BNWL-1196

UC-70

3 -

11-69

AN EVALUATION OF PREDICTIVE METHODS
OF DETERMINING THE EFFECTS
OF SOLID-LIQUID PHASE INTERACTIONS
ON THE MOVEMENT OF SOLUTES IN SOILS

November 1969

AEC RESEARCH &
DEVELOPMENT REPORT

NAME TO	P.R.NO.	LOCATION	FILED UNDER

BNWL-1196

BATTELLE

NORTHWEST

BATTELLE MEMORIAL INSTITUTE

PACIFIC NORTHWEST LABORATORIES

BATTELLE BOULEVARD, P. O. BOX 999, RICHLAND, WASHINGTON 99352

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

operated by

BATTELLE MEMORIAL INSTITUTE

for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

3 3679 00061 8324

BNWL-1196
UC-70, Waste Disposal
and Processing

AN EVALUATION OF PREDICTIVE METHODS
OF DETERMINING THE EFFECTS OF SOLID-LIQUID
PHASE INTERACTIONS ON THE MOVEMENT OF SOLUTES IN SOILS

By

R. C. Routson
Water and Land Resources Department
Environmental and Life Sciences Division

November 1969

NOT UNRESTRICTED
CLASSIFICATION

DEC 5 '69

BATTELLE MEMORIAL INSTITUTE
PACIFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON 99352

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

TABLE OF CONTENTS

INTRODUCTION	1
SUMMARY	1
RESULTS AND DISCUSSION	2
SINGLE DISPERSIVE MECHANISM MODELS	3
MULTIDISPERSIVE MECHANISM MODELS	4
RESEARCH PROGRAM	7
REFERENCES	9

AN EVALUATION OF PREDICTIVE METHODS OF
DETERMINING THE EFFECTS OF SOLID-LIQUID PHASE
INTERACTIONS ON THE MOVEMENT OF SOLUTES IN SOILS

INTRODUCTION

Development of a transport model for the prediction of the movement of radionuclides through the Hanford soils requires that all first-order solid-liquid phase interactions be mathematically described. Upon completion, the transport model will have the capability to predict the concentration of radionuclides as a function of time and space for the Hanford flow system within known limits of error. This report is a progress report, literature review, and evaluation of the work performed under part job 9-26 of the "Revised Critical Path Analysis of the Movement of Radionuclides Through Hanford Soils Research Program" (Water Resources Systems Section, 1968).

Solutes move in natural systems due to the convective movement of the transporting solution (solvent). In addition, other natural phenomena also act to control the movement of solutes relative to the transporting solution. These other phenomena are collectively entitled solute dispersion and include hydrodynamic dispersion, diffusion and solid phase sorption. This report predominately considers the effects of solid phase sorption on solute movement in porous natural media.

Hanford studies have shown that radionuclides are generally present in trace concentration and the presence of one solute radionuclide does not measurably affect the sorption of other solute radionuclides. In contrast the solution concentration of all the ions present in macroamounts does affect the sorption of trace components.⁽¹⁾ Thus, for any theoretical approach to describe adequately the sorption of trace solutes the solid-liquid interactions which control the solution concentration of macroions must also be described. With this as criteria, a review and evaluation of available sorption approaches was conducted.

SUMMARY

An evaluation was made of the available methods, theories, and models which have been used to describe solid-liquid phase interactions which take

place in porous media. Only the discontinuous-fixed plate model of Dutt was found to be a multiton approach which prior work on the Hanfsrd project has shown to be necessary for a successful sorption description. The combination of Dutt's macroton approach and an empirical-statistical method of measuring trace radionuclide sorption was deemed to be the most fruitful approach for describing radionuclide concentration as a function of position and time. A computer program has been written and experiments have been designed to measure model parameters for testing the aforementioned approach.

RESULTS AND DISCUSSION

According to Hougen and Marshall [1], a completely general partial differential equation which entirely describes the movement of the ith solution component in a one-dimensional system is

$$-\bar{V}_x \frac{\partial c}{\partial x} + \epsilon \delta_i \frac{\partial c}{\partial x \partial x} + \frac{\partial}{\partial x} (D \epsilon \frac{\partial c}{\partial x}) = \frac{\partial c}{\partial t} + \frac{\beta}{\epsilon} \frac{\partial G_i}{\partial t} \quad [1]$$

where

$\bar{V}_x$ = average seepage velocity of solution

c = concentration of the ith component in liquid phase

δ_i = diffusion coefficient

D = hydrodynamic dispersion coefficient

G_i = concentration of the ith component in the solid phase

β = bulk density of the soil

ϵ = porosity of the soil

t = elapsed time.

Equation [1] is a mass balance expression which considers all possible fates of the ith solute component with respect to space and time. The first term of Equation [1] is a convective term which accounts for the changes in solution concentration due to the movement of the liquid phase. Term two is a diffusional term which accounts for the changes in solution concentration due to a concentration gradient. Term three is a hydrodynamic dispersion term which accounts for changes in solution concentration due to microdifferences in geometry causing dispersion on a microscale. The sum of the first three terms is equal to the rate of change of concentration with respect to time plus the change in solution concentration due to reactions with the solid phase with respect

to time. Solid phase reactions include all of the first-order sorption reactions including ion exchange, precipitation, and other surface sorption reactions. A general solution for Equation [I] would completely describe solid and liquid phase concentration of a given solute in both space and time.

Solute movement theories can be divided into two general categories; viz, those which consider only solid phase sorption as dispersive mechanisms and those which consider convection, diffusion, hydrodynamic dispersion and solid phase sorption as dispersive mechanisms.

SINGLE DISPERSIVE MECHANISM MODELS

Single dispersive mechanism theories include the plate theories of Glueckauf,⁽⁸⁾ Michaels,⁽¹⁶⁾ Thornwaite et al.,⁽¹⁸⁾ Dutt and Tanji,⁽⁵⁾ and the rate-plate theory of Vermeulen and Hiester.⁽¹⁹⁾ The theories of Meyer and Tompkin,⁽¹⁵⁾ Glueckauf, Michaels and Vermeulen and Hiester are all variable-plate, two or three parameter theories which include equilibrium and kinetic (nonequilibrium effects) parameters. These theories are generally designed to describe chromatographic separation in fixed beds and are based on linear sorption isotherms. The variable plate theories have proven to be adequate for fixed-bed, fixed flow rate, large particle-sized, and simple ion exchange systems where the effects of hydrodynamic dispersion and diffusion can be neglected or inferred. However, in low capacity natural soil systems the parameters obtained on small columns were found to be column length dependent. For any theory to be useful in describing the Hanford soil system, the system parameters must remain constant or be determinable as a function of column length to allow the extrapolation of short laboratory column data to the much longer Hanford project sediment column.⁽¹⁷⁾ Thus, none of these theories would seem to be useful for describing the soil reactions which take place on the Hanford project, which can be considered as a column many miles in length. In addition the assumption of a linear sorption isotherm has been shown to be inadequate for the Hanford soils.⁽¹⁾

The fixed plate theory of Thornwaite et al also assumes a linear sorption isotherm and was found to be inadequate by Frissel and Poelstra.⁽⁶⁾ Dutt's fixed plate model differs somewhat from the other plate theories: it is a one-dimensional discontinuous-model in which the number of theoretical plates

are preselected. In contrast to the other plate theories, Dutt's treatment is essentially a simulation model which considers all of the known first order chemical reactions which occur in natural soil systems. This model incorporates the exchange reactions of Ca, Mg, Na, and K, the solubility reactions of CaSO_4 , CaCO_3 , and the solution of readily soluble salts from an initially dry soil into the model. A further treatment of Dutt's model will be given later in this paper.

MULTIDISPERSIVE MECHANISM MODELS

Although no general solution for Equation [1] has been developed, a special solution has been found which describes limited systems.^(3,14,9) The special solution is:

$$C/C_0 = 1/2 \left(1 - \operatorname{erf} \left[\frac{x - \bar{V}_x \tau a}{2 \sqrt{D_m \bar{V}_x \tau / a}} \right] \right) \quad [2]$$

where

$$a = 1 + \frac{\beta - \theta}{\theta} K_d$$

C = effluent concentration of radionuclide

C_0 = influent concentration of radionuclide

β = bulk density of exchanger

θ = pore fraction in the exchanger

K_d = equilibrium distribution coefficient between the solid and liquid phase

D_m = dispersion coefficient

$\bar{V}_x$ = average solution velocity

x = distance from the influent end of the column

τ = elapsed time measured from initial disposal

Equation [2] considers that hydrodynamic dispersion and diffusion can be accounted for with a single dispersion coefficient. In addition, several other assumptions must be met for Equation [2] to be valid including: 1) the porosity of the exchanger must remain constant, 2) the K_d must remain constant in both time and space; 3) the column's solution and solid phases must be at instantaneous equilibrium; 4) the flow rate must remain constant. Any deviation from the above conditions will result in an error between measurement and theory.

The first condition that the porosity must remain constant throughout the column requires that the exchanger packing be uniform. Errors of 0.01 and 0.2

in porosity cause errors of 3% and 31% in C/C_0 , respectively. Thus, the column homogeneity is critical. For sands this source of error will be relatively minor, but for heavier sediments this error may severely limit the usefulness of the equation

The second condition that the equilibrium constant (K_d) must remain constant in space and time requires that the exchange capacity be homogeneous with respect to column Length, and the accompanying ions in solution be in continuous equilibrium with the solid phase. This latter condition is not often met in field systems. For example, at Hanford waste solutions which contain essentially Na^+ are disposed through an exchanger which is initially Ca^{++} saturated, and ion exchange decreases the solution concentration of Na^+ , while increasing the solution concentration of Ca^{++} .

The condition that equilibrium between solid and liquid phases must occur at all points in the column requires that the flow rate be less than some given rate. This given rate is probably a function of both the exchange capacity and the texture of the sediment. In addition, this given flow rate may not be a constant at all points on a given breakthrough curve, as is evidenced by the tendency of many measured breakthrough curves to be asymmetrical^(17, 7, 9). However, equilibrium is probably generally occurring in natural flow systems.

The final condition that a steady-flow rate must be maintained is attained in laboratory columns but seldom strictly attained in natural field systems. When all of the above conditions occur good agreement is obtained between measured and predicted (Equation [2]) breakthrough.^(2, 14, 9)

Houghton⁽¹³⁾ used a diffusional approach to obtain a solution for Equation [1]. It was assumed that sorption would be adequately described by a nonlinear isotherm of the form

$$q = K_1 + K_2 C + K_3 C^2 \quad [3]$$

where

q = amount of radionuclide sorbed in the solid phase

K_1, K_2, K_3 = empirical constants for curve matching

C = concentration of radionuclide in solution

A complex solution was obtained:

$$C/C_0 = \{\exp(g)[\operatorname{erf}(p + h) - \operatorname{erf}(g + h)]\} / \{1 - \operatorname{erf}(p) + \exp(g)[\operatorname{erf}(p + h) - \operatorname{erf}(g + h)] + \exp(m)[1 + \operatorname{erf}(g)]\}$$

where

$$p = \frac{X}{2(D_x t)^{1/2}}$$

$$q = \frac{X}{2(D_x t)^{1/2}}$$

$$g = \frac{\lambda n C_0 \bar{V}_x R_F}{4 D_x t}$$

$$h = \frac{\lambda n C_0 \bar{V}_x R_F}{2(D_x t)^{1/2}}$$

$$m = \frac{\lambda n C_0 \bar{V}_x R_F}{2 D_x}$$

$$\lambda n = 2K_3 / \theta(1 + K_2)$$

θ = fractional pore size

$\bar{V}_x$ = average liquid flow velocity

$$R_F = 1 / (1 + K_d \beta / \theta)$$

K_d = equilibrium distribution coefficient

β = bulk density

t = elapsed time

D_x = dispersion coefficient

X = distance from influent end of the column.

In Houghton's treatment the nonlinearity coefficients result from a knowledge of the exact shape of the sorption isotherm and his solution is valid only if this form holds. Studies of sorption of radionuclides on the Hanford project show that Cs and Sr sorption can not be described by an equation of the form of Equation [3] and thus this model would seem to be inadequate.

In conclusion, all of the models previously discussed above, except the simulation model of Dutt, assume that the sorption of radionuclides is a determinable function only of the concentration of the respective nuclide in solution and of the composition of the solid phase upon which sorption takes place. However, it has been demonstrated that this is an unwarranted assumption for the Hanford Project soils. Hajek and Ames⁽¹¹⁾ showed that the equilibrium distribution coefficients (Kd) for Sr and Cs were a function of all of the cations in solution including Na^+ , K^+ , Ca^{++} , Mg^{++} , and H^+ . These authors also developed an empirical technique to predict the sorption of radioactive Sr and Cs on a given soil as a function of solution concentration of the macroions. Thus, any model which fails to determine the solution concentration of all of the macroions can be expected to give only an approximation of sorption of radionuclides in soils. Therefore, the simulation model of Dutt was selected as giving the greatest chance of successfully describing the solution and soil phase concentrations of macroions, and a research program was initiated to develop a model for radionuclide sorption, based on his model, which later could be incorporated into the transport model,

RESEARCH PROGRAM

The following research program is designed to integrate the fixed plate model of Dutt which describes the distribution of macroions in solution and solid phases with the statistical-empirical method of Ames and Hajek which predicts the sorption of trace ions (radioactive ions) for a given exchanger as a function of the solution concentration of macroions. These two models are described more completely below.

Dutt's model divides a column of dry homogeneous soil of length L and of unit cross sectional area along the X coordinate into n equal segments AX in length, then

$$L = \sum_{i=1}^n \Delta X_i \quad [4]$$

where i is a variable which denotes the segment number. The concentration of the solutes entering the column are designated as $C_1, C_2, C_3, \dots, C_J$

where j denotes the number of the species present. If the amount of solution q in each segment i is identical during percolation, the final concentration of component j , C_j^1 ; in the first aliquot q_1 , coming from the column will be

$$C_j^1 = C_j + \sum_{i=1} \Delta C_i; \quad [5]$$

where ΔC_i is the change in concentration of solute j when aliquot q_1 is equilibrated with the solid phase in segment i . By the application of known ion-exchange, carbonate, sulfate, and solution ion interaction equilibria and use of an iterative computer program the breakthrough and column distribution of macroions can be described.⁽⁴⁾ Thus, Dutt's procedure is essentially a discontinuous, equilibrium procedure in which a pore volume of solution containing up to several solutes is equilibrated with a fixed volume of soil in a column and is then moved successively to all following segments and equilibrated with the solid phase in each of these segments.

The Ames and Hajek statistical-empirical sorption technique is a two-level factorial design method in which the sorption of radionuclides is measured as a function of the concentration of all solution ions. Sorption of radionuclides is measured by directly counting small columns equilibrated with given radionuclide and solute concentrations. This procedure can be used to derive a linear equation in which the sorption of radionuclides is given as a function of all macroion concentrations. To be valid, the range of macroion concentration must be small enough that a linear equation does adequately describe the sorption,

By combining this empirical technique with Dutt's model, the sorption of radionuclides in a column can be predicted. Dutt's technique will be used to describe the concentration of all the macroions in each segment as a function of column distance and time (aliquot added) and the empirical sorption equations will then be used to describe the sorption of a given radionuclide in each segment as a function of column distance and time. A computer program has been written to integrate these two techniques,

Experiments will be designed to evaluate all the equilibrium parameters in Dutt's model and to measure the sorption of radionuclides as a function of macroion concentration,

REFERENCES

1. L. L. Ames, Jr. and B. F. Hajek. Statistical Analysis of Cesium and Strontium Adsorption on Soils, BNWL-CC-539, Battelle-Northwest. 1966.
2. L. J. Baetsele. "Computational Methods for the Prediction of Underground Movement of Radionuclides." Nuclear Safety, 8:576-588. 1967.
3. R. B. Banks and S. Jerasate. "Dispersion in Unsteady Porous Media Flow." J. Hydraulic Div., Proc. Am. Soc. Civil Eng., 88 HY3:1-22. 1962.
4. G. R. Dutt. "Effects of Small Amounts of Gypsum in Soils on the Solutes in Effluents." Soil Sci. Soc. Amer. Proc., 28:754-757. 1964.
5. G. R. Dutt and K. K. Tanji. "Predicting Concentrations of Solutes in Water Percolated Through a Column of Soil." J. Geophys. Res., 67:3437-3439. 1963.
6. M. J. Frissel and P. Poelstra. "Chromatographic Transport Through Soils. II. Column Experiments with Sr and Ca Isotopes," Plant and Soil, 27: 20-32. 1967.
7. H. S. Gile. The Application of Some Ion Exchange Theories to the Adsorption of Trace Elements. HW-32461 TH. Available from Clearinghouse for Federal Scientific and Technical Information, U.S. Dept. of Commerce, Springfield, Virginia, 1954.
8. E. Glueckauf. "Principles of Operation of Ion Exchange Columns, in Ion Exchange and Its Applications," Society of the Chemical Industry, p. 34-36, London, England. 1955.
9. B. F. Hajek. Dispersion Characteristics of Strontium in Soil Column, BNWL-235-3. Battelle-Northwest. 1966.
10. B. F. Hajek. Unpublished Data. Battelle-Northwest, 1968. (preliminary Report: Waste Disposal to the Ground at 100-N) .
11. B. F. Hajek and L. L. Ames. Trace Strontium and Cesium Equilibrium Distribution Coefficients: Batch and Column Determinations, BNWL-SA-843. Battelle-Northwest. 1968.
12. O. A. Hougen and W. R. Marshall, Jr. "Adsorption from a Fluid Stream Flowing Through a Stationary Granular Bed," Chem. Eng. Progr., 43:197-208. 1947.
13. G. Houghton. "Band Shapes in Non-Linear Chromatography with Axial Dispersion," J. Phys. Chem., 67:84-88. 1963.
14. Y. Ionue and W. J. Kaufmann. Studies of Injection Disposal, TID-7628. 1962.

15. S. W. Meyer and E. R. Tompkin. "Ion Exchange as a Separations Method. IV. A Theoretical Analysis of the Column Separation Process." Jour. Amer. Chem. Soc., 69:2866-2874. 1947.
16. A. S. Michaels "Simplified Method of Interpreting Kinetic Data in Fixed-Bed Ion Exchange," Indust. and Eng. Chem., 44:1922-1930. 1952.
17. J. L. Nelson. Soil Column Studies with Radiostrontium. I. Effects of Temperature and Accompanying Ions, HW-62035. 1959.
18. C. W. Thornwaite, J. R. Mather, and J. K. Nakamura. "Movement of Radiostrontium in Soil," Sci., 131:1015-1019. 1960.
19. T. Vermeulen and N. K. Hiester. "Ion Exchange Chromatography of Trace Components," Ind. Eng. Chem., 44:636-651. 1952.
20. Water Resources Systems Section, Water and Land Resources Dept. Unpublished Data. Battelle-Northwest, 1968. (preliminary Data: Critical Path Analysis of the Movement of Radionuclides Through Hanford Soils Research program).

DISTRIBUTION

Number
of Copies

OFFSITE

1 AEC Chicago Patent Group

G. H. Lee

178 AEC Division of Technical Information Extension

ONSITE-HANFORD

1 AEC Chicago Patent Group

R. K. Sharp (Richland)

2 AEC RDT Site Representative-PNL

3 AEC Richland Operations Office

C. L. Robinson

O. J. Elgert (2)

14 Atlantic Richfield Hanford Company

S. J. Beard

G. E. Benedict

D. J. Brown (6)

W. L. Godfrey

G. I. Hanson

R. E. Isaacson

L. M. Richards

P. W. Smith

R. E. Tomlinson

39 Battelle-Northwest

F. W. Albaugh

E. I. Alpen

R. E. Burns

D. B. Cearlock

J. J. Fuquay

W. A. Haffey

B. W. Mercer

D. E. Olesen (3)

R. C. Routson (20)

C. J. Townhill

R. E. Wildung

Technical Information Files (5)

Technical Publications (1)

Battelle Memorial Institute