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Migration of Actinide Elements
in Representative U.S. Soils

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Abstract

Diffusion data indicate the Am, Cm, and Np migrate 1.2, 0.8, and 26 centimeters, respectively, in a thousand years. Thus, excluding mass transport by moving water or wind, actinide elements, such as Cm, Am, and Np that find their way to the soil-aquatic environment are relatively immobile. Measured diffusion coefficients, corrected for distribution between the aqueous and soil phases, tortuosity, negative absorption, and relative fluidity are in reasonable agreement with aqueous diffusion coefficients. However, agreement depends strongly on measurement method used to determine distribution ratios.

INTRODUCTION

Knowledge about the mobilities of actinide elements in the ground-water environment is essential for the evaluation of potential radiological hazards associated with the release of radionuclides from nuclear facilities. In the absence of mass transport by water or wind, determinations of cationic diffusion coefficients of actinide elements provide limiting estimates of the rates that radioelements may migrate in the soil-aquatic environment. This research was initially directed toward the measurement of diffusion coefficients of the actinide ions in the soil-aquatic environment with the objective of establishing limiting migration rates of these radionuclides in representative U.S. soils. Another objective was to calculate aqueous diffusion coefficients for actinide ions using their diffusion coefficients in moist soils, distribution ratios or K_d 's and other data. However, recent research (1,2) has demonstrated that a continuum of actinide species--ions, humic acid complexes and larger and less mobile actinide-bearing soil colloids--are transported through the soil-aquatic environment. The evidence for a continuum of species makes it very difficult to obtain aqueous diffusion coefficients from these measurements, but it is still possible to determine the distance that a continuum of actinide species can migrate in a moist soil in a given time in the absence of flowing water.

MATERIALS AND METHODS

Table I summarizes the physical and chemical properties of the soils used. The radiochemical and chemical purity of the ^{241}Am , ^{244}Cm , and ^{237}Np were established by conventional methods (2,3). Gamma and x-ray counting were done with Si(Li) and Ge(Li) detectors (2). All samples were counted

at least twice and counting times were such that errors were generally less than 3%.

MIGRATION MEASUREMENTS

Migration experiments for $^{241}\text{Am}(\text{III})$, $^{244}\text{Cm}(\text{III})$ and $^{237}\text{Np}(\text{V})$ were similar to those used to measure diffusion coefficients of $\text{Zn}(\text{III})(4)$, $\text{Fe}(\text{III})(5)$, $\text{Pu}(\text{IV})(6)$ in moist soils. Approximately 8.0 grams of soil were added to a vial containing 10 ml of distilled water and 25 μl of actinide tracer. A like amount of soil was also added to a vial containing 10 ml of water but no tracer. Vials were equilibrated on a shaker for three to four weeks. Subsequently, the solutions were centrifuged and the supernatant decanted. The water-saturated soils were loaded into Teflon half-cells. Tagged and untagged half-cells were prepared for each soil and subjected to identical pressures of approximately one bar to force out excess water, thereby ensuring that both half-cells had the same moisture tension and content. The cells were clamped together with a thin open-weave nylon netting separating them, and placed in a water-saturated atmosphere for approximately 30 days at room temperature to allow diffusion to take place.

At the end of the migration period, half-cells were separated, covered with a thin Teflon window, and counted with a $\text{Ge}(\text{Li})$ or $\text{Si}(\text{Li})$ spectrometer coupled to a 1024 channel analyzer to measure their radionuclide content.

To determine if the actinide tracer was transferred from the tagged to the untagged cell through accidental bulk transfer rather than diffusion, two half-cells, one containing ^{241}Am , were clamped together for approximately one hour, separated, and counted to determine the amount of $^{241}\text{Am}(\text{III})$ transferred. Less than 0.1% of the $^{241}\text{Am}(\text{III})$ was transferred to the

Table I. Physical and Chemical Properties of Soils Studied

soil code	sand, %	silt, %	clay, %	soil class	pH	C.E.C., mequiv/100 g	org material, %
MUS	12.6	65.8	21.6	silt loam	5.3	16.88	3.61
BUR	76.0	21.2	2.8	loamy sand	8.1	5.94	0.43
HF-A	65.2	29.0	5.8	sandy loam	8.1	6.14	0.45
HF-B	83.6	12.6	3.8	loamy sand	8.4	4.95	0.17
RITZ	32.0	56.0	12.0	silt loam	6.5	10.76	0.84
FO-1	91.2	7.8	1.0	sand	4.0	2.01	1.19
FO-2	91.6	5.4	3.0	sand	6.7	1.79	0.99
FO-3	94.6	1.6	3.8	sand	5.2	0.69	0.21
ID-A	42.6	39.4	18.0	loam	8.3	15.04	0.60
ID-B	60.4	19.4	20.2	sandy clay loam	8.4	10.44	0.18
ID-C	83.4	8.8	7.8	loamy sand	8.4	6.38	0.16
ID-D	49.2	28.4	22.4	sandy clay loam	7.7	18.36	0.98

untagged cell, compared to the 5 to 10% that normally diffuses from one cell to the other in 30 days, indicating minimal bulk transfer of $^{241}\text{Am}(\text{III})$.

Both ^{241}Am and ^{237}Np have gamma rays that can be easily counted with a Ge(Li) detector. The 40 keV gamma emitted by ^{244}Cm has a low abundance and because of a very large conversion ratio is very difficult to detect. Self-absorption precluded alpha counting, making it necessary to count ^{244}Cm L x-rays with an Si(Li) detector. Since ^{244}Cm x-rays are strongly attenuated by the soil, equations below were derived to correct for the self-absorption.

EQUATIONS USED TO CALCULATE DIFFUSION COEFFICIENTS

To calculate diffusion coefficients of x-ray emitting tracers such as ^{244}Cm , the normal equation used for the half-cell method (4,5,6) cannot be used because of the attenuation of the x-rays by the soil and must be modified to include corrections of x-ray attenuation. For the limiting case where $R \gg \sqrt{Dt}$, minimal diffusion of an x-ray emitting radionuclide from the tagged to untagged cell can be called as "low" diffusion with significant x-ray attenuation. Including exponential attenuation of the x-rays, the solution to the diffusion equation for this case is

$$\frac{C_2}{C_1} = \frac{1}{2} \frac{\{1 - e^{-\mu^2 Dt}\} [1 - \text{erf}(\mu\sqrt{Dt})]}{1 - e^{-\mu R}}, \quad (1)$$

where μ = x-ray attenuation coefficient, cm^{-1} ,

R = half-cell thickness, cm

C_1 = x-ray counting rate of tagged half-cell at time t ,

C_2 = x-ray counting rate of initially untagged half-cell at t seconds, and

D = apparent diffusion coefficient for soil under investigation.

For small values of $\mu\sqrt{Dt}$ and μ^2Dt , $\text{erf}(\mu\sqrt{Dt}) = 2\mu\sqrt{\frac{Dt}{\pi}}$ and $e^{\mu^2Dt} \rightarrow 1$, equation (1) becomes

$$D = \frac{\pi}{t} \left(\frac{1 - e^{-\mu R}}{\mu} \right)^2 \left(\frac{C_2}{C_1} \right)^2 \text{ cm}^2\text{sec}^{-1}. \quad (2)$$

Equation (2) and linear x-ray attenuation coefficients calculated for moist soils were used to calculate ^{244}Cm diffusion coefficients in Table II.

Two additional limiting cases can be obtained from equation (1). When $\mu R \rightarrow 0$, equation (1) reduces to

$$D \approx \frac{\pi}{t} R^2 \left(\frac{C_2}{C_1} \right)^2, \quad (3)$$

the equation used for most half-cell determinations of diffusion coefficients when gamma attenuation is negligible (4,5,6). When μR becomes very large, as it does for very low energy x-rays, $e^{-\mu R} \rightarrow 0$, and equation (1) becomes

$$D \approx \frac{\pi}{t} \frac{1}{\mu^2} \left(\frac{C_2}{C_1} \right)^2. \quad (4)$$

Equation (3) was used to calculate ^{241}Am and ^{237}Np diffusion coefficients found in Table II.

EXPERIMENTAL DATA

Examination of the data in Table II suggests: 1) For a given soil,

TABLE II

Apparent Diffusion Coefficients of a Continuum of $^{241}\text{Am}(\text{III})$,
 $^{244}\text{Cm}(\text{III})$, $^{237}\text{Np}(\text{V})$ in Moist U.S. Soils

		Am	Cm	Np
SOIL		cm^2/sec	cm^2/sec	cm^2/sec
silt loam	MUS	5.1×10^{-11}	1.4×10^{-11}	8.9×10^{-9}
loamy sand	BUR	5.0×10^{-11}	1.2×10^{-11}	2.3×10^{-8}
	HF-A	6.0×10^{-11}		3.0×10^{-8}
	HF-B	8.5×10^{-11}		
	Ave.(a)	$(6.5 \pm 1.8) \times 10^{-11}$		$(2.7 \pm 0.4) \times 10^{-8}$
silt loam	RITZ	1.4×10^{-11}	1.9×10^{-11}	2.3×10^{-8}
loam	ID-A	1.1×10^{-11}		5.0×10^{-9}
to	ID-B	$(3.4 \pm 2.3) \times 10^{-11}$	6.2×10^{-11}	
sandy				
clay loam	ID-C	$(6.1 \pm 4.3) \times 10^{-11}$	1.2×10^{-11}	2.3×10^{-9}
	ID-D	1.5×10^{-11}		
	Ave.(b)	$(3.8 \pm 2.3) \times 10^{-11}$		
sand	FUQ	$(4.8 \pm 5.5) \times 10^{-11}$	0.6×10^{-11}	$(5.5 \pm 3.9) \times 10^{-8}$
clay loam	AHN	6.1×10^{-11}		3.2×10^{-9}
clay loam	RKS	3.8×10^{-11}		3.8×10^{-9}
	Grand Ave. (c)	$(4.0 \pm 2.1) \times 10^{-11}$	$(2.1 \pm 2.1) \times 10^{-11}$	$(1.7 \pm 1.8) \times 10^{-8}$

a) Average of BUR, HF-A, and HF-B.

b) Average of ID-C and ID-D.

c) Grand average of all apparent diffusion coefficients.

the apparent diffusion coefficients are in reasonable agreement if relatively large measurement errors are accepted. Some abnormally low diffusion coefficients were thought to be caused by poor contact between the two half-cells. An average diffusion coefficient for Am(III) and Cm(III) is $(3.6 \pm 3.0) \times 10^{-11}$ cm²/sec, and compares favorably with the 3.0×10^{-11} cm²/sec (5) found for another plus three cation, Fe(III).

2) Diffusion coefficients for Am and Cm, and to a lesser extent Np, are independent of ^{soil} texture and other properties.

3) Within the rather large error limits for the Am and Cm data, these trivalent actinides have identical diffusion coefficients. Because Am and Cm are adjacent actinide elements, such agreement is expected.

4) The large difference between Np(V) and Am(III) and Cm(III) diffusion coefficients is due, most likely, to ionic charge and extensive humic acid complexing of Am(III) and Cm(III).

DISCUSSION

The most important information that can be obtained from Table II is the distance that an actinide migrates in a given time. This distance can be estimated by

$$\text{Distance} \sim \sqrt{Dt} \text{ cm} \quad (5)$$

where D is the observed diffusion coefficient. Using average diffusion coefficients in Table II, ²⁴¹Am, ²⁴⁴Cm, and ²³⁷Np will diffuse 1.2, 0.8, and 26 centimeters, respectively, in ¹⁰⁰⁰ Cm years, assuming that physical and chemical properties of the soil and these actinide elements are unchanged and there is no mass transport. From the standpoint of nuclear hazards, the

distances that these actinide elements migrate in a given time are by far the most important aspects of these measurements. Flowing water (7,8) or resuspension of dry actinide-bearing soils profoundly increase the mobility of these radioelements. Even without mass transport by water or wind, radioactive decay (7) and chemical factors such as complexing (2,9) and adsorption on mobile soil particles (1,2,10,11) must be considered. For example, in a thousand years an average of 48% of the $^{244}\text{Am}(\text{III})$ will be transformed into the more mobile ^{237}Np . Also, almost all of the ^{242}Cm and ^{244}Cm will have decayed to ^{238}Pu and ^{240}Pu , respectively. In the same time, less than 0.03% of the ^{237}Np will be transformed to ^{233}Pa .

Chemically, complex formation of ^{241}Am and ^{244}Cm by humic and fulvic acids should enhance the migration of these actinide cations, but the extent is unknown. The formation constant data of Bertha and Choppin (12) suggest that humic acid complexing has the potential to enhance the transport of $\text{Am}(\text{III})$, $\text{Eu}(\text{III})$ and presumably other actinide elements. However, complex formation of any $\text{Pu}(\text{IV})$ and $\text{Np}(\text{IV})$ may be important in other ways; for example, complex formation of any $\text{Np}(\text{IV})$ by humic acid certainly has the potential to shift the $\text{Np}(\text{V}) \rightarrow \text{Np}(\text{IV}) + \text{Np}(\text{VI})$ disproportionation reaction to the right.

However, these diffusion data can be used to obtain additional insights on the migration of cations in soils. In the absence of complicating factors, the porous and aqueous (or bulk) diffusion coefficients should be equal. Diffusion of cations in moist soils may be viewed as the migration from one site on the soil particle's surface to another through an intervening aqueous phase. Current models (2,4,7,11) incorporate those factors thought to inhibit cation migration: distribution between the soil and aqueous phases, tortuosity, retardation or negative adsorption factor, relative fluidity or

viscosity, complex formation, and adsorption on small-mobile soil particles. For most cations, the most important factor is the distribution between phases, which inhibits cation migration by a factor of 10 to 10⁴. It is expressed as a partition coefficient, K_d , or a distribution ratio, R . K_d (or R) are measures of the average relative time that a cation spends in one phase or the other. Actinides spend greater than 99.9% of their time attached to soil particles, thus any process that removes them from the soil phase is important. Complexing by humic acid and man-made compounds like nitrilo acetic acid, for example, reduce the average time that an actinide cation spends in the soil phase, thereby accelerating the migration of these radioelements. Experiments have demonstrated that a spectrum of particles ranging from uncomplexed ions, humic acid complexes, polymeric humic acid complexes, and actinide-bearing soil particles influence the determination of K_d s and R s. Thus, inclusion of these factors introduce uncertainties which vary with the measurement method used. Tortuosity, retardation, and relative fluidity collectively inhibit cation migration by a factor of about 0.5. The tortuosity factor, T , is usually most important and corrects for the longer path that cations traverse in the presence of soil particles and voids. Typically, tortuosity, which is related to the soil's moisture content, has a value of approximately 0.5 (13) to 0.8 (14). Other correction factors include the retardation or negative adsorption factor, γ , and a relative fluidity or viscosity factor, α . Depending on the soil, the product $T\gamma\alpha$ varies between 0.5 and 0.2 with an average of 0.4 (13). Thus the aqueous or bulk diffusion coefficient, D_0 , is related to the porous diffusion coefficient D_p by

$$D_p = D_0 T \gamma \alpha = D_{obs} K_d = \frac{D_{obs}}{R} .$$

Consequently, the bulk and observed diffusion coefficients of cations in moist soils are given by the equation

$$D_0 = \frac{D_{\text{obs}} K_d}{T\gamma\alpha} = \frac{D_{\text{obs}}}{RT\gamma\alpha}$$

If the D_0 obtained by the application of these correction factors agrees with directly measured diffusion coefficients, the model is considered satisfactory.

Now consider the following calculations of D_0 using distribution ratios determined by two different methods, gel filtration and centrifugation (1,2). Gel filtration distribution measurements probably yield close approximations to the K_d s of uncomplexed cations, because mobile cation complexes can be recognized and excluded from the K_d calculation. K_d s measured by methods employing centrifugation for phase separation include variable contributions from humic acid complexing and in some soils adsorption of cations on small, mobile soil particles. Examination of Table III clearly shows that K_d s determined by gel filtration are larger than those found by the centrifugation method, demonstrating the influence of humic acid complexing and adsorption of actinides on mobile soil particles. This comparison emphasizes the importance of the measurement methods used to determine K_d s and Rs and shows the relative insignificance of the $T\gamma\alpha$ correction factor.

Another approach for the interpretation of these K_d s is to consider a multi-group calculation of D_{mix} using particle size distributions similar to those found by Sheppard et al (2). In this case the particle size distribution would be broken into several groups to calculate an average diffusion coefficient, D_{mix} . Because the diffusion coefficient of a species is roughly inversely proportional to the square root of its molecular weight, D_{mix} should

Table III

Comparison of Aqueous Am(III) Diffusion Coefficients
obtained by the use of K_d s measured by Different Methods

Soil	D_{obs} (cm ² sec ⁻¹)	K_d (cm ³ g ⁻¹)	D_o (expt) cm ² sec ⁻¹ (a)	D_o calc.)(b)
IDB	3.4×10^{-11}	43500	4.0×10^{-6}	3.1×10^{-6}
		1660	1.4×10^{-7}	
Ritz	1.4×10^{-11}	3850	1.3×10^{-7}	3.1×10^{-6}
		1380	4.8×10^{-8}	
AHN	6.1×10^{-11}	35700	5.4×10^{-6}	3.1×10^{-6}
		10200	1.6×10^{-6}	
RKS	3.8×10^{-11}	23300	2.2×10^{-6}	3.1×10^{-6}
		1700	1.6×10^{-6}	

(a) D_o calculated using K_d s in column 2 and a value of 0.4 for $T_{\gamma\alpha}$ obtained from Van Schaik, Kemper, and Olsen (13).

(b) D_o was calculated with the Nernst equation relation (15).

(c) Measured using gel filtration (2).

(d) Centrifuge conditions used to measure K_d (or R) were: International 856 centrifuge head, 4500 rpm for 30 min., sampling depth of aqueous phase 4 ± 1 mm (1).

be less than D_0 . If D_{mix} rather than D_0 is used for comparisons, $T\gamma\alpha$ must be adjusted to a larger value. Such adjustments serve to emphasize the problems associated with the interpretation of the diffusion of a mixture of diffusing species in the soil-aquatic environment. More elegant interpretations await data not presently available.

CONCLUSIONS

Excluding mass transport by moving water or wind, actinide elements that find their way into the soil-aquatic environment are relatively immobile. Diffusion coefficient data indicate that Am, Cm, and Np migrate only a few centimeters in 10^3 years. Measured diffusion coefficients in moist soils can be related to aqueous value (D_0) if gel filtration distribution ratios (or K_d 's), tortuosity, etc., are taken into account. However, agreement depends strongly on the techniques employed to measure the K_d .

Finally, it should be mentioned that the centrifuge method may yield K_d 's that are closer approximations to natural conditions of the soil aquatic environment. The gel filtration method, however, comes closer to the measurement of distributions of uncomplexed cations and yields better estimates of D_0 .

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