sample (dry weight basis) of soil was added to the reaction vessel. The vessel was filled with 792 ml of equilibrating solution (see Table 7 for solution compositions) and the experimental apparatus was assembled as shown in Figure 9. The assembled apparatus was placed in a constant temperature bath (see Table 7 for experimental temperatures), the stirrer was turned on, the N_2 flow was begun, and the auto-titrator was started to adjust the pH to the preset level (see Table 7 for experimental pH values). The suspension was allowed to equilibrate until thermal equilibrium was reached as measured by a thermometer and the pH was constant. At time zero 8.0 ml of 1000 $\mu\text{g/ml}$ Cr(III) solution was rapidly added. This resulted in a total volume of 800 ml, a soil concentration of 12.5 g/l, and an initial Cr(III) concentration of 10 $\mu\text{g/ml}$. At periodic intervals the suspension was sampled by means of the syringe sampler, filtered through 0.2 μm membrane filters, and the filtrates analyzed for total Cr by AAS and Cr(VI) by the s-diphenylcarbazide method. Typically, sampling took less than 5 to 10 sec while filtering took 15 to 25 sec per sample. Temperature control was generally $\pm 1^\circ\text{C}$. The pH and ml of NaOH added after the addition of Cr(III) were monitored on strip-chart recorders.

Figure 9. Experimental apparatus for studying the kinetics of Cr oxidation by moist Hagerstown silt loam and manganese oxide suspensions.

Kinetics of Cr Oxidation by MnO₂ Minerals

A summary of the reaction conditions for experiments on the kinetics of Cr oxidation by manganese oxide minerals is given in Table 8. The experimental set-up was identical to that used for the soil experiments. A typical kinetic run for experiments where MnO₂ was in excess consisted of the following procedure. The MnO₂ mineral was weighed into the reaction vessel and the equilibrating solution was added. The MnO₂ mineral concentrations and solution compositions used in the various experiments are listed in Table 8. The experimental apparatus was assembled and placed in a constant temperature bath (see Table 8 for experimental temperatures), the stirrer was turned on, the N₂ flow begun, and the auto-titrator was started to adjust the pH to the present level (see Table 8 for experimental pH values). The suspension was allowed to equilibrate until the temperature and pH were constant. At time zero a measured volume of 1000 µg/ml Cr(III) solution was rapidly added to achieve the desired initial Cr(III) concentration (see Table 8). At periodic intervals the suspension was sampled by means of the syringe sampler, filtered through 0.2 µm membrane filters, and the filtrates analyzed for total Cr by AAS and Cr(VI) by the s-diphenylcarbazide method. Typically, sampling took less than 5 to 10 sec and filtering took 15 to 25 sec. Temperature control was generally $\pm 1^{\circ}\text{C}$. The pH and ml of NaOH added after the addition of Cr(III) were monitored on strip-chart recorders. For experiments in which the pH stat was not used the NaOH delivery tube, pH electrode, N₂ gas diffuser, and auto-titrator were omitted from the experimental set-up. However, an initial pH adjustment of the suspension was performed before the Cr(III) was added. Perchloric acid and NaOH were used for pH adjustments. For

Table 8. Summary of reaction conditions for experiments on the kinetics of Cr oxidation by manganese oxide minerals.

MnO ₂ Mineral	MnO ₂ Amount	Solution Volume	Solution Composition	[MnO ₂]	[Cr(III)] ₀	Mn(IV)/Cr(III)	pH	Temp.
	mg	ml		mg/l	μmole/l			°C
δ-MnO ₂	200	800	10 ⁻³ M NaClO ₄	250	24.0	86	5.5	2
δ-MnO ₂	200	800	10 ⁻³ M NaClO ₄	250	24.0	86	5.5	28
δ-MnO ₂	200	800	10 ⁻³ M NaClO ₄	250	24.0	86	5.5	50
δ-MnO ₂	100	400	0.1 M HClO ₄	250	24.0	86	1.0**	28
δ-MnO ₂	500	500	0.1 M HClO ₄	1000	38.4	215	1.0**	2
δ-MnO ₂	500	500	0.1 M HClO ₄	1000	38.4	215	1.0**	24
δ-MnO ₂	500	500	0.1 M HClO ₄	1000	38.4	215	1.0**	48
δ-MnO ₂	100	400	10 ⁻³ M HClO ₄	250	24.0	86	3.0**	28
δ-MnO ₂	200	800	10 ⁻³ M NaClO ₄	250	24.0	86	7.5	28
δ-MnO ₂	200	800	10 ⁻³ M NaClO ₄	250	24.0	86	10**	26
δ-MnO ₂	200	800	0.1 M NaClO ₄	250	24.0	86	5.5	29
δ-MnO ₂	200	800	2.5 x 10 ⁻⁴ m KCl 10 x 10 ⁻⁴ m MgCl ₂ 50 x 10 ⁻⁴ m CaCl ₂	250	24.0	86	5.5	26
δ-MnO ₂	200	800	2.5 x 10 ⁻⁴ m KCl 10 x 10 ⁻⁴ m MgCl ₂ 50 x 10 ⁻⁴ m CaCl ₂ 4 x 10 ⁻⁴ m DTPA	250	24.0	86	5.5	26

Table 8 (Continued).

MnO ₂ Mineral	MnO ₂ Amount	Solution Volume	Solution Composition	[MnO ₂]	[Cr(III)] ₀	Mn(IV)/Cr(III)	pH	Temp.
	mg	ml		mg/l	μmole/l			°C
δ-MnO ₂	200	800	2.5 x 10 ⁻⁴ m KCl 10 x 10 ⁻⁴ m MgCl ₂ 50 x 10 ⁻⁴ m CaCl ₂ 5 μg/ml Mn, 3 μg/ml Fe, 1 μg/ml Al and Zn, 0.5 μg/ml Cu, 0.1 μg/ml Ni, Cd, and Ca	250	24.0	86	5.5	23
δ-MnO ₂	200	800	1000 μg/ml Fe	250	24.0	86	5.5	29
δ-MnO ₂	20	500	10 ⁻³ M NaClO ₄	40*	19.2	17.2	~7**	28
δ-MnO ₂	10	500	10 ⁻³ M NaClO ₄	20*	19.2	8.6	~7**	28
δ-MnO ₂	5	500	10 ⁻³ M NaClO ₄	10*	19.2	4.3	~7**	28
δ-MnO ₂	2.8	500	10 ⁻³ M NaClO ₄	5.6*	19.2	2.4	~7**	28
δ-MnO ₂	10	500	1000 μg/ml Cr(III)	20*	19,230***	0.0086	2.6**	28
δ-MnO ₂	1	500	1000 μg/ml Cr(III)	2	19,230***	0.00086	1.0**	25
δ-MnO ₂	1	500	1000 μg/ml Cr(III)	2	19,230***	0.00086	1.0**	48
Mn(II)- manganite	200	800	10 ⁻³ M NaClO ₄	250	24.0	87	5.5	28
Mn(II)- manganite	10	500	10 ⁻³ M NaClO ₄	20*	19.2	8.7	~7**	28
α-MnO ₂	200	800	10 ⁻³ M NaClO ₄	250	24.0	98	5.5	27

Table 8 (Continued).

MnO ₂ Mineral	MnO ₂ Amount	Solution Volume	Solution Composition	[MnO ₂]	[Cr(III)] ₀	Mn(IV)/Cr(III)	pH	Temp.
	mg	ml		mg/l	μmole/l			°C
α-MnO ₂	200	800	2.5 x 10 ⁻⁴ m KCl 10 x 10 ⁻⁴ m MgCl ₂ 50 x 10 ⁻⁴ m CaCl ₂ 5 μg/ml Mn, 3 μg/ml Fe, 1 μg/ml Al and Zn, 0.5 μg/ml Cu, 0.1 μg/ml Ni, Cd, and Co	250	24.0	98	5.5	29
β-MnO ₂	200	800	10 ⁻³ M NaClO ₄	250	24.0	115	5.5	30
β-MnO ₂	1000	800	0.1 M HClO ₄	1250	481	29	1.0**	25
β-MnO ₂	1000	800	10 ⁻³ M NaClO ₄	1250	601	23	8.0	26

*MnO₂ hydrosonically dispersed

**pH stat not used

***Cr(III) in excess

experiments in which Cr(III) was in excess, the pH stat was not used and a typical kinetic run consisted of the following. The Cr(III) solution was measured into the reaction vessel and the pH adjusted (see Table 8 for Cr(III) concentrations and pH levels). The reaction vessel was placed in a constant temperature bath and allowed to reach thermal equilibrium (see Table 8 for temperatures). At time zero a measured volume of a 1000 mg/l δ -MnO₂ suspension in deionized water was added to achieve the desired initial MnO₂ concentration (see Table 8). At periodic intervals the suspension was sampled, filtered through 0.2 μ m membrane filters, and analyzed for Mn(II) by AAS.

Kinetics of Cr Oxidation by δ -MnO₂ in the Presence
of Fulvic Acid and the Kinetics of Cr and Mn
Reduction by Fulvic Acid

A summary of the reaction conditions for experiments on the kinetics of Cr oxidation by δ -MnO₂ in the presence of fulvic acid and the kinetics of Cr and Mn reduction by fulvic acid is given in Table 9. A typical kinetic run consisted of the following. Fulvic acid solution was added to the reaction vessel and the pH was adjusted to the desired level (see Table 9 for fulvic acid concentrations and pH levels). If the experiment called for δ -MnO₂ it was weighed out and added to the fulvic acid solution followed by mixing (see Table 9 for MnO₂ concentrations used). At time zero Cr(III) or Cr(VI) solution was added to give the desired initial Cr concentration (see Table 9). At periodic intervals the solution was sampled, filtered through 0.2 μ m membrane filters if necessary, and analyzed for Cr(VI) or Mn(II). For the experiment involving moist Hagerstown silt loam, deionized water was used in place of fulvic acid solution and no pH adjustment was done.

Table 9. Summary of reaction conditions for experiments on the kinetics of Cr oxidation in the presence of fulvic acid and the kinetics of Cr and Mn reduction by fulvic acid.

Soil or MnO ₂ Amount	Fulvic Acid Amount	Solution Volume	[Soil] or [MnO ₂]	[Fulvic Acid]	[Cr(VI)] ₀	[Cr(III)] ₀	pH	Temp.
		ml			-----μmole/l-----			°C
40 g moist Hagerstown silt loam	--	200	200 g/l	--	96.2	--	5.0	25
--	90 ml 944 mg/l soil fulvic acid	100	--	850 mg/l	96.2	--	1.0	25
--	90 ml 944 mg/l soil fulvic acid	100	--	850 mg/l	96.2	--	5.5	25
--	90 ml 944 mg/l soil fulvic acid	100	--	850 mg/l	96.2	--	5.5	50
--	90 ml 12.4 g/l leather dust fulvic acid	100	--	11.2 g/l	96.2	--	1.0	25
--	90 ml 12.4 g/l leather dust fulvic acid	100	--	11.2 g/l	96.2	--	5.5	25
--	90 ml 12.4 g/l leather dust fulvic acid	100	--	11.2 g/l	96.2	--	5.5	50

Table 9 (Continued).

Soil or MnO ₂ Amount	Fulvic Acid Amount	Solution Volume	[Soil] or [MnO ₂]	[Fulvic Acid]	[Cr(VI)] ₂	[Cr(III)] ₀	pH	Temp.
		ml			-----μmole/l-----			°C
100 mg δ-MnO ₂	200 ml 12.4 g/l leather dust fulvic acid	200	500 mg/l	12.4 g/l	--	96.2	7.0	25
100 mg δ-MnO ₂	200 ml 12.4 g/l leather dust fulvic acid	200	500 mg/l	12.4 g/l	--	--	5.5	25

RESULTS AND DISCUSSION

Plutonium Experiments

Chemical Fractionation of Soil Pu

The Pu extracted with $\text{Na}_4\text{P}_2\text{O}_7$, NaOCl , H_2O_2 , $\text{NH}_2\text{OH}\cdot\text{HCl}$, or DCB from the Area 11C soil samples is listed in Table 10 along with coefficients of variation for duplicate extractions and analysis. The wide range in variances is a reflection of the non-uniform distribution of Pu in NTS soils, the error in sampling from the storage bottle, and the difficulty in precisely replicating trace level analyses.

Bremner and Lees (1948) originally discovered that $\text{Na}_4\text{P}_2\text{O}_7$ was able to extract large amounts of soil organic matter although extractions were not 100% complete. Although NTS soils are expected to be relatively low in organic matter, $\text{Na}_4\text{P}_2\text{O}_7$ was included in this study to extract Pu associated with the small amount of organic matter present. However, pyrophosphate anions are excellent complexers of metal ions, so any Pu sorbed to the surfaces of any soil component, organic or inorganic, will be desorbed by the pyrophosphate if the binding strength of Pu to pyrophosphate is stronger than the binding strength of Pu to the soil. Thus, pyrophosphate may not be selective for organo-Pu complexes.

The results in Table 10 indicate that essentially all of the pyrophosphate extractable Pu was Pu(IV). This is not surprising, since any Pu associated with the extracted organic matter would be expected to be in a reduced state. Also, any Pu(V/VI) sorbed to mineral components could be reduced by the extracted organic matter during desorption and complexation by the pyrophosphate. The level of Pu extracted with pyrophosphate amounted to only a few percent of the total soil Pu (Table 4). The total soil Pu measurements listed in Table 4 are in terms of nCi/g.

Table 10. Plutonium extracted from a soil sample from Area 11C (NTS) using various extracting reagents.

Extractant	Valence	Valence Method	^{239}Pu	C.V.
			nCi/cm ³	
0.1 M $\text{Na}_4\text{P}_2\text{O}_7$	IV	PrF_3 -TTA-xylene [†]	34.3	42
"	all	$\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene	40.2	25
pH 9.5, 5.25% NaOCl	IV	TTA-xylene	0.08	53
"	V + VI	$\text{Ca}(\text{NO}_3)_2$ -hexone	69.2	5.7
"	all	$\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene	69.7	14
pH 7, 10% H_2O_2	IV	TTA-xylene	0.49	126
"	V + VI	$\text{Ca}(\text{NO}_3)_2$ -hexone	0.10	64
"	all	$\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene	0.14	71
pH 2, 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$	IV	TTA-xylene	0.23	--
"	III + IV	PrF_3 -TTA-xylene	0.35	--
DCB	IV	PrF_3 -TTA-xylene [†]	41.1	36
"	III + IV	PrF_3 -TTA-xylene	46.4	37

[†] NaNO_3 omitted from procedure

However, soil volume measurements were used in the fractionation experiments. To convert total soil Pu in nCi/g to nCi/cm³ the values are multiplied by 1.3 g/cm³, the average bulk density of soil. When this was done for the sample from Area 11C used in the fractionation experiments, an estimated value of 976 nCi/cm³ for total soil Pu was obtained. Thus, very little of the Pu in this sample was associated with organic matter or desorbable from mineral components with pyrophosphate.

Sodium hypochlorite was originally proposed by Anderson (1963) as a good oxidizing agent for destroying organic matter from soil and Lavkulich and Wiens (1970) showed that NaOCl was more efficient than H₂O₂ in destroying soil organic matter and less destructive of mineral constituents. Therefore, it was included in this study as an extractant for soil Pu associated with organic matter. Because NaOCl can oxidize Pu(III/IV) to Pu(V/VI), any Pu associated with the soil organic matter would likely be oxidized as the organic matter was destroyed and would more readily remain in solution. Surface sorbed Pu would likely be oxidized as well. The results in Table 10 indicate that NaOCl extractable Pu was only slightly greater than pyrophosphate extractable Pu. This tends to confirm the conclusion that only a very small fraction of the soil Pu was associated with the soil organic matter or was surface sorbed, and therefore potentially oxidizable. As expected virtually all of the Pu in the NaOCl extracts was oxidized.

Hydrogen peroxide was also tried as an extractant for Pu associated with soil organic matter or potentially oxidizable Pu sorbed to soil surfaces. At acid pH levels besides oxidizing organic matter, H₂O₂ will reduce manganese oxides (Taylor and McKenzie, 1966) and Pu(V/VI) (Cleveland, 1970). At neutral to alkaline pH levels, H₂O₂ will not

reduce manganese oxides and can oxidize Pu(III/IV) (Cleveland, 1970).

Thus, by using a neutral 10% H_2O_2 solution it was hoped that soil organic matter could be destroyed releasing any associated Pu which would then be oxidized and more readily remain in solution. However, the results in Table 10 show that H_2O_2 was not a good extracting agent for Pu. This probably reflects the inability of H_2O_2 to oxidize the Pu despite the predicted results, or because metal ions readily cause the catalytic decomposition of H_2O_2 at higher pH levels, the H_2O_2 may have been destroyed before it had a chance to be an effective oxidizing agent.

Chao (1972) originally showed that $\text{NH}_2\text{OH}\cdot\text{HCl}$ was an effective reducing agent for soil manganese oxides, thus releasing any associated metal ions, and that it did not readily reduce iron. Thus, one could distinguish between metal ions occluded by manganese or iron oxides. Any metal ions sorbed to the surface of iron oxides would likely be extracted, however, since the reagent is not perfectly selective. The results in Table 10 suggest that very little Pu was associated with the manganese oxide minerals in the soil sample. The $\text{NH}_2\text{OH}\cdot\text{HCl}$ was apparently unable to extract surface sorbed Pu that $\text{Na}_4\text{P}_2\text{O}_7$ and NaOCl were able to extract. It is not surprising to find little Pu associated with the manganese oxide minerals. At the high pH levels of the NTS soils and with sufficient carbonate anions present the formation of $\text{PuO}_2\text{CO}_3\text{OH}^-$ ions is likely. Since these ions are negatively charged, they will be repelled by the surfaces of the minerals which have a net negative charge at the pH levels typical of NTS soils. Existing as the cations PuO_2^+ or PuO_2^{2+} , oxidized Pu could be sorbed to manganese oxide minerals. This is the basis for using MnO_2 cartridges as scavengers for Pu in water (Wong et al., 1978).

The dithionite-citrate-bicarbonate procedure of Mehra and Jackson (1960) was used to remove free iron oxides in the soil sample from Area 11C. Sodium dithionite will reduce Fe(III) to Fe(II) which is then complexed by citrate ions and kept in solution. Buffering is provided by bicarbonate. Any metal ions associated with the iron oxides are also released and complexed by the citrate ions. This reagent is non-selective, however, in that manganese oxides are also reduced and the citrate and bicarbonate can extract organic matter. Thus, this reagent should extract Pu associated with organic matter, Pu sorbed to and occluded by iron and manganese oxides, and perhaps any non-crystalline Pu in the soil. The results in Table 10 demonstrate that DCB extracted practically the same amount of Pu as did the $\text{Na}_4\text{P}_2\text{O}_7$. Thus, there seems to have been no occluded Pu in this soil sample and all of the extractable Pu is probably surface sorbed. Virtually all of the DCB extractable Pu was Pu(IV) which is not surprising, since the reducing nature of the reagent would keep the Pu in a reduced state.

The reasonable agreement between the extractable Pu values for the $\text{Na}_4\text{P}_2\text{O}_7$, NaOCl, and DCB reagents indicates that the extractable Pu could be associated with organic matter, sorbed to mineral surfaces, or both since the nonselectivity of the reagents does not allow one to distinguish between the potential sources. However, it is clear that only a very small fraction of the total soil Pu content would be readily bioavailable which is in keeping with what is already known about Pu in these soils (White and Dunaway (eds.), 1975, 1976, 1977a, 1977b, and 1978). Tamura (1975) has shown that Pu in NTS soils is extremely stable to attack from HNO_3 and citrate and these latest results are in agreement with this observation. This unusual stability appears to be

kinetic rather than thermodynamic, however, since PuO_2 should be unstable in all the reagents used. Therefore, the time of extraction is an important experimental variable.

Extraction of Soil Pu(V/VI)

To see whether any Pu(V/VI) species existed in the soil sample from Area 11C, extractions were carried out using KH_2PO_4 , Na_2CO_3 , $\text{Na}_4\text{P}_2\text{O}_7$, and $\text{Na}_4\text{P}_2\text{O}_7 + \text{Na}_2\text{CO}_3$ and the results are listed in Table 11. Potassium phosphate was chosen as an extractant because Bartlett and James (1979) had already demonstrated that it was a good extractant for Cr(VI) species, so it was presumed that it would also be a good extractant for Pu(V/VI). It did extract a small amount of Pu(V/VI), but it also extracted more Pu(IV) than Pu(V/VI). There is a discrepancy between the results obtained with the TTA-xylene/ $\text{Ca}(\text{NO}_3)_2$ -hexone valence state separation methods and the results obtained with the PrF_3 -TTA-xylene/ $\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene methods. The TTA-xylene/ $\text{Ca}(\text{NO}_3)_2$ -hexone methods yielded less Pu(IV) and more Pu(V/VI) than did the methods using PrF_3 coprecipitation. The total amount of Pu extracted was the same for both methods. It appears that the TTA-xylene solution failed to completely extract the Pu(IV), so that it was then extracted by the $\text{Ca}(\text{NO}_3)_2$ -hexone solution and was counted as Pu(V/VI). By using a PrF_3 coprecipitation step all of the Pu(IV) that could be precipitated was removed from solution resulting in more reliable results. For this reason the PrF_3 -TTA-xylene/ $\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene methods are thought to be the more reliable methods.

Sodium carbonate was selected as an extractant because carbonate solutions are excellent solvents for uranium (U) minerals (Garrels and Christ, 1965), and it was assumed that Pu is enough like U to make it

Table 11. Plutonium extracted from a soil sample from Area 11C (NTS) using various extracting reagents.

Extractant	Valence Method	²³⁹ Pu			Total
		IV	IV	V + VI	
-----nCi/cm ³ -----					
0.01 M KH ₂ PO ₄	TTA-xylene/Ca(NO ₃) ₂ -hexone	0.139	--	0.143	0.282
"	PrF ₃ -TTA-xylene/NH ₂ OH·HCl- PrF ₃ -TTA-xylene	--	0.201	0.081	0.282
0.2 M Na ₂ CO ₃	TTA-xylene/Ca(NO ₃) ₂ -hexone	6.78	--	3.17	9.95
"	PrF ₃ -TTA-xylene/NH ₂ OH·HCl- PrF ₃ -TTA-xylene	--	7.27	1.25	8.52
0.1 M Na ₄ P ₂ O ₇	PrF ₃ -TTA-xylene/NH ₂ OH·HCl- PrF ₃ -TTA-xylene	--	38.5	3.32	41.8
0.05 M Na ₄ P ₂ O ₇ + 0.1 M Na ₂ CO ₃	PrF ₃ -TTA-xylene/NH ₂ OH·HCl- PrF ₃ -TTA-xylene	--	19.2	2.92	22.1

worthwhile to try a carbonate extracting solution. Also, carbonate is one of the constituents of the hydroxy-carbonate Pu species, $\text{PuO}_2\text{CO}_3\text{OH}^-$, and the high pH NTS soils contain appreciable levels of carbonate (Leavitt, 1970). Sodium carbonate was able to extract a significant amount of Pu with most of that being Pu(IV). However, an appreciable amount of Pu(V/VI) was also extracted. Again, it appears that the TTA-xylene method alone failed to extract all of the Pu(IV) which allowed the remainder to be extracted with the Pu(V/VI) by the $\text{Ca}(\text{NO}_3)_2$ -hexone. However, there is a discrepancy between the total Pu results obtained with the two sets of methods. It appears that the Pu(V/VI) results using the $\text{NH}_2\text{OH}\cdot\text{HCl}$ - PrF_3 -TTA-xylene methods may have been too low. A second PrF_3 -TTA-xylene extraction after the first yielded negligible amounts of Pu. After adding the $\text{NH}_2\text{OH}\cdot\text{HCl}$ reducing agent, Pu was extracted with the PrF_3 -TTA-xylene methods, so it seems that the remaining Pu was definitely Pu(V/VI), but for some reason extraction was incomplete in this case.

Another sodium pyrophosphate extraction was carried out followed by a complete Pu valence state separation scheme. Mostly Pu(IV) was found, but somewhat surprisingly, some Pu(V/VI) was also found. This was unexpected, since the organic matter extracted by the pyrophosphate was expected to keep the Pu in a reduced state. Perhaps the amount of organic matter extracted was too low and the rate of reduction too slow to assure all Pu(IV).

A mixed $\text{Na}_2\text{CO}_3 + \text{Na}_4\text{P}_2\text{O}_7$ extractant was also tried with each salt at half the concentration as the individual extractants. Interestingly, at half the concentration of $\text{Na}_4\text{P}_2\text{O}_7$, half as much Pu(IV) was extracted

by the mixed extractant as compared to $\text{Na}_4\text{P}_2\text{O}_7$ alone, but the amount of Pu(V/VI) extracted was about the same with the two extractants.

At this point it is necessary to discuss what was happening during the extractions. There are several possibilities. The extracted amounts of each valence state may represent the actual valence state distribution in the soil, but this does not seem likely, since there was ample opportunity for the extracted Pu to react with soil components and added reagents. All of the extractable Pu might have been Pu(V/VI) in the soil at one time, but most of it became reduced during storage of the soil or during extraction. Equally or more likely, the extractable Pu might have been all Pu(IV) initially and during the extraction the dissolved Pu(IV) reacted with manganese oxide minerals yielding Pu(V/VI). Also highly likely is that both oxidation and reduction were occurring during extraction. The extractions performed do not allow one to distinguish between the various possibilities unequivocally. Additional experiments would be necessary. One experiment was performed in which the effect of extraction time on Na_2CO_3 extraction of Pu was studied in order to test the possibility of oxidation during extraction and the results are listed in Table 12. There was a relatively greater increase in the amount of Pu(V/VI) extracted after a longer extraction time as compared to the increase in the amount of Pu(III/IV) extracted. These results indicate that additional extraction time was needed to oxidize the Pu because Pu(V/VI) should be weakly held by soil and readily extractable regardless of extraction time. Whatever the case, Pu(V/VI) either exists or can readily be produced in Area 11 soils.

Oxidation of Carbonate-Soluble Pu

To see whether oxidation of carbonate-soluble Pu could be enhanced, a sample of soil from Area 11C was incubated with a large excess of $\delta\text{-MnO}_2$ before extraction with Na_2CO_3 . The results of this experiment are shown in Table 13 along with the results from the Na_2CO_3 extraction alone for comparison. Virtually all of the extracted Pu was oxidized by the $\delta\text{-MnO}_2$ and the incubation with $\delta\text{-MnO}_2$ also increased the solubility of the Pu. It is not difficult to conceive of situations where carbonate-bearing water coming into contact with PuO_2 and MnO_2 would lead to increased mobility of Pu in a localized environment. In order to further stabilize the PuO_2 in the NTS soils, everything possible should be done to encourage revegetation of contaminated areas. This would not only stabilize the soils against erosion, but also add more organic matter to the soil to help keep the Pu in a reduced state. If any contaminated areas need to be filled in, materials containing ferromagnesian minerals should be used with a minimum of manganese oxide minerals present.

Extraction of Soil Am

Some results for the extraction of ^{241}Am are presented in Table 14. Sodium pyrophosphate and DCB were the two best extractants. Unlike the case with Pu, NaOCl was a poor extractant for Am indicating Am is not readily oxidized in soils which is in keeping with what is known about the redox reactions of this element. As with Pu, the amount of Am extracted was only a few percent of the total soil Am which was about 123 nCi/Cm^3 .

Table 12. Effect of extraction time on Na_2CO_3 extractable Pu in a soil sample from Area 11C (NTS).

Extractant	Extraction Time	²³⁹ Pu		
		III + IV*	V + VI**	Total
		-----nCi/cm ³ -----		
Na ₂ CO ₃	5 min	4.25	0.20	4.45
Na ₂ CO ₃	1 hr	7.27	1.25	8.52

* PrF_3 -TTA-xylene

** $\text{NH}_2\text{OH} \cdot \text{HCl}$ - PrF_3 -TTA-xylene

Table 13. Oxidation of Na_2CO_3 soluble Pu in a soil sample from Area 11C (NTS) using $\delta\text{-MnO}_2$.

Sample	Extractant	²³⁹ Pu		
		III + IV*	V + VI**	Total
-----nCi/cm ³ -----				
11C-2	Na ₂ CO ₃	7.27	1.25	8.52
11C-2 + δ-MnO ₂	Na ₂ CO ₃	0.22	14.5	14.7

* PrF_3 -TTA-xylene

** $\text{NH}_2\text{OH} \cdot \text{HCl}$ - PrF_3 -TTA-xylene

Chromium Experiments

Chemical Fractionation of Soil Cr and Mn

The water content, pH, and organic matter content of the Hagerstown and Murrill silt loam samples are shown in Table 15. The water content increased with increasing organic matter content reflecting the excellent water-holding capacity of organic matter. The high pH of the Murrill soil was a result of lime added to the sludge during sludge processing at the treatment plant.

Sodium hydroxide is a good extractant for soil organic matter (Stevenson, 1965). The humic and fulvic acid components of organic matter are soluble in NaOH. Any Cr associated with humic and fulvic acids would be extracted as well. Because of the high pH involved, the Cr would be expected to be insoluble, so in order to stay in solution it would have to be complexed by the organic acids. Results of NaOH extractions of the sludge used on the field plots and two of the soil samples are listed in Table 16. About 28% of the Cr in the sludge was soluble in strong base indicating a substantial amount of complexation of Cr by organic matter, since this is a highly insoluble element. Significant amounts of Cr in the two soil samples were soluble in NaOH, although the fraction of total Cr in the soil that was NaOH soluble was much less than the fraction of total Cr in sludge that was NaOH soluble. However, more Cr might have been associated with the organic matter than what the NaOH extracts indicated, since extraction of soil organic matter with NaOH is incomplete.

The results from the chemical fractionation of soil Cr are presented in Table 17. The order of extractants in terms of their ability to extract Cr was $\text{NaOCl} > \text{H}_2\text{O}_2 > \text{Na}_4\text{P}_2\text{O}_7 > \text{NH}_2\text{OH} \cdot \text{HCl}$. All the extractants

Table 14. Americium extracted from a soil sample from Area 11C (NTS) using various extracting reagents.

Extractant	^{241}Am nCi/cm ³
0.1 M $\text{Na}_4\text{P}_2\text{O}_7$	10.05
pH 9.5, 5.25% NaOCl	1.47
pH 2, 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$	0.74
DCB	7.68

Table 15. Water content (θ_{dw}), pH, and organic matter (O.M.) content of collected Hagerstown silt loam and Murrill silt loam samples.

Soil Series	Total Sludge Treatment MT/ha	θ_{dw} %	pH	O.M. %
Hagerstown	0	22.2	5.51	1.6
	11.2	24.1	5.52	2.1
	22.4	24.6	5.36	2.2
	44.8	25.4	5.98	2.2
Murrill	89.6	27.6	7.17	2.4

Table 16. Chromium in 0.5 M NaOH extractable organic matter from sludge and moist Hagerstown silt loam and Murrill silt loam amended with sludge.

Sample	0.5 M NaOH Extractable Cr	
	µg/g	% of Total Cr
Sludge	187.5	28.4
Hagerstown silt loam amended with 44.8 MT/ha sludge	2.8	3.4
Murrill silt loam amended with 89.6 MT/ha sludge	4.6	--

Table 17. Chemical fractionation of soil Cr.

Soil Series	Total Sludge Treatment	pH 10, 0.1 M Na ₄ P ₂ O ₇ **		pH 9.5, 5.25% NaOCl**		pH 2, 0.1 M NH ₂ OH·HCl*				pH 3, 10% H ₂ O ₂ **		pH 2, 10% H ₂ O ₂ *		Total
						Soil/Solution Ratio				Soil/Solution Ratio				
						1:5		1:50		1:5		1:50		
	MT/ha	µg/g	% of Total	µg/g	% of Total	µg/g	% of Total	µg/g	% of Total	µg/g	% of Total	µg/g	% of Total	µg/g
Hagerstown	0	--	—	3.6	5.5	0.10	0.2	0.75	1.2	0.40	0.6	0.50	0.8	65
	11.2	2.55	3.7	8.6	12.6	0.20	0.3	1.00	1.5	0.52	0.8	3.00	4.4	68
	22.4	4.70	6.1	13.7	17.8	0.25	0.3	1.00	1.3	0.62	0.8	5.00	6.5	77
	44.8	6.45	7.8	19.8	23.9	0.17	0.2	1.25	1.5	0.87	1.0	7.25	8.7	83
Murrill	89.6	6.45	—	18.0	--	0.12	--	1.50	--	2.30	--	8.75	--	--
Chrome	--	0.55	0.05	66	6.0	0.10	0.01	--	--	6.2	0.56	--	--	1100

*1 extraction

**3 extractions

reflected the increase in Cr in the Hagerstown and Murrill soils as a result of increasing sludge additions. The low amounts of Cr extracted by $\text{NH}_2\text{OH}\cdot\text{HCl}$ are not surprising, since this extractant reduces manganese oxides and any Cr coming into contact with manganese oxides would be oxidized and leached out of the soil. The Cr that was extracted by the $\text{NH}_2\text{OH}\cdot\text{HCl}$ was likely sorbed to other soil components and dissolved by the low pH of the extractant. The other extractants were able to extract or destroy soil organic matter and dissolve any associated Cr. Surface sorbed Cr was also undoubtedly extracted. It is unknown whether the small amount of Cr in the Chrome soil that was extracted with NaOCl or H_2O_2 actually represented organic matter Cr or inorganic Cr that was oxidized by the NaOCl or H_2O_2 . In any case the amount extracted was a small fraction of the total reflecting the known high degree of resistance to weathering of chromite ore in surface environments.

Potassium phosphate extractions were run on all the collected soil samples to see if any Cr(VI) was present in any of the soils indicating that Cr oxidation was taking place. However, no detectable Cr(VI) was found in any of the samples. This is not surprising for the Hagerstown and Murrill samples where the added Cr came from an organic source. The organic matter would be expected to keep the Cr in a reduced state. The Cr in the Chrome soil is inorganic, however, existing as the mineral chromite. At first it might be expected that this Cr would be oxidizable by manganese oxides. This would mean that chromite would be a soluble mineral and that Cr would be a geochemically mobile element. However, this conclusion contrasts sharply with reality. Chromite is very resistant to weathering and thus Cr is considered to be a geochemically immobile element. The answer may lie in the chemical formula of the

mineral, FeCr_2O_4 . Both iron and chromium are in a reduced state in this mineral and this might lend extra resistance to weathering to the mineral. The reduced Fe might help keep the Cr in a reduced state and thus the rate of oxidation is so slow as to be negligible.

The various extracts were also analyzed for Mn and these results are presented in Table 18. The most remarkable thing about this data is the very low $\text{NH}_2\text{OH}\cdot\text{HCl}$ and H_2O_2 extractable Mn in the Chrome soil as compared to the Hagerstown and Murrill soils. The lack of reducible Mn in the Chrome soil may also contribute to the high resistance to weathering of chromite ore, since little manganese oxide is present to oxidize the Cr. Perhaps the manganese oxide is depleted by the reducing action of the chromite.

As the results in Table 17 already indicated, NaOCl was able to reflect the increased Cr content of the soils as a result of sludge addition. This reagent shows promise in being able to distinguish between added Cr that is readily oxidizable and natural soil Cr which is not as readily oxidizable, since the amount of NaOCl extractable Cr found in the sample from the plot with no sludge was only about 5% of the total. But the question remains as to how well this extractant can account for all of the added Cr. This question is answered in Tables 19 and 20. In Table 19 the amount of Cr added as determined by total analysis and NaOCl extraction of the moist Hagerstown samples is presented. These results were obtained by subtracting the results for the plot not receiving any sludge from the results for the plots amended with sludge. The results indicate that the NaOCl extraction accounted for the added Cr fairly well. However, the moist samples were only grab samples from one set of plots. To obtain a more reliable sampling,

Table 18. Chemical fractionation of soil Mn.

Soil Series	Total Sludge Treatment	pH 10, 0.1 M Na ₄ P ₂ O ₇ **	pH 9.5, 5.25% NaOCl**	pH 2, 0.1 M NH ₂ OH-HCl*				pH 3, 10% H ₂ O ₂ *		pH 2, 10% H ₂ O ₂ *		Total		
				Soil/Solution Ratio				Soil/Solution Ratio		Soil/Solution Ratio				
				1:5		1:50		1:5		1:50				
	MT/ha	µg/g	% of Total	µg/g	% of Total	µg/g	% of Total	µg/g	% of Total	µg/g	% of Total	µg/g	% of Total	µg/g
Hagerstown	0	--	--	43	3.7	550	47	747	64	185	16	915	78	1170
	11.2	10.3	0.6	55	3.5	750	47	1150	72	242	15	1370	86	1590
	22.4	10.7	0.8	38	2.7	650	47	850	61	347	25	1020	73	1390
	44.8	9.6	0.6	37	2.5	775	53	1018	69	290	20	1282	87	1475
Murrill	89.6	7.4	--	30	--	675	--	940	--	237	--	1190	--	--
Chrome	--	--	--	--	--	80	--	--	--	52.5	--	--	--	--

*1 extraction

**3 extractions

Table 19. Total and NaOCl extractable Cr in moist Hagerstown silt loam amended with sludge.*

Total Sludge Treatment	Cr added as determined by:	
	Total Analysis**	NaOCl Extraction
MT/ha	-----µg/g-----	
11.2	3	5.0
22.4	12	10.1
44.8	18	16.2

*Samples collected from the first set of plots, only

**HF-HNO₃-H₂SO₄-HClO₄ digestion

Table 20. Total and NaOCl extractable Cr in air-dried Hagerstown silt loam amended with sludge.*

Total Sludge Treatment	Cr added as determined by:		
	Calculation***	Total Analysis**	NaOCl Extraction
MT/ha	-----µg/g-----		
11.2	6.5	6	5.5
22.4	13	11	11.2
44.8	26	23	23.9

*Samples collected from all four sets of plots

**HNO₃-H₂O₂-HCl digestion

***Calculated from Cr content of sludge and amount of sludge added to soil

composite samples from all the plots were analyzed for total and NaOCl extractable Cr and these data are listed in Table 20. By comparing the amount of Cr added as determined by calculation to the amount of Cr added as determined by total analysis, it can be seen that nearly all the added Cr is still in the top 20 cm of the soil profile four years after sludge addition ceased. In addition the NaOCl extraction fairly well accounted for this added Cr. Chromium not extracted by the NaOCl was probably occluded in iron oxides.

From the soil fractionation data we can conclude that Cr from organic sources is not oxidized in soils and remains associated with the soil organic matter where it is very stable to oxidation. This is supported by the facts that no Cr(VI) was found in the soil samples from the field plots amended with sludge contaminated with Cr, nearly all the added Cr remained in the top 20 cm of the soil profile as determined by the total analysis data, and NaOCl which oxidizes soil organic matter was able to extract most of the added Cr. It is also possible that some of the Cr became associated with the soil iron oxides, but the association was such as to keep the Cr in a reduced state. Perhaps organo-Cr complexes are sorbed to iron oxides. This possibility needs further study.

Fate of Cr from Sludge and Leather Dust Applied to Soil in Laboratory Incubation Experiments

The results of the analysis of the samples from the field plots are also supported by the results of laboratory incubation studies with leather dust and sludge. Leather dust is an excellent source of Cr in that it contains 2.6% Cr. Potassium phosphate extractions were run on samples from soil incubation studies using leather dust and sludge and

the results are presented in Table 21. The results, not surprisingly, are all negative. In the experiment using 50 g of leather dust a water content of 50% was established in the incubated soils. Due to the high affinity of organic matter for water and the large amount of leather dust used in the experiment, this high water content was needed to achieve good mixing between the soil and leather dust. At this high water content and with that much organic matter, anaerobic conditions were virtually assured. At low Eh levels oxidation of Cr is not possible, thus the results are not surprising. In the experiment using 10 g of sludge or leather dust, no additional water was added to the soil samples, and thus more oxidizing conditions were maintained. However, no oxidation of Cr was observed in this experiment either.

Although not susceptible to oxidation by MnO_2 , the Cr in the sludge and leather dust could be oxidized and extracted using NaOCl as the results in Table 22 show. Three extractions with NaOCl were insufficient to remove all of the added Cr. Five extractions were necessary to remove all of the added Cr. The greater than 100% recoveries are probably due to non-representative sampling as well as some extraction of natural Cr. The amount of Cr extracted appears more related to the amount of organic matter added to the soil than the amount of Cr added. When 10 g of leather dust or sludge were added, the same fraction of Cr (83%) was extracted after three NaOCl extractions even though much more Cr was added with the leather dust than with the sludge. When 50 g of leather dust were added the fraction of added Cr extracted after three extractions decreased to 63%. Thus, additional extractions are necessary to remove all the added Cr at high organic matter levels. It was observed that a pink color probably due to Mn(VII) was found in the NaOCl solution

Table 21. Potassium phosphate extractable Cr(VI) in moist Hagerstown silt loam samples treated with sludge and leather dust in laboratory incubation studies.

Original Sludge Amendment in the Field	Amendment in Laboratory	Time	0.01 M KH_2PO_4 Extractable Cr(VI)
MT/ha	g/500 g of soil	months	
22.4	10 g of sludge	3	none detected
	10 g of leather dust	3	none detected
44.8	50 g of leather dust	0.5	none detected
		1.5	none detected
		7	none detected

Table 22. Sodium hypochlorite extractable Cr in moist Hagerstown silt loam samples treated with sludge and leather dust in laboratory incubation studies.

Original Sludge Amendment in the Field	Amendment in Laboratory	Cr added in:			pH 9.5, 5.25% NaOCl Extractable Cr			
					Number of Extractions			
		Field	Lab	Total	3X	5X	3X	5X
MT/ha	g/500 g of soil	-----µg/g-----			----µg/g----		% of Cr added	
22.4	10 g sludge*	12	13	25	21	28	84	112
	10 g leather dust**	12	520	532	440	542	83	102
44.8	50 g leather dust**	18	2600	2618	1643	3122	63	119

*660 µg/g Cr

**2.6% Cr

after all the organic matter was apparently destroyed. This observation would be useful for routine analyses to decide when enough extractions had been performed.

Effect of Drying, Storage Time, and Organic Matter

Removal on the Ability of Soil to Oxidize Cr

Although Cr(III) in organic matter and chromite is not oxidized in soil, Cr(III) from inorganic sources such as CrCl_3 solutions is oxidized in soils as Bartlett and James (1979) first demonstrated. A modified version of their Cr oxidation test was used to study the effects of drying, storage time, and organic matter removal on the Cr oxidizing ability of Hagerstown and Murrill soils and to compare the Cr oxidizing ability of the Chrome soil with the Hagerstown and Murrill soils. The results are summarized in Table 23. The effects of drying and Cr oxidation on Mn reduction are also summarized in Table 23. The first thing to note is the strong effect drying had on the Cr oxidizing ability of the soils. Air-drying the soils led to a substantial loss of Cr oxidizing ability. Oven-drying virtually destroyed the Cr oxidizing ability of the soils. There was also a loss of Cr oxidizing ability with storage over time. There was no loss of Cr oxidizing ability of the moist soils for the first three months of storage. Beyond three months the ability of the soils to oxidize Cr declined. After 1 year the moist Hagerstown soils were able to oxidize about one-third as much Cr as they did at three months. The Cr oxidizing ability of the Murrill soil declined more slowly even though it contained more organic matter. The air-dried soils lost most of their Cr oxidizing ability during the initial stage of drying, but small losses also occurred during storage

Table 23. Chromium oxidizing ability of Hagerstown, Murrill, and Chrome soils as affected by drying, storage time, and organic matter removal.

Soil Series	Total Sludge Treatment	Drying	Storage Time	0.01 M KH ₂ PO ₄ Extractable		0.5 M CaCl ₂ Extractable Mn(II) After Cr Oxidation Test	Total Mn(II)	Initial 0.5 M CaCl ₂ Extractable Mn(II)	Net Total Mn(II) Produced	Mn(II)/Cr(VI)	
				Cr(VI)	Mn(II)						
			MT/ha	mcnths	-----nmole/g-----						
Hagers-town	0	no	3	117	13.8	167	181	34.2	147	1.3	
			4	86.1	8.0	138	146	34.9	111	1.3	
			12	36.9	--	--	--	--	--	--	
			air-dry	3	27.7	94.5	400	494	465	29	1.0
				4	9.2	74.9	465	540	451	89	9.7
				12	--	--	--	--	--	--	--
			oven-dry	3	0.0	945	2836	3781	3636	144	--
				4	0.0	873	3418	4291	4291	0	--
				12	--	--	--	--	--	--	--
		11.2	no	3	129	10.9	175	186	34.2	152	1.2
				4	111	7.3	153	160	33.5	126	1.1
				12	43.1	--	--	--	--	--	--
			air-dry	3	36.9	87.3	458	545	393	152	4.1
				4	15.4	75.6	531	607	487	120	8.0
				12	2.3	--	--	--	--	--	--
			oven-dry	3	1.5	800	2982	3782	4000	-218	--
				4	1.5	727	3782	4509	4873	-364	--
				12	--	--	--	--	--	--	--

Table 23 (Continued).

Soil Series	Total Sludge Treatment	Drying	Storage Time	0.01 M KH_2PO_4 Extractable		0.5 M CaCl_2 Extractable Mn(II) After Cr Oxidation Test	Total Mn(II)	Initial 0.5 M CaCl_2 Extractable Mn(II)	Net Total Mn(II) Produced	Mn(II)/Cr(VI)
				Cr(VI)	Mn(II)					
	MT/ha		months	-----mmole/g-----						
Hagers-town	22.4	no	3	86.2	15.3	175	190	49.5	141	1.6
			4	67.7	10.2	116	126	62.5	63	0.9
			12	21.5	--	--	--	--	--	--
		air-dry	3	30.8	94.5	473	567	436	131	4.2
			4	13.8	94.5	553	647	516	131	9.4
			12	1.5	--	--	--	--	--	--
		oven-dry	3	1.5	1164	3200	4364	4218	146	--
			4	0.0	872	4145	5017	6400	-1383	--
			12	--	--	--	--	--	--	--
	44.8	no	3	129	7.3	109	116	10.2	106	0.8
			4	92.3	3.6	80	84	13.1	71	0.8
			12	40.0	--	--	--	--	--	--
		air-dry	3	49.2	27.6	240	268	167	101	2.1
			4	21.5	28.4	291	319	218	101	4.8
			12	2.3	--	--	--	--	--	--
		oven-dry	3	0.0	945	2982	3927	3782	145	--
			4	0.0	527	3273	4000	4655	-655	--
			12	--	--	--	--	--	--	--

Table 23 (Continued).

Soil Series	Total Sludge Treatment	Drying	Storage Time	0.01 M KH_2PO_4 Extractable		0.5 M CaCl_2 Extractable Mn(II) After Cr Oxidation Test	Total Mn(II)	Initial 0.5 M CaCl_2 Extractable Mn(II)	Net Total Mn(II) Produced	Mn(II)/Cr(VI)
				Cr(VI)	Mn(II)					
-----nmole/g-----										
Murrill	89.6	no	3	92.3	2.2	35.6	38	2.9	35	0.4
			4	80.0	1.5	27.6	29	5.8	23	0.3
			12	64.6	--	--	--	--	--	--
		air-dry	3	50.8	5.1	109	114	30.5	84	1.6
			4	27.7	5.1	138	143	72.7	70	2.5
			12	3.8	--	--	--	--	--	--
		oven-dry	3	1.5	276	1818	2094	1964	130	--
			4	4.6	247	1818	2065	2109	-44	--
			12	--	--	--	--	--	--	--
Hagers-town*	44.8	no	3	127	--	--	--	--	--	
Chrome	--	no	4	75	--	--	--	--	--	

*Organic matter removed using pH 9.5, 5.25% NaOCl

over time. Air-dried soil samples are normally considered stable, but these data indicate that even air-dried soils change over time.

The reason for the loss of Cr oxidizing ability can be found by examining the Mn data. It is clear that air-drying the soils led to an increase in extractable Mn(II) ions. Oven-drying led to an even greater increase. Storage also generally resulted in an increase. The explanation is that as the soil was dried changes in the organic matter occurred that led to a decrease in the Eh of the soil. As the Eh fell the manganese oxides were reduced yielding Mn(II) (Bartlett and James, 1980). If enough of the manganese oxides are reduced, none are left to oxidize any added Cr which is why this reaction was unknown in soils until the discovery of Bartlett and James (1979). It is the almost universal practice of virtually every soils lab to dry soil samples before studying them. Such a practice must be discontinued if an accurate determination of the redox properties of soils is to be made.

It was also possible to evaluate the amount of Mn that was reduced during Cr oxidation. The Mn(II) content of each 0.01 M KI_2PO_4 extractant was added to the Mn(II) extractable with 0.5 M CaCl_2 after each Cr oxidation test to give the total extractable Mn(II) in each soil. From the total Mn(II) was subtracted the initial 0.5 M CaCl_2 extractable Mn(II) in each soil before the Cr oxidation test was run. The calculated result gave the net Mn(II) produced as a result of Cr oxidation. Assuming that all of the soil manganese oxide is $\delta\text{-MnO}_2$, then the stoichiometry of the reaction:

predicts that 1.5 moles of Mn(II) will be produced for every mole of HCrO_4^- yielded. The ratio of Mn(II) to Cr(VI) for each soil is shown in

Table 23. Since no Cr was oxidized by the oven-dry soils, the total Mn(II) and net total Mn(II) in oven-dry soils should theoretically be the same. Any discrepancies were due to sample variability. For the case of the air-dry soils the variability of the net Mn(II) produced was too great to deduce anything useful from the Mn(II)/Cr(VI) ratio. However, for three of the moist soils the Mn(II)/Cr(VI) ratio seems reasonably close to the theoretically predicted 1.5 value. These soils contained less organic matter and had lower pH values than the two soils where the Mn(II)/Cr(VI) ratios were less than one. The higher pH levels and/or organic matter contents of those two soils may have caused less Mn(II) to be extracted with the CaCl_2 .

Removal of organic matter from a sample of Hagerstown soil amended with 44.8 MT/ha sludge did not result in an increase in the amount of Cr oxidized as compared to an untreated soil. Evidence contradicting this result will be presented later.

Despite the low level of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and H_2O_2 reducible Mn in the Chrome soil, there was apparently enough manganese oxide there to yield only slightly less oxidized Cr than the Hagerstown and Murrill soils yielded. However, the Cr added to the soils was a highly soluble form easily oxidized by MnO_2 coatings over soil particles, so this finding may not be significant.

The effect of water removal by various treatments on the Cr oxidizing ability of Murrill silt loam was examined and the results are presented in Table 24. Each sample was amended with Cr(III), treated to remove water, and then analyzed for 0.01 M KH_2PO_4 extractable Cr(VI). It is apparent that oven-drying was able to reverse the oxidation process. However, water removal by washing with an organic solvent resulted in

Table 24. Effect of water removal by various treatments on the Cr oxidizing ability of Murrill silt loam.

Treatment	0.01 M KH_2PO_4 Extractable Cr(VI)
	$\mu\text{g/g}$
none	4.16
oven drying at 105°C	0.08
alcohol wash	1.92
alcohol wash + oven dry	0.40
acetone wash	3.04
acetone wash + oven dry	2.00

incomplete reversal of the Cr oxidation reaction. Even with oven-drying following the washing with solvent, the reaction could not be entirely reversed. No completely satisfactory explanation of these observations is available yet, but it may be related to the rate or completeness of water removal. Oven-drying results in slow water removal while solvent washing results in rapid water removal. Chromium reduction may be slow upon drying.

Effect of Cr Concentration on Cr Oxidation by Soil

At this point it might be useful to ask what is the relationship between the amount of Cr(III) added to soil and the amount of Cr(VI) produced. This question is partially answered by Figures 10 and 11. In Figure 10, the amount of Cr oxidized expressed as a percent of the amount of Cr(III) added is shown as a function of the amount of Cr(III) added. This experiment covered a wide range of added Cr(III) amounts and it clearly shows that as the amount of added Cr(III) increased the fraction of added Cr that was oxidized decreased. In no case did the amount of Cr oxidized amount to more than a few percent of the amount of added Cr. According to the Mn fractionation data the soil used in this experiment contained about 1300 $\mu\text{g/g}$ of reducible Mn (using pH 2, 10% H_2O_2 at 1:50 soil/solution ratio). Assuming this was all $\delta\text{-MnO}_2$ and all accessible to the Cr, this much reducible Mn should have been able to oxidize about 800 $\mu\text{g/g}$ of Cr. This would have been enough to oxidize all of the added Cr except for the highest rate added (1000 $\mu\text{g/g}$). The fact that only a small fraction of the added Cr was actually oxidized indicates that either very little of the manganese oxides present were actually accessible to the Cr, or that only a small fraction of the Cr added was available for oxidation or both. The fraction of added Cr

Figure 10. Effect of varying Cr(III) concentrations on the fraction of added Cr that is sorbed or oxidized by moist Hagerstown silt loam.

that was sorbed by the soil is also plotted in Figure 10 as a function of the amount of Cr added. It is clear that most of the added Cr was sorbed by the soil reaching a maximum at 100 $\mu\text{g/g}$ of added Cr. If all of the sorbed Cr was sorbed by organic matter and iron oxides and was unavailable for oxidation, then the amount remaining in solution would account for the small fraction that was oxidized. Sorption by organic matter and iron oxides is the most likely explanation for immobilization of added Cr(III), since Schnitzer (1980, Agronomy Abstracts, p. 159) has shown humic acids have a high affinity for Cr(III) and Grove and Ellis (1980) have shown that when Cr(III) was added to soil a large fraction of added Cr was extracted with the free iron oxides.

In Figure 10 the fractions of added Cr that were oxidized and sorbed were plotted against the amount of added Cr. In Figure 11 the amounts of soil solution total Cr and Cr(VI), extractable Cr(VI), and total Cr(VI) produced are plotted against the amount of added Cr. At lower amounts of added Cr most of the Cr(VI) produced remained in the soil solution. As the amount of Cr added increased the fraction of Cr(VI) that became sorbed to the soil, and hence extractable with KH_2PO_4 increased until the Cr(VI) was approximately equally distributed between soil and solution. At lower amounts of added Cr, Cr(VI) accounted for nearly all of the solution Cr, but as the amount of added Cr increased, the fraction of solution Cr that was Cr(VI) decreased. Assuming that only the Cr(III) remaining in solution was available for oxidation, then there was sufficient MnO_2 in the soil to oxidize all of the solution Cr(III). Since it was not all oxidized, all of the reducible Mn must not be available for oxidizing the Cr. The total Cr(VI) produced seemed to have reached a maximum far below what the soil was theoretically

Figure 11. Effect of varying Cr(III) concentrations on the amount of soil solution total Cr and Cr(VI), KH_2PO_4 extractable Cr(VI), and total Cr(VI) produced in moist Hagerstown silt loam.

capable of producing. Thus, soils probably have a finite capacity to oxidize Cr that is below the theoretical maximum. The theoretical maximum is given by the amount of reducible Mn in the soil and the stoichiometry of the reaction between Cr and Mn.

Cr Oxidizing Capacity of Soil

Figures 10 and 11 imply a finite capacity of soil to oxidize Cr. This is demonstrated in Figure 12 where a sample of Hagerstown soil amended with 44.8 MT/ha sludge was repeatedly equilibrated with a 1000 $\mu\text{g/ml}$ Cr(III) solution. The fraction of added Cr sorbed, the Cr(VI) in the 1000 $\mu\text{g/ml}$ Cr(III) solution after each equilibration, and the concentration of Mn(II) released to solution are all plotted as a function of the number of equilibrations (extractions). With each extraction, the fraction of added Cr that was sorbed decreased approximately by a factor of two. The Cr(VI) in solution decreased but not by a uniform factor. The Mn(II) concentration of the equilibrating solution increased almost linearly for the first four extractions and then declined as the capacity of the soil to oxidize Cr was almost exhausted. Thus, the soil's capacity to oxidize Cr was nearly exhausted after a total of 234 $\mu\text{mole/l}$ of solution Cr(VI) were produced.

Extractability of Soil Cr(VI) with KH_2PO_4

Many of the experiments have relied on data obtained using KH_2PO_4 extractions of the soil. However, little is known about the details of a KH_2PO_4 extractable Cr(VI) test for soils. Therefore, a series of experiments were run to study the nature of Cr(VI) extraction from soils using KH_2PO_4 . In the first experiment Cr(VI) was extracted from a moist Hagerstown silt loam previously treated with Cr(III) using solutions of

Figure 12. Exhaustion of Cr oxidizing capacity of moist Hagerstown silt loam.

varying KH_2PO_4 concentrations and the results are given in Table 25. There was no significant difference in the amount of Cr(VI) extracted by the three solutions. A solution containing 0.01 M KH_2PO_4 is sufficient to extract Cr(VI). If it is assumed that H_2PO_4^- ions replace HCrO_4^- ions on the soil and the exchange reaction is governed by a mass action formulation, then if the 0.01 M KH_2PO_4 did not extract all the Cr(VI), solutions with higher concentrations of KH_2PO_4 would have. Since this did not happen, the 0.01 M KH_2PO_4 solution must be adequate.

Apparently contradictory evidence was obtained by running successive KH_2PO_4 extractions for Cr(VI) on moist Hagerstown silt loam treated with three levels of Cr(III) as shown in Figure 13. This diagram apparently shows that one extraction with 0.01 M KH_2PO_4 was not sufficient to remove all of the Cr(VI). However, it is possible that the first extraction did remove nearly all of the Cr(VI) and that the Cr(VI) removed by subsequent extractions was mostly produced through oxidation during those extractions. If the KH_2PO_4 was able to desorb some of the added Cr(III) that was originally unavailable for oxidation, thereby making it available for oxidation, this would account for the discrepancy between the results in Table 25 and Figure 13.

To further characterize the extraction of Cr(VI) using KH_2PO_4 , the effect of the soil to extracting solution ratio on the results was studied. In the first experiment the soil/solution ratio was varied by holding the amount of soil constant while varying the KH_2PO_4 solution volume and the results are presented in Table 26. The results show that a 1:1 soil/solution ratio did not give as much extractable Cr(VI) as did the other three ratios. The 1:1 ratio was used in the experiment where the concentration of KH_2PO_4 was varied and in the successive extraction

Table 25. Chromium(VI) extracted from moist Hagerstown silt loam using various concentrations of KH_2PO_4 in solution.

KH_2PO_4 Concentration	Cr(VI) Extracted
	$\mu\text{g/g}$
0.1 M	8.4
0.05 M	8.0
0.01 M	8.1

Figure 13. Successive KH_2PO_4 extractions of Cr(VI) from moist Hagerstown silt loam treated with three levels of Cr(III).

Table 26. Effect of soil/solution ratio on the KH_2PO_4 extraction of Cr(VI) from moist Hagerstown silt loam. Soil/solution ratio varied by holding soil amount constant while varying KH_2PO_4 solution volume.

Soil Amount	0.01 M KH_2PO_4 Solution Volume	Soil/Solution	0.01 M KH_2PO_4 Extractable Cr(VI)	
			$\mu\text{g/g}$	μg
g	ml	g/ml		
5	5.0	1	6.2	31
5	10.0	0.5	8.8	44
5	15.0	0.33	9.6	48
5	20.0	0.25	8.8	44

experiment, so the results of Table 26 may support the first explanation of the results shown in Figure 13 which is that not all of the Cr(VI) was extracted on the first extraction with 0.01 M KH_2PO_4 at a 1:1 soil/solution ratio. However, it is entirely possible that incomplete extraction was obtained the first time and subsequent extractions removed both the Cr(VI) missed the first time plus freshly generated Cr(VI). Also possible is desorption and oxidation of Cr(III) when a smaller soil/solution ratio was used.

In Figure 14 the results of an experiment whereby the soil/solution ratio was changed by holding the KH_2PO_4 solution volume constant and varying the amount of soil are shown. Since the amount of soil was varied, the amount of manganese oxide available for oxidizing the Cr was also varied. As the amount of soil increased, the amount of manganese oxide increased, and so did the amount of Cr(VI) produced. The concentration of extractable Cr(VI) in the soil did not vary much with soil/solution ratio when the ratio was above 1:1. At a ratio of 1:1 incomplete extraction of Cr(VI) again seemed likely or else desorption and oxidation of Cr(III) at the other ratios occurred.

In another experiment the amounts of soil and KH_2PO_4 solution were varied, but the ratio was held constant at 1:1. The results are diagrammed in Figure 15. As expected there was a linear increase in the amount of Cr(VI) extracted as the amount of soil increased. The concentration of extractable Cr(VI) in the soil did not vary much with the amount of soil used and theoretically should have been independent of amount. Why it was not invariant is unknown.

Figure 14. Effect of soil/solution ratio on KH_2PO_4 extraction of Cr(VI) from moist Hagerstown silt loam. Soil/solution ratio varied by holding KH_2PO_4 solution volume constant while varying soil amount.

Figure 15. KH_2PO_4 extraction of Cr(VI) from moist Hagerstown silt loam at constant soil/solution ratios.

Oxidation of Cr from Different Sources at Selected
Concentrations in Soil with Time

In addition to the experiments already described a series of incubation experiments were run to study the effects of Cr(III) source and amount on Cr oxidation with time. In the first of these, the oxidation of three levels of Cr(III) added to Murrill soil was followed over a period of 29 hr by determining Cr(VI) in the soil solution extracted using an immiscible displacement-centrifugation technique (Mubarak and Olsen, 1976) and by determining 0.01 M KH_2PO_4 extractable Cr(VI). The results are summarized in Table 27. At the lowest rate of added Cr(III) there was little change in the amount of soil solution Cr(VI) or KH_2PO_4 extractable Cr(VI) over a period of a day. The oxidation of Cr(III) apparently occurred rapidly, reaching the maximum in the first couple of hours before any samples were taken. At the two higher rates of added Cr(III) there was an increase in soil solution Cr(VI) and KH_2PO_4 extractable Cr(VI) with time. Most of the Cr(VI) produced was produced during the first couple of hours with the next largest increase occurring between 7 and 26 to 29 hrs. Again, as with previously described experiments only a small fraction of added Cr was oxidized. Most of the rest was presumably sorbed to various soil components and unavailable for oxidation. Again, most, but not all of the soil solution Cr was Cr(VI). At the lowest level of added Cr virtually all the soil solution Cr was Cr(VI), but as the amount of added Cr(III) was increased, the fraction of soil solution Cr existing as Cr(VI) decreased. Even though there was more than enough manganese oxide in the soil to oxidize all of the soil solution Cr, complete oxidation was not achieved indicating that all of the manganese oxide was not accessible to the Cr. Or perhaps reduction

Table 27. Effect of varying Cr(III) concentration on the oxidation of Cr in moist Murrill silt loam with time.

<u>0.01 M KH₂PO₄ Extractable Cr(VI)</u>					
<u>Cr(III) Added</u>	<u>Time, hrs</u>				
	<u>2.5</u>	<u>4.5</u>	<u>7.5</u>	<u>15.5</u>	<u>29</u>
	<u>-----µg/g-----</u>				
10	0.78	0.51	0.56	0.60	0.49
50	2.71	1.93	2.93	2.91	4.64
100	3.60	4.57	4.45	6.08	6.88

<u>Soil Solution Cr(VI)</u>				
<u>Cr(III) Added</u>	<u>Time, hrs</u>			
	<u>5</u>	<u>6.5</u>	<u>8</u>	<u>26</u>
<u>µg/g</u>	<u>-----µg/ml-----</u>			
10	0.67	0.53	0.50	0.53
50	1.88	1.80	2.41	2.45
100	3.69	3.41	3.59	4.65

<u>Soil Solution Total Cr</u>				
<u>Cr(III) Added</u>	<u>Time, hrs</u>			
	<u>5</u>	<u>6.5</u>	<u>8</u>	<u>26</u>
<u>µg/g</u>	<u>-----µg/ml-----</u>			
10	0.68	0.52	0.55	0.58
50	2.20	2.11	2.83	2.77
100	5.04	5.18	4.46	5.94

of Cr(VI) by the soil organic matter was also occurring. This matter will be considered later. The 0.01 M KH_2PO_4 extractable Cr(VI) in this experiment actually included soil solution Cr(VI) as well as Cr(VI) sorbed to the soil, since wet soils were extracted. At the lowest level of added Cr soil solution Cr(VI) accounted for about 50% of the extractable Cr(VI) while at the highest level it accounted for about 30% of the extractable Cr(VI).

The results in Table 27 suggest rapid oxidation of Cr(III), but no samples were taken before 2.5 hrs of incubation. Therefore, another experiment was run to study the oxidation of Cr in Merrill silt loam over a shorter time span. The results of this experiment are presented in Figure 16. The chief difference between this experiment and the previous one was in the water content (50% for the previous experiment, 100% for this one), but this should not have made much difference. The level of added Cr was 192 $\mu\text{mole/l}$ which was equivalent to 10 $\mu\text{g/g}$ of Cr. The graph shows that the fastest rate of Cr oxidation occurred rather early on (less than 1 hr). Between 2 and 4 hrs only a small increase in Cr(VI) was observed.

It was also desirable to compare the oxidation of Cr from different sources at different levels of added Cr and to follow the Cr over a longer time span. Such an experiment was carried out using Hagerstown silt loam and is summarized in Table 28. The oxidation of the relatively soluble CrCl_3 was compared to the oxidation of the relatively insoluble $\text{Cr}(\text{OH})_3$. The more readily soluble compound was more easily oxidized as expected, but the important point is that even a compound like $\text{Cr}(\text{OH})_3$ which would normally be considered insoluble in soil was oxidized to a small degree. This has implications for the land disposal of wastes

Figure 16. Kinetics of Cr oxidation in moist Murrill silt loam.

Table 28. Effect of Cr(III) source and amount on the oxidation of Cr in moist Hagerstown silt loam with time.

<u>0.01 M KH₂PO₄ Extractable Cr(VI)</u>				
<u>Cr Source</u>	<u>Cr Added</u>	<u>Time</u>		
		<u>1 Day</u>	<u>1 Week</u>	<u>1 Month</u>
		-----µg/g-----		
CrCl ₃ solution	10	0.85	0.07	0.07
	100	6.40	2.00	0.07
Cr(OH) ₃ suspension	10	0.10	0.00	0.02
	100	1.65	0.45	0.05

<u>Soil Solution Cr(VI)</u>				
<u>Cr Source</u>	<u>Cr Added</u>	<u>Time</u>		
		<u>1 Day</u>	<u>1 Week</u>	<u>1 Month</u>
	µg/g	-----µg/ml-----		
CrCl ₃ solution	10	0.56	0.20	0.01
	100	5.56	3.20	0.15
Cr(OH) ₃ suspension	10	0.07	0.01	0.00
	100	1.11	0.80	0.06

from the metal finishing industry. Such wastes normally consist of metals precipitated as the hydroxides including $\text{Cr}(\text{OH})_3$. It might be surmised that such wastes could safely be disposed of on soil because of low solubility, but the results in Table 28 indicate otherwise, since $\text{Cr}(\text{VI})$ from the oxidation of $\text{Cr}(\text{OH})_3$ in soil would be toxic to plants, aquatic life, and possibly humans. Again, the amount of Cr oxidized in this experiment amounted to only a small fraction of the total, but measurable levels persisted for a period of at least a month. It appeared that the maximum level of $\text{Cr}(\text{VI})$ that was reached occurred in about a day and the decline in $\text{Cr}(\text{VI})$ after that was due to reduction by organic matter. Using some of the KH_2PO_4 extractable $\text{Cr}(\text{VI})$ data the half-life for $\text{Cr}(\text{VI})$ reduction was estimated to be 8 days. Using some of the soil solution $\text{Cr}(\text{VI})$ data the half-life for $\text{Cr}(\text{VI})$ reduction was estimated to be 17 days. It is apparent that Cr oxidation was fairly rapid while Cr reduction was slow. This will be examined in detail later.

The oxidation of the very insoluble Cr_2O_3 in moist Hagerstown silt loam was also examined and the results are listed in Table 29. A high level of Cr_2O_3 was used representing a severe contamination situation. Small amounts of $\text{Cr}(\text{VI})$ were found over an 11-month period. When an insoluble Cr compound is added to moist soil a source of oxidizable Cr is provided for a long period of time and oxidation will occur as long as the manganese oxide supply holds out. Thus, caution is urged in the land disposal of inorganic Cr compounds.

The incubation experiments implied that the oxidation of Cr is fairly rapid and that reduction is slow. A series of kinetic experiments

Table 29. Potassium phosphate extractable Cr(VI) in moist Hagerstown silt loam amended with Cr_2O_3 .

Cr Source	Cr Added	Time			
		1 Week	1.5 Months	5 Months	11 Months
	mg/g	-----µg/g-----			
Cr_2O_3	68.4	0.96	1.04	0.60	0.52

was designed in order to study these reactions in more detail and the results of these experiments are described next.

Kinetics of Cr Oxidation and Sorption by

Moist Hagerstown Silt Loam

Sorption reactions are normally considered to be quite rapid--too fast to even measure. In Figure 17 the sorption of Cr(III) by a suspension of moist Hagerstown silt loam with time is shown. As expected the sorption reaction was too rapid to measure and was complete in 30 sec when the first sample was taken. No change in solution total Cr was observed over the period of 30 sec to 15 min.

The kinetics of Cr oxidation as affected by temperature in a dilute suspension of Hagerstown silt loam are shown in Figure 18. The suspension concentration used in this experiment was considerably less than that used in the incubation experiments. Therefore, this experiment was analogous to Cr contaminating a sediment-laden stream or river. In the incubation experiments the amount of manganese oxide was far in excess of that needed to oxidize all the added Cr. In this experiment the amount of soil used was such that its reducible Mn content was just enough to oxidize all of the added Cr. Of course not all of the manganese oxide was accessible to the Cr and about half of the added Cr was sorbed and unavailable for oxidation, so the actual amounts able to react differed from the theoretical maximum. As with the incubation experiments most of the oxidation occurred during the first hour with only small increases observed after that. It is clear from the figure that temperature exerts a major effect on Cr oxidation in soil. At low temperature (2°C) the oxidation of Cr was following zero order kinetics

Figure 17. Kinetics of Cr sorption by moist Hagerstown silt loam.

Figure 18. Effect of temperature on the kinetics of Cr oxidation in moist Hagerstown silt loam.

([Cr(VI)] plotted against time yielded a straight line) with a rate coefficient of $0.046 \mu\text{mole/l/min}$. Beyond about 1 hr deviations from the straight line were observed. Zero order kinetics in which the rate of the reaction does not depend upon the concentrations of reactants are not unusual for reactions involving surfaces. In the present case at low temperature the oxidation reaction was sufficiently slowed down so that the manganese oxide surface was "saturated" with Cr undergoing oxidation. Higher concentrations of Cr(III) will not speed up the reaction, since the reaction can only proceed as fast as the amount of manganese oxide surface available for oxidation will allow. At higher temperatures an initial rapid increase in Cr(VI) was quickly followed by a fall-off in reaction rate. The fall-off was greater at a higher temperature. There are two possible explanations for this observation. One is that side-reactions involving Cr(VI) became more important as time goes on and were more important at higher temperatures. The other explanation is that not all of the manganese oxide was available for oxidation and the surface was "used up" as the reaction proceeded, or perhaps both situations were occurring. In any case as with the incubation experiments the reaction "shuts off" before reaching the maximum allowable amount of Cr(VI) produced if all the soil manganese oxide was used up. More will be said about this later.

The effect of removing organic matter on the kinetics of Cr oxidation by moist Hagerstown silt loam was also examined and the results are illustrated in Figure 19. This experiment revealed that organic matter removal did increase the rate of reaction whereas in the Cr oxidation test no difference was found between untreated Hagerstown silt loam and Hagerstown treated to remove organic matter. The Cr oxidation

Figure 19. Effect of organic matter removal on the kinetics of Cr oxidation in moist Hagerstown silt loam.

test used a 15 min shaking time so any differences would have had time to show up. The discrepancy between the two results may be due to the amount of soil used. In the Cr oxidation test an excess of soil theoretically needed to oxidize all of the added Cr was used. Perhaps this was enough to mask any differences. Another explanation would be that all of the NaOCl used to destroy the organic matter was not washed out of the soil used in the kinetic experiment. Sodium hypochlorite is capable of oxidizing Cr so the results in Figure 19 may actually be an experimental artifact and not a real difference at all. Further work to settle this matter is needed.

Kinetics of Cr Oxidation by MnO_2 Minerals

Experiments on the kinetics of Cr oxidation in moist soil are clouded by the sorption and reduction reactions involving Cr and other soil components. To avoid this problem the oxidation of Cr by manganese oxide minerals was studied and the results of these experiments are now discussed. Most of the experiments made use of $\delta\text{-MnO}_2$, a hydrated, amorphous form of MnO_2 thought to be the most common MnO_2 mineral in the environment.

The effect of temperature on Cr oxidation by $\delta\text{-MnO}_2$ was studied first and the results are shown in Figure 20. The general shape of the kinetic curves was the same as the soil kinetic curves, an initial rapid oxidation of Cr followed by a rapid fall-off in oxidation rate. Both the rate and the amount oxidized increased with temperature. Even though there was a large excess of $\delta\text{-MnO}_2$ used, the reaction did not go to completion, that is, all of the Cr(III) was not used up. This rapid fall-off in the reaction rate and lack of complete oxidation could only occur if the surface of the $\delta\text{-MnO}_2$ available for oxidizing Cr was

Figure 20. Effect of temperature on the kinetics of Cr oxidation by $\delta\text{-MnO}_2$ at pH 5.5.

"used-up" as the reaction proceeded. However, there should have been more than enough surface area available to complete the reaction. An explanation of the observed results can be inferred by consideration of what happened to the Mn reduced during the reaction. As Cr was oxidized Mn(IV) was reduced to Mn(II). However, instead of being released to solution and exposing fresh Mn(IV) for oxidizing Cr, the Mn(II) was retained on the surface, thus blocking access to the Mn(IV) below it. This explanation is strongly supported by not finding any increase in the Mn(II) content of the solution surrounding the MnO_2 as the reaction proceeded. Morgan and Stumm (1964) and Posselt et al. (1968) have found that $\delta\text{-MnO}_2$ has a high affinity for its own divalent metal ion. Protons are also a product of the reaction between $\delta\text{-MnO}_2$ and Cr and these would also be retained on the surface, thus blocking access to fresh Mn(IV). During the reaction it was found that no Cr was sorbed to the $\delta\text{-MnO}_2$ surface, since all of the added Cr was found in solution at any point in time. Thus, Cr(III) only forms a "loose" association with the surface while being oxidized and oxidation occurs so quickly that it is rapidly released. The negatively charged chromate ions are repelled by the negatively charged $\delta\text{-MnO}_2$ surface. This lack of sorption of Cr on $\delta\text{-MnO}_2$ is in dramatic contrast to the known high affinity of $\delta\text{-MnO}_2$ for cations such as Co, Cu, Zn, and Cd (Morgan and Stumm, 1964; Posselt et al., 1968; Murray et al., 1968; Loganathan and Burau, 1972). An excess of $\delta\text{-MnO}_2$ needed to oxidize all the Cr(III) was used in this experiment to try and determine the reaction order for formation of Cr(VI). However, it is obvious that the reaction was much too fast when $\delta\text{-MnO}_2$ actually was in excess for the experimental technique to follow. Fast flow or instrumental techniques must be used. It is also clear that predicted

levels of Cr(VI) will probably never be achieved in soils if the manganese oxide surface area is limiting. This is a most fortunate occurrence, since severe environmental contamination with Cr(VI) would occur and would probably already have been observed. The effect of $\delta\text{-MnO}_2$ amount on Cr oxidation will be reconsidered later.

It might be worthwhile to ask what is the effect of pH on Cr oxidation by $\delta\text{-MnO}_2$. Bartlett and James (1979) had discovered that the amount of Cr oxidized in soil increased with decreasing pH. The effect of pH on Cr oxidation by $\delta\text{-MnO}_2$ is shown in Figure 21. At low pH the rate of Cr oxidation was less than the rate at higher more environmentally realistic pH levels. At pH 1 the rate of oxidation is approaching a zero order level qualitatively similar to the case with soil at 2°C . The reason the rate is slowed down at low pH can be explained on the basis of the zero point of charge (ZPC) of the $\delta\text{-MnO}_2$. The zero point of charge is the pH at which a surface is electrically neutral and will not migrate to a cathode or an anode when an electrical potential is applied to the suspension. For $\delta\text{-MnO}_2$ the zero point of charge is about pH 2.5. Above this the mineral carries a net negative charge due to OH^- groups at the mineral surface and below this the mineral carries a net positive charge. At pH 1 the mineral carried a net positive charge due to excess protons. These tended to repel the Cr thus slowing down the rate of reaction because the Cr had to replace the protons before the oxidation could occur. At pH 3 (slightly above the ZPC) the rate of oxidation increased, but was still slowed down somewhat. At pH 5.5 to 7.5 the rate was not significantly affected by pH. At first it might seem that this evidence contradicts the Bartlett and James data. However, the increase in Cr oxidation at low pH in soils might simply be

Figure 21. Effect of pH on the kinetics of Cr oxidation by δ -MnO₂.

due to less sorption or precipitation of Cr at low pH. More Cr remains in solution to be oxidized. It seems that the effect of pH on Cr oxidation is indirect, controlling sorption and solubility rather than a direct control of oxidation at least at environmentally meaningful pH levels.

In Figure 22 the effect of temperature on Cr oxidation by $\delta\text{-MnO}_2$ at pH 1 is shown. A huge excess of $\delta\text{-MnO}_2$ was maintained. At low temperature the reaction was sufficiently slowed down to follow zero-order kinetics. However, a low pH was needed to slow the reaction down even at this low temperature which is in contrast to the case with the soil. At room temperature the reaction began by following zero-order kinetics but fell off as the mineral surface was "used up". At high temperature the reaction occurred so quickly that the mineral surface was rapidly "used up". However, at higher temperatures the thermal motion allows more of the surface to be used than at the lower temperature. Thus, the amount of MnO_2 surface available for oxidation is temperature dependent. The rate coefficients were $0.31 \mu\text{mole/l/min}$ at 2°C and $2.61 \mu\text{mole/l/min}$ at 24°C . The activation energy was 14.9 kcal/mole .

The metal finishing industry often relies on precipitating out metals in their wastewater as hydroxides and then disposes of the metal hydroxide sludge. As already seen Cr(OH)_3 can be oxidized in soil. One might ask what is the rate of oxidation of Cr(OH)_3 by $\delta\text{-MnO}_2$ at high pH and such a curve is shown in Figure 23. Although much slower than the oxidation of CrCl_3 at lower pH levels, the oxidation of Cr(OH)_3 at high pH could pose a problem in the land disposal of such a waste. Caution is urged in this matter.

Figure 22. Effect of temperature on the kinetics of Cr oxidation by δ -MnO₂ at pH 1.0.

Figure 23.. Kinetics of Cr(OH)_3 oxidation by $\delta\text{-MnO}_2$ at pH 10.

The effect of ionic strength on the rate of Cr oxidation was also examined and the results are presented in Figure 24. As expected an increase in solution ionic strength lowered the oxidation rate due to a decrease in the ionic activity of Cr(III). However, the effect was a small one and could be ignored in dilute solutions.

The effects of solution composition on the rate of Cr oxidation are shown in Figure 25. The previously described experiments all used a 10^{-3} M NaClO_4 solution for suspending the $\delta\text{-MnO}_2$. However, wastewaters and soil solutions are not dilute perchlorate solutions, so the effect of different solution compositions on oxidation rate must be known. Using a solution containing KCl , MgCl_2 , and CaCl_2 to approximate the "average" soil solution, it can be seen that the oxidation rate was substantially decreased initially. However, this decrease was certainly not enough to lead one to expect to observe much of an effect "in the field", since most of the Cr was oxidized within 15 min anyway. Adding other metal salts decreased the rate only slightly more. Adding DTPA, a chelating agent, decreased the rate substantially. Probably because the DTPA lowered the Cr(III) activity substantially and also may have affected the $\delta\text{-MnO}_2$ surface. Natural chelators would be expected to also slow down the oxidation rate. When the $\delta\text{-MnO}_2$ was suspended in a 1000 $\mu\text{g/ml}$ Fe(III) solution and the pH raised to 5.5, the Fe(III) precipitated as Fe(OH)_3 occluding the $\delta\text{-MnO}_2$ and completely preventing oxidation when the Cr(III) was added. This suggests a way to treat and dispose of metal finishing wastes. By adding FeCl_3 to the acidic waste and then raising the pH the metals precipitate and are trapped in the amorphous Fe(OH)_3 . Since Fe(OH)_3 is stable in well-oxidized soils, the Fe(OH)_3 sludge with the entrained metals can be added to a well-drained soil.

Figure 24. Effect of ionic strength on the kinetics of Cr oxidation by δ -MnO₂.

Figure 25. Effect of solution composition on the kinetics of Cr oxidation by δ -MnO₂.

As long as oxidizing conditions prevail the $\text{Fe}(\text{OH})_3$ will remain stable in the soil.

Earlier it was suggested that all of the solution $\text{Cr}(\text{III})$ was not oxidized in any of the experiments because the $\text{Mn}(\text{IV})$ at the mineral surface was "used up". The effect of surface area available for oxidizing Cr on the rate of Cr oxidation by $\delta\text{-MnO}_2$ can be seen in Figure 26. The surface area of $\delta\text{-MnO}_2$ available for oxidizing Cr was varied by using different amounts of $\delta\text{-MnO}_2$ while holding the initial $\text{Cr}(\text{III})$ concentration constant. In this experiment the $\delta\text{-MnO}_2$ was hydrosonically dispersed to achieve the maximum possible surface area. In previous experiments dispersion was by rapidly mixing in solution so the maximum surface area was not achieved. The graph clearly shows that there was an initial rapid production of $\text{Cr}(\text{VI})$ which then quickly fell off. This fall-off occurred within a few minutes. In each case there was more than enough $\delta\text{-MnO}_2$ to oxidize all of the added $\text{Cr}(\text{III})$, but the amount actually oxidized fell short of the total possible. The amount oxidized decreased with the amount of $\delta\text{-MnO}_2$ used.

It would now seem that the only way to oxidize more Cr would be to use an excess amount of $\text{Cr}(\text{III})$, and thus begin dissolving the mineral. Such an occurrence can be seen by examining Figure 27 where the oxidation of $\text{Cr}(\text{III})$ and reduction of $\text{Mn}(\text{IV})$ was followed upon dissolving $\delta\text{-MnO}_2$ in excess CrCl_3 solution. A plateau was reached on the Cr oxidation curve after a few minutes which corresponded to using up the surface $\text{Mn}(\text{IV})$. The reaction would have stopped here if $\delta\text{-MnO}_2$ was in excess of Cr, but with excess Cr present the reaction rate began accelerating again and did not slow until most of the mineral was dissolved. The Mn reduction rate also started off slowly and then quickly accelerated

Figure 26. Effect of varying amounts of $\delta\text{-MnO}_2$ on the kinetics of Cr oxidation by $\delta\text{-MnO}_2$.

Figure 27. Kinetics of Cr oxidation by $\delta\text{-MnO}_2$ and Mn reduction by Cr(III) with excess Cr present.

as the mineral was dissolved. The normal environmental situation in the case of soils would probably be excess $\delta\text{-MnO}_2$ over Cr except in localized regions. Excess Cr over $\delta\text{-MnO}_2$ might occur when highly Cr-contaminated wastewater is discharged into a natural body of water.

The reduction of $\delta\text{-MnO}_2$ by excess Cr as affected by temperature at low pH is shown in Figure 28. The initial reaction rate at this pH was obviously following zero-order kinetics. This is not surprising, since Cr was in excess and the reaction could proceed only as fast as the available surface area would allow. The low pH assured that as the Mn(II) was produced it was released to solution, thus the S-shaped curve of Figure 27 was avoided. The rate coefficients were 0.46 $\mu\text{mole/l/min}$ at 25°C and 6.26 $\mu\text{mole/l/min}$ at 48°C. The activation energy was 21.5 kcal per mole.

The mineral $\delta\text{-MnO}_2$ is not the only MnO_2 mineral capable of oxidizing Cr as the results in Figure 29 demonstrate. At a MnO_2 concentration of 250 mg/l and without hydrosonic dispersion both $\delta\text{-MnO}_2$ and Mn(II)-manganite oxidized Cr rather rapidly with Mn(II)-manganite producing complete oxidation of the added Cr(III). However, at 20 mg/l and with hydrosonic dispersion the larger surface area of $\delta\text{-MnO}_2$ revealed itself in that it oxidized Cr faster than did the Mn(II)-manganite. The mineral $\alpha\text{-MnO}_2$ oxidized Cr much more slowly than did $\delta\text{-MnO}_2$ or Mn(II)-manganite. The α form of MnO_2 exhibits ion-exchange properties and the rate of oxidation could be slowed even further by adding competing cations to the suspension to block the access of Cr to the sites where oxidation occurred. The oxidation of Cr by $\beta\text{-MnO}_2$ (pyrolusite) was so slow that it could not even be shown on the figure. Experiments were run at different pH levels and amounts of Cr and $\beta\text{-MnO}_2$, but no

Figure 28. Effect of temperature on the kinetics of Mn reduction by Cr(III) at pH 1.0 with excess Cr present.

Figure 29. Kinetics of Cr oxidation by various MnO_2 minerals under selected conditions.

significant amount of oxidation by $\beta\text{-MnO}_2$ was ever observed even after many days. Pyrolusite is the most stable form of MnO_2 and the most crystalline form. However, its occurrence in soils is apparently limited (McKenzie, 1977).

Many of the experiments made use of an autotitrimer to return the pH to a preset level after the Cr(III) solution was added. The suspensions were acidified upon adding Cr(III) because of hydrolysis. The amount of base needed to return the pH to the preset level over the course of the experiment is known as OH^- demand and examples of OH^- demand curves are presented in Figures 30 and 31. In Figure 30 the effect of temperature on OH^- demand during Cr oxidation in moist Hagerstown silt loam is shown. As the diagram shows temperature had a large effect on OH^- demand which was not yet satisfied even after one hour. Because the added Cr was trivalent, one would expect three protons to need neutralized for every Cr(III) ion added. Thus, when fully satisfied the $\text{OH}^-/\text{Cr}^{3+}$ ratio should be 3 to 1. However, after one hour the OH^- demand was not yet satisfied and the $\text{OH}^-/\text{Cr}^{3+}$ ratio was 2 to 1. These observations were due to reactions of H^+ , OH^- , and Cr^{3+} ions with soil other than simple neutralization reactions. This depressed the OH^- demand. However, the effect of temperature on OH^- demand during Cr oxidation by $\delta\text{-MnO}_2$ was slight compared to the temperature effect when soil was used. The OH^- demand was mostly satisfied in 15 min with the $\text{OH}^-/\text{Cr}^{3+}$ ratio approaching the 3 to 1 value predicted. Apparently, the OH^- ions added only had to neutralize the protons from Cr(III) hydrolysis and did not have time to react with the $\delta\text{-MnO}_2$.

Figure 30. Effect of temperature on OH⁻ demand during Cr oxidation and sorption in moist Hagerstown silt loam.

Figure 31. Effect of temperature on OH⁻ demand during Cr oxidation by δ -MnO₂.

Kinetics of Cr Oxidation by δ -MnO₂ in the Presence
of Fulvic Acid and the Kinetics of Cr and Mn
Reduction by Fulvic Acid

A number of times it has been suggested that the rate of Cr reduction in soil is slow. A number of experiments were designed to study the rate of Cr reduction in soil and by soluble organic matter to determine the reaction rates. In the first experiment the rate of Cr reduction in moist Hagerstown silt loam was studied and the results are presented in Figure 32. Unlike the complicated case of Cr oxidation, Cr reduction kinetics are straightforward. Reduction follows first order kinetics. Under the conditions shown in Figure 32 the rate coefficient for reduction was 0.012 day^{-1} and the half-life was about 55 days. In contrast with this, a half-life of 17 days was calculated from the results of the incubation experiment (Table 28). However, in the incubation experiment more soil was used than in the kinetic experiment, so there was a greater opportunity for the incubation experiment to become more reducing due to more organic matter being present. Also, the Mn(IV)/Cr(III) ratio was greater in the incubation experiment than in the kinetic experiment. In both the kinetic and incubation experiments only the loss of solution Cr(VI) was measured. However, the Hagerstown silt loam does sorb some Cr(VI), so in order to study Cr reduction in the absence of side reactions, Cr reduction by fulvic acid, the soluble portion of soil organic matter, was studied.

In the first experiment the kinetics of Cr reduction by fulvic acid extracted from Murrill silt loam were studied under varying pH and temperature conditions and the results are diagrammed in Figure 33. It is clear that reduction by fulvic acid is slow at environmentally

Figure 32. Kinetics of Cr reduction in moist Hagerstown silt loam.

Figure 33. Effects of temperature and pH on the kinetics of Cr reduction by soil fulvic acid.

important pH and temperature levels. The rate of reduction could be increased by increasing the temperature, but the most dramatic rate increase was produced by lowering the pH of the solution. This large rate increase occurred because protons are one of the reactants in the reduction reaction (Bartlett and Kimble, 1976b):

The increase in the rate of Cr reduction by fulvic acid upon acidification of fulvic acid agrees qualitatively with the increase in the rate of Cr reduction by manure that Bartlett and Kimble (1976b) observed upon acidifying the manure. Observed rate coefficients for Cr reduction by soil fulvic acid were 0.15 hr^{-1} at 25°C and pH 1, 0.037 day^{-1} at 25°C and pH 5.5, and 0.23 day^{-1} at 50°C and pH 5.5. The half-lives were 4.6 hrs at 25°C and pH 1, 19 days at 25°C and pH 5.5, and 3 days at 50°C and pH 5.5. The 19-day half-life at 25°C and pH 5.5 agrees very well with the 17-day half-life from the incubation experiment run at 25°C and pH 5.1. The activation energy for reduction was 13.9 kcal/mole.

The kinetics of Cr reduction by leather dust fulvic acid was also studied and these results are graphed in Figure 34. It is obvious that leather dust fulvic acid reduced Cr faster than soil fulvic acid. Since both soil and leather dust fulvic acids were in excess of that needed to reduce all of the initial Cr(VI) added, the faster rate with the leather dust fulvic acid was probably due to the greater catalytic activity of the microorganisms in the leather dust. Filamentous microorganism growths were observed in the leather dust fulvic acid solutions. The slope changes in the diagram were due to pH changes. The solutions were initially adjusted to pH 5.5, but the microorganisms kept buffering the pH up toward 7 as time went on as periodic pH measurements demonstrated.

Figure 34. Effects of temperature and pH on the kinetics of Cr reduction by leather dust fulvic acid.

Rate coefficients were not calculated for these curves because of the uncertainties in the data due to the microorganism activities.

The experiments on Cr reduction by fulvic acid demonstrated the slow rate of the reaction. The question now remains as to whether fulvic acid can actually prevent the oxidation of Cr by $\delta\text{-MnO}_2$. This question is answered by Figures 35 and 36. A fulvic acid extract of leather dust after removing the humic acid and β -humus impurities was found to contain 70 $\mu\text{g/ml}$ of Cr. When mixed with $\delta\text{-MnO}_2$ no oxidation of the Cr in the leather dust fulvic acid was observed. Apparently the fulvic acid-Cr complex is stable toward oxidation. However, when a soluble CrCl_3 solution was added oxidation did occur as shown in Figure 35. The characteristic rapid initial increase in Cr(VI) was observed followed by the rapid fall-off in oxidation rate. Obviously, the fulvic acid was unable to prevent this oxidation. Oxidation is only prevented if a stable organo-Cr complex is formed before the Cr has a chance to contact the $\delta\text{-MnO}_2$. The maximum amount of Cr(VI) was reached after several hours, but this amount was much less than the amount that would have been reached if the fulvic acid was not present, so the fulvic acid was able to prevent some of the Cr(III) from being oxidized. Eventually the rate of reduction of the Cr(VI) dominated. All of the Cr reduction experiments showed that substantial amounts of Cr(VI) could persist for long periods of time in soil, probably long enough to be leached out and contaminate ground water.

Besides the oxidation of Cr(III) by $\delta\text{-MnO}_2$ and the reduction of Cr(VI) by organic matter, the reduction of $\delta\text{-MnO}_2$ by organic matter should be considered. In Figure 37 are shown the kinetics of $\delta\text{-MnO}_2$ reduction by leather dust fulvic acid. Although reduction was slow it

Figure 35. Kinetics of Cr oxidation by $\delta\text{-MnO}_2$ in the presence of leather dust fulvic acid over a short time period.

Figure 36. Kinetics of Cr oxidation by $\delta\text{-MnO}_2$ in the presence of leather dust fulvic acid over a long time period.

Figure 37. Kinetics of Mn reduction by leather dust fulvic acid.

is apparent that if the soluble organic matter concentration is high enough, MnO_2 coatings in the soil can be destroyed thereby eliminating the danger of Cr oxidation. High soluble organic matter concentrations are expected in reduced soils high in organic matter content.

SUMMARY AND CONCLUSIONS

As a result of atmospheric testing of nuclear devices at the Nevada Test Site in southern Nevada, the soil and vegetation of several areas on the test site are contaminated with transuranic elements, particularly Pu and Am. Although particulate movement through erosion by the forces of wind and water is the most important mechanism of dispersing Pu at the test site, there is some evidence of Pu migration through some soil profiles perhaps due to dispersion of water soluble species. Under the direction of the Nevada Applied Ecology Group of the U.S. Department of Energy, a program is being developed to monitor the dispersion and bioavailability of transuranics, especially Pu, in the environment.

However, because Pu is toxic, usually insoluble, not uniformly distributed in the soil, and can exist in four oxidation states in the environment, it is a difficult element to study. Therefore, Cr reactions in soil were investigated as a possible general model for Pu reactions in soil, since it was postulated that the redox chemistries of the two elements should be similar. An evaluation of data from the literature indicated that the reduced forms of both elements are usually relatively immobile in soils while the oxidized forms are usually relatively mobile and hence more bioavailable. The redox chemistries of both elements appear to be controlled by organic matter, minerals containing Fe(II), and manganese oxides. Thermodynamic calculations revealed that both elements should be highly soluble in the presence of manganese oxides. In addition, the solubility of Pu can be enhanced by radiolytic oxidation. Reduction of both elements by organic matter and oxidation of Cr by manganese oxides have already been demonstrated, and it was postulated

that the conditions necessary for oxidation of Pu by manganese oxides exist in Nevada Test Site soils. These conditions are low organic matter levels and negligible amounts of Fe(II) in order to avoid reduction of Pu and high levels of HCO_3^- and the presence of manganese oxides in order to form the $\text{PuO}_2\text{CO}_3\text{OH}^-$ species.

In the present study, chemical fractionation methods were used to determine the redox states of Pu in a Nevada Test Site soil and the amounts of Pu associated with various soil components in order to deduce possible reactions between the various Pu species and soil components so that weathering and dispersion by chemical mechanisms can be predicted. Chemical fractionation and kinetics experiments were performed to study reactions of Cr with soil, manganese oxides, and fulvic acids in order to provide information to eventually develop a qualitative, predictive model for Pu reactions in soil.

The results of the experiments in this thesis, as well as those from other investigators, lead to the following conclusions by the author regarding the general behavior of Cr and Pu in soils as summarized by the diagrams in Figures 38 and 39.

- 1) Plutonium oxide is thermodynamically unstable in many soil environments as calculations revealed. However, PuO_2 is resistant to weathering since all the available evidence indicates that weathering is slow and reagents that should dissolve PuO_2 are able to extract only a small fraction of the total soil Pu. This is especially true of NTS soils. The Pu that is extracted is probably initially sorbed to soil surfaces.
- 2) The Pu(IV) released by the weathering of PuO_2 can undergo several possible reactions. Two of these reactions are sorption to iron

Figure 38. Idealized diagram of Pu reactions in soil.

Figure 39. Idealized diagram of Cr reactions in soil.

oxides and the formation of stable soluble and insoluble complexes with organic matter. The Pu remains in a reduced state in these reactions. These types of reactions are normally considered fast.

- 3) If the PuO_2 particles are large enough, then radiolytic oxidation can occur. If the particles are submicron in size, then oxidation is probably caused by manganese oxides. Carbonate complexes can form and be oxidized. The available evidence indicates that the oxidation of solution Pu species is relatively fast on a geologic time scale of hundreds to thousands of years. Thus, the rate limiting step in the weathering of PuO_2 must be the breakdown of the PuO_2 lattice and initial formation of the soluble Pu species.
- 4) Once oxidized Pu species are formed they are available to migrate through the soil profile, become sorbed to soil components without reduction, or be reduced by minerals containing Fe(II) and/or organic matter. Reduction and sorption by minerals with Fe(II) and/or organic matter would serve to effectively immobilize the weathered Pu. Thus, some enrichment of Pu in these soil components is to be expected.
- 5) The immediate bioavailability of Pu would seem to be dictated by the presence of the relatively more mobile oxidized Pu species which are controlled by manganese oxides and/or radiolytic effects. Mobilization of Pu by way of oxidation would serve to deliver Pu to the plant root vicinity. Reduction by root exudates and other organic matter would then undoubtedly occur. The mobility near the root would then be controlled by soluble organo-Pu complexes.
- 6) When soluble Cr(III) is added to soils several reactions are possible. If the solubility of Cr(III) is exceeded, Cr(OH)_3 can be formed.

The formation of $\text{Cr}(\text{OH})_3$ likely occurs fairly rapidly, but dissolution appears to be slow even under conditions favoring dissolution.

- 7) Sorption of $\text{Cr}(\text{III})$ by iron oxides and formation of soluble and insoluble complexes with organic matter also occur. The organo-Cr complexes appear especially stable to oxidation and other forms of weathering.
- 8) The $\text{Cr}(\text{III})$ not sorbed by iron oxides and organic matter is oxidized by soil manganese oxides. Oxidation is relatively fast, but complete oxidation is not achieved if the mineral surface available for oxidation is limited.
- 9) Reduction of $\text{Cr}(\text{VI})$ by organic matter will eventually dominate, but significant levels of $\text{Cr}(\text{VI})$ can persist for weeks.
- 10) Immediate bioavailability of Cr would be controlled through oxidation by manganese oxides, but long-term control would probably be exerted by organic matter and iron oxides. Some enrichment in these soil components is to be expected.
- 11) Qualitatively, it appears that much of the soil chemistry of Cr is sufficiently similar to that of Pu, so that it could be used as a general model for Pu behavior in soil under certain conditions. This is supported by the fact that even though soils with dissimilar properties were used in the experiments, both elements underwent similar reactions. However, there are insufficient data available for both elements to formulate a mathematical model for Pu dispersion based on experiments with Cr.
- 12) The main points of similarity between Cr reactions in soil and Pu reactions in soil are:

- a) Even though the oxides and hydroxides of both elements are unstable in many soil environments they are resistant to weathering so dissolution is slow.
 - b) The lower valence states of both elements can be sorbed by iron oxides and other soil minerals and can form stable soluble and insoluble organometallic complexes. In these forms the elements cannot be oxidized by manganese oxide minerals.
 - c) Even though the total amounts and concentrations of Cr would typically be higher in cases of Cr contamination of soils than in cases of Pu contamination, only a small fraction of the amount of each element is oxidized by manganese oxide minerals.
 - d) The oxidation of Cr and Pu by manganese oxides could effectively serve to deliver these elements to the vicinity of plant roots for possible uptake.
- 13) Major points of difference between the two elements are:
- a) If the Cr concentration is high enough, the amount of Cr oxidized can be limited by the amount of MnO_2 surface area available for oxidation. It is doubtful that Pu concentrations in soil solutions would ever be high enough to use up the available MnO_2 surface area.
 - b) Radiolytic effects from PuO_2 are absent from Cr.

LITERATURE CITED

- Allison, L. E. 1965. Organic carbon. In C. A. Black (ed.) Methods of soil analysis. Part II: Chemical and microbiological properties. Agronomy Monograph 9:1367-1378. Am. Soc. of Agron., Madison, Wis.
- Anderson, J. V. 1963. An improved pretreatment for mineralogical analysis of samples containing organic matter. *Clays Clay Miner.* 10:380-388.
- Baes, C. F., Jr. and R. F. Mesmer. 1976. The hydrolysis of cations. John Wiley and Sons, New York.
- Baker, D. E., M. C. Amacher, and W. T. Doty. 1977. Monitoring sewage sludges, soils, and crops for zinc and cadmium. p. 261-281. In R. C. Loehr (ed.) Proc. 1976 Cornell Agri. Waste Mngmt. Conf. Rochester, N.Y. Oct. 1976. Ann Arbor Science, Ann Arbor, Mich.
- Baker, D. E., M. C. Amacher, and R. M. Leach. 1979. Sewage sludge as a source of cadmium in soil-plant-animal systems. *Environ. Health Persp.* 28:45-49.
- Baker, D. E., K. K. S. Pillay, A. W. Rose, and E. J. Ciolkosz. 1978. Development of an approach for monitoring the plant availability of transuranics in Nevada Test Site soils. p. 157-176. In M. G. White and P. B. Dunaway (eds.) Selected environmental plutonium research reports of the NAEG. USDOE Rep. NVO-192.
- Barber, S. A. 1962. A diffusion and mass-flow concept of soil nutrient availability. *Soil Sci.* 93:39-45.
- Bartlett, R. J. 1981. Oxidation-reduction status of aerobic soils. p. 77-102. In R. H. Dowdy (ed.) Chemistry in the soil environment. ASA Special Publication No. 40. Am. Soc. of Agron., Madison, Wis.
- Bartlett, R. J. and B. James. 1979. Behavior of chromium in soils: III. Oxidation. *J. Environ. Qual.* 8:31-35.
- Bartlett, R. J. and B. James. 1980. Studying dried, stored soil samples--some pitfalls. *Soil Sci. Soc. Am. J.* 44:721-724.
- Bartlett, R. J. and J. M. Kimble. 1976a. Behavior of chromium in soils: I. Trivalent forms. *J. Environ. Qual.* 5:379-383.
- Bartlett, R. J. and J. M. Kimble. 1976b. Behavior of chromium in soils: II. Hexavalent forms. *J. Environ. Qual.* 5:383-386.
- Bondietti, E. A. and S. A. Reynolds. 1976. Field and laboratory observations on plutonium oxidation states. p. 505-537. In L. L. Ames (ed.) Proc. Workshop on Actinide-Sediment Interactions. Seattle, Wash. 10-11 Feb. 1976. Battelle Pacific Northwest Lab, Richland, Wash. USDOE Rep. BNWL-2117.

- Bondietti, E. A., S. A. Reynolds, and M. H. Shanks. 1975. Interactions of plutonium with complexing substances in soils and natural waters. p. 273-287. In Int. Atomic Energy Agency, Vienna (ed.) Transuranium nuclides in the environment. IAEA-SM-191/51.
- Bondietti, E. A. and F. H. Sweeton. 1977. Transuranic speciation in the environment. p. 449-476. In M. G. White and P. B. Dunaway (eds.) Transuranics in natural environments. Proc. Symp. on Transuranics in Terrestrial and Aquatic Environ. Gatlinberg, Tenn. 5-7 Oct. 1976. USDOE Rep. NVO-178.
- Bremner, J. M. and H. Lees. 1949. Studies on soil organic matter: II. The extraction of organic matter from soil by neutral reagents. J. Agr. Sci. 39:274-279.
- Chao, L. L. 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. Soil Sci. Soc. Am. Proc. 36:764-768.
- Cleveland, J. M. 1970. The chemistry of plutonium. Gordon and Breach Sci. Publ., New York.
- Dahlman, R. C., E. A. Bondietti, and L. D. Eyman. 1976. Biological pathways and chemical behavior of plutonium and other actinides in the environment. p. 47-80. In A. M. Friedman (ed.) Actinides in the environment. Am. Chem. Soc. Symp. Series No. 35. Am. Chem. Soc., Washington, D.C.
- Doty, W. T., D. E. Baker, and R. F. Shipp. 1977. Chemical monitoring of sewage sludge in Pennsylvania. J. Environ. Qual. 6:421-426.
- Essington, E. H., R. O. Gilbert, L. L. Eberhardt, and E. B. Fowler. 1976. Plutonium, americium, and uranium concentrations in Nevada Test Site soil profiles. p. 157-173. In Int. Atomic Energy Agency, Vienna (ed.) Transuranium nuclides in the environment. IAEA-SM-199/76.
- Fiskell, J. G. A. 1965. Copper. In C. A. Black (ed.) Methods of soil analysis. Part II: Chemical and microbiological properties. Agronomy Monograph 9:1078-1089. Am. Soc. of Agron., Madison, Wis.
- Gardner, W. H. 1965. Water content. In C. A. Black (ed.) Methods of soil analysis. Part I: Physical and mineralogical properties. Agronomy Monograph 9:82-127. Am. Soc. of Agron., Madison, Wis.
- Garrels, R. M. and C. L. Christ. 1965. Solutions, minerals, and equilibria. Freeman, Cooper, and Co. San Francisco, Cal.
- Grove, J. H. and B. G. Ellis. 1980. Extractable chromium as related to soil pH and applied chromium. Soil Sci. Soc. Am. J. 44:238-242.
- Healy, T. W., A. P. Herring, and D. W. Fuerstenau. 1965. The effect of crystal structure on the surface properties of a series of manganese dioxides. J. Coll. Interf. Sci. 21:435-444.

- Jacobsen, L. and R. Overstreet. 1948. The uptake of plutonium and some products of nuclear fission adsorbed on soil colloids. *Soil Sci.* 65:129-134.
- Lavkulich, L. M. and J. H. Wiens. 1970. Comparison of organic matter destruction by H_2O_2 and $NaOCl$ and its effect on selected mineral constituents. *Soil Sci. Soc. Am. Proc.* 34:755-758.
- Leavitt, V. D. 1970. Soil survey of Area 18, Nevada Test Site. Public Health Service. USDHEW, Washington, D.C.
- Lindsay, W. L. 1979. Chemical equilibria in soils. John Wiley and Sons, New York.
- Loganathan, P. and R. G. Burau. 1973. Sorption of heavy metal ions by a hydrous manganese oxide. *Geochim. Cosmochim. Acta.* 37: 1277-1293.
- McKenzie, R. M. 1977. Manganese oxides and hydroxides. p. 181-193. In J. B. Dixon and L. B. Weed (eds.) *Minerals in soil environments*. Soil Sci. Soc. of Am., Madison, Wis.
- Mehra, O. P. and M. L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system with sodium bicarbonate. *Clays Clay Miner.* 7:317-327.
- Morgan, J. J. and W. Stumm. 1964. Colloid-chemical properties of manganese dioxide. *J. Colloid Sci.* 19:347-359.
- Mubarak, A. and R. A. Olsen. 1976. Immiscible displacement of the soil solution by centrifugation. *Soil Sci. Soc. Am. Proc.* 40: 327-329.
- Murray, D. J., T. W. Healy, and D. W. Fuerstenau. 1968. The adsorption of aqueous metal ions on colloidal manganese oxide. *Adv. Chem. Ser.* 79:74-81.
- Pearre, N. C. and A. V. Heyl. 1960. Chromite and other mineral deposits in serpentine rocks of the Piedmont Upland Maryland, Pennsylvania, and Delaware. U.S. Geol. Sur. Bull. 1082-K. U.S. Gov. Printing Office, Washington, D.C.
- Posselt, H. S., F. J. Anderson, and W. J. Weber, Jr. 1968. Cation sorption on colloidal hydrous manganese dioxide. *Environ. Sci. Tech.* 2:1087-1093.
- Rai, E. and R. J. Serne. 1977. Plutonium activities in soil solutions and the stability and formation of selected plutonium minerals. *J. Environ. Qual.* 6:89-95.
- Rai, D. R., R. J. Serne, and D. A. Moore. 1980. Solubility of plutonium compounds and their behavior in soils. *Soil Sci. Soc. Am. J.* 44:490-495.

- Rai, D., R. J. Serne, and J. L. Swanson. 1980. Solution species of plutonium in the environment. *J. Environ. Qual.* 9:417-420.
- Stevenson, F. J. 1965. Gross chemical fractionation of organic matter. In C. A. Black (ed.) *Methods of soil analysis. Part II: Chemical and microbiological properties.* Agronomy Monograph 9:1409-1421. Am. Soc. of Agron., Madison, Wis.
- Tamura, T. 1974. Distribution and characterization of plutonium in soils from the Nevada Test Site. p. 29-42. In M. G. White and P. B. Dunaway (eds.) *The dynamics of plutonium in desert environments.* USDOE Rep. NVO-142.
- Tamura, T. 1975. Characterization of plutonium in surface soils from Area 13 of the Nevada Test Site. p. 27-41. In M. G. White and P. B. Dunaway (eds.) *The dynamics of plutonium in desert environments.* USDOE Rep. NVO-153.
- Taylor, R. M. and R. M. McKenzie. 1966. The association of trace elements and manganese minerals in Australian soils. *Aust. J. Soil Res.* 4:29-39.
- United States Environmental Protection Agency. 1980. Reviews of the environmental effects of pollutants: III. Chromium. ORNL/EIS-80. EPA-600/1-78-023.
- Wedepohl, K. H. (ed.). 1970. *Handbook of geochemistry.* Springer-Verlag, Berlin.
- White, M. G. and P. B. Dunaway (eds.). 1975. *The radioecology of plutonium and other transuranics in desert environments.* USDOE Rep. NVO-153.
- White, M. G. and P. B. Dunaway (eds.). 1976. *Studies of environmental plutonium and other transuranics in desert ecosystems.* USDOE Rep. NVO-159.
- White, M. G. and P. B. Dunaway (eds.). 1977a. *Environmental plutonium on the Nevada Test Site and environs.* USDOE Rep. NVO-171.
- White, M. G. and P. B. Dunaway (eds.). 1977b. *Transuranics in desert ecosystems.* USDOE Rep. NVO-181.
- White, M. G. and P. B. Dunaway (eds.). 1978. *Selected environmental plutonium research reports of the NAEG.* USDOE Rep. NVO-192.
- Wong, K. M., V. E. Noshkin, and T. A. Jokela. 1978. Preconcentration of plutonium radionuclides from natural waters. p. 583-592. In M. G. White and P. B. Dunaway (eds.) *Selected environmental plutonium research reports of the NAEG.* USDOE Rep. NVO-192.