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INFLUENCE OF HUMIC-ACID COMPLEXING
ON THE MOBILITY OF AMERICIUM
IN THE SOIL-AQUATIC ENVIRONMENT

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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.

Two sets of experiments with ^{241}Am and ^{152}Eu tracers have been done to measure distribution ratios as a function of the aqueous humic acid concentration. In the first experiments the solid phase was kaolinite and in the second series of distribution ratios were measured with Burbank sandy loam. Both of these experiments indicated that Am(III) and Eu(III) form very strong humic acid complexes with formation constants of approximately 10^5 . Additional experiments are being done to establish the average number of Am(III)s or Eu(III)s bound to the humic acid polymer.

I. Introduction

This period's research has had two principal components, the first involving the analysis of previous diffusion data for Am, Cm, and Np in several soils, and a second part dealing with the formation of the Am-humic acid complexes. The results of these research components are summarized below.

II. Results

The previous diffusion data for eight different soils were analyzed and the following conclusions were reached.

1) For a given soil the apparent diffusion coefficients, obtained from multiplicate experiments, were in reasonable agreement if the low diffusion coefficients ($\sim 3 \times 10^{-11}$ cm²/sec) and the relatively large measurement errors are accepted.

2) An average diffusion coefficient in moist soils for Am (III) and Cm(III) of 3.6×10^{-11} cm²/sec compares favorably with a value of 3.0×10^{-11} for Fe(III)(1).

3) Diffusion coefficients of Am and Cm, and to a lesser extent Np, are independent of soil texture and other properties of soil.

4) Within rather large error limits Am(III) and Cm(III) have identical diffusion coefficients, as expected for adjacent plus three actinide cations.

5) The large difference between Np(V) diffusion coefficients ($\sim 2 \times 10^{-8}$ cm²/sec) and those for Am(III) and Cm(III) is due, most likely to ionic charge and humic acid complexing of Am(III) and Cm(III).

The most important information that can be obtained from the diffusion data is the distance that an actinide migrates in moist soils in a given

time. This migration distance in soils can be estimated from

$$\text{Distance} \sim \sqrt{Dt} \text{ cm}$$

where D is the observed diffusion coefficient. Using average diffusion coefficients, Am(III) and Cm(III) will diffuse 1.0 centimeter in a moist soil in 1000 years. Np(V) will migrate 26 centimeters in the same time. It is assumed that physical and chemical properties of the soil and these actinides are unchanged and there is no mass transport. From the standpoint of nuclear hazards, the distances these actinide elements migrate in a given time are by far the most significant aspect of these measurements. Flowing water or resuspension of dry actinide-bearing soils profoundly increase the mobility of these radioelements. Even without mass transport by water or wind, radioactive decay and chemical factors such as complexing and adsorption on mobile soil particles must be considered. For example, in a thousand years an average of 48% of the $^{244}\text{Am(III)}$ 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 suggest that humic acid complexing has the potential to enhance the transport of Am(III), Eu(III) and presumably other actinide elements. However, complex formation of any Pu(IV) and Np(IV) may be important in other ways; for example, complex formation of any Np(IV) by humic acid certainly has the potential to shift the $\text{Np(V)} \rightarrow \text{Np(IV)} + \text{Np(VI)}$ disproportionation reaction to the right.

Additional analysis of diffusion data for actinide elements in moist soils indicate that the observed or uncorrected diffusion coefficient can be related to aqueous diffusion coefficients (D_0) if gel filtration distribution ratios, tortuosity, negative adsorption (retardation), and relative fluidity (viscosity) are taken into account. However, agreement depends most strongly on the techniques employed to measure K_d 's. The diffusion coefficient data, in the form of a manuscript entitled "Migration of Actinide elements in Representative U. S. Soils," has been submitted to Environmental Science and Technology and is being reviewed.

Because of the potential importance of humic acid complexing on the transport of actinide elements in most soils and aquifers, a series of experiments have been started to attempt to measure the formation constant(s) of Am(III)-humic acid complex(es). Bertha and Choppin (2) have shown that Am(III) and its chemical analogue Eu(III) are strongly bound by humic acid. In our experiments we are attempting to measure the extent of humic acid complexing of Am(III) and Eu(III) under conditions approaching those moist in soils. Two series of experiments have been done. The first involved the affect of varying humic acid concentration on the distribution of Am(III) between a clay (kaolinite) and the aqueous phase. These measurements indicated the the distribution data obeyed the relationship

$$\frac{R}{R_0} = 1 + 4.2 [\text{HA}] + 0.58 [\text{HA}]^2$$

over a humic acid range of 0 to about 10^{-4} M. Analysis, very rough, suggests a formation constant of about 10^6 for the Am(III)-humic acid complex. This indicates that Am(III) forms a very strong humic acid complex and the extent of complexing is close to that observed by Bertha and Choppin (2).

To more closely approximate environmental conditions, a similar series of distribution experiments were done with the Burbank soil. In these experiments Eu(III) was used as a chemical stand-in for Am(III). Europium-152 tracer was used because approval and delivery of ^{241}Am from Hanford has taken almost a year. [This delay has really held back the past year's research. It is not clear why it took so long to obtain the ^{241}Am , but it appeared that the approval process was very slow. The university has a license for ^{241}Am and on-campus approval was fairly prompt.] Also, the research of Bertha and Choppin indicate that Eu(III) behaves very much like Am(III), thus distribution experiments can be done more conveniently and with an additional safety margin. Over a humic acid concentration range of zero to $4 \times 10^{-5}\text{M}$, it was found that the apparent Eu(III)-humic acid formation constant has a value of $(8 \pm 6) \times 10^5$. Table I contains a summary of the distribution ratios and formation constants obtained from the Burbank data. These data are in qualitative agreement with the value of 10^5 found by Bertha and Choppin (2) who measured the distributions of Am(III) and Eu(III) between Dowex-50 cation exchange resin and the aqueous phase.

All the experiments described above were performed under conditions that were not strictly comparable. For example, the kaolinite experiments were done at a pH of 2.5, the Burbank experiments had a pH of 9.6, and the Dowex-50 experiments of Bertha and Choppin were carried at a pH of 4.5. Since the hydrogen ion dependence of the Am-humic acid complex is unknown, there is no satisfactory way of comparing these data.

Table I
DISTRIBUTION RATIOS AND APPARENT FORMATION CONSTANTS
FOR THE AU-HUMIC AND COMPLEX

[Humic Acid](1)	D (2)	$x_{\beta_x} [M]^{x-1}$ (3)
0	7.2×10^{-3}	--
10^{-5}	10.8×10^{-2}	1.4×10^6
2×10^{-5}	10.1×10^{-2}	6.5×10^5
4×10^{-5}	9.7×10^{-2}	3.1×10^5
		Ave $(8 \pm 6) \times 10^5$

(1) Calculated assuming that humic acid has an average molecular weight of 1000.

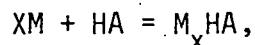
(2)
$$D = \frac{\text{cpm of } ^{152}\text{Eu per cm}^3 \text{ of aqueous phase}}{\text{cpm of } ^{152}\text{Eu per gram of Burbank soil}}$$

These values are an averages of D's obtained from each of the prominent ^{152}Eu gammas.

(3) This is an apparent formation constant for the Eu-humic acid complex at a pH of 9.6. The metal ion and hydrogen ion dependence are unknown, thus the apparent formation constant is highly uncertain.

Accepting that humic acid is a polyelectrolyte and that it can be considered as a polymer of humic acid and assuming that these polymers have the following composition(3) $[C_{20}H_{12}(COOH)_6(OH)_5(CO)_2]_n$, where n is the number of humic acid monomer units per polymer [polyelectrolyte], humic acid polymers have the potential to complex many Am(III) cations. However, a significant number of the carboxyl and phenol groups must be involved in the hydrogen bonding that stabilizes the humic acid polymer. Assuming that half of the carboxyl and phenol groups are hydrogen bonded, the molecular weight ranges from 8000 to 50,000 (4) and only the carboxyl groups are involved in the complexing of metal cations, each polymer can complex 12 to 75 Am(III)s. However, in the soil aquatic environment a significant number of these sites are occupied by Ca^{2+} and Fe^{3+} , and other cations, hence fewer Am(III) cations can be complexed, the actual number being rather uncertain. Thus humic acid polymers have varying capacities for Am(III) which depend on the factors mentioned above.

We are performing distribution experiments to test this hypothesis. Now assume that the following reaction takes place between x cations (either Am^{3+} or Eu^{3+}) and the humic acid polymer, HA, and that the reaction is



where $M = Eu^{3+}$ or Am^{3+} .

M_xHA = the humic acid polymer complex of M . The equilibrium quotient for this reaction is

$$\beta_x = \frac{[M_xHA]}{[M]^x[HA]} \quad (1)$$

and material balance equation for M in the aqueous phase is

$$[M]_{\text{tot}} = [M] + x[M_x\text{HA}]. \quad (2)$$

Substituting equation 1 into 2 we obtain

$$[M]_{\text{tot}} = [M] + x\beta_x[M]^x [\text{HA}]. \quad (3)$$

For distribution experiments the distribution ratio is defined as

$$D = \frac{[M]_{\text{org}}}{[M]_{\text{tot}}} = \frac{\text{metal ion concentration in organic phase, cation exchange resin, etc.}}{\text{total metal ion concentration in aqueous phase}}$$

$$= \frac{[M]_{\text{org}}}{[M]} \cdot \frac{1}{1 + x\beta_x[M]^{x-1}[\text{HA}]} \quad (4)$$

and where

$$D_o = \frac{[M]_{\text{org}}}{[M]} = \text{Distribution ratio in absence of humic acid.} \quad (5)$$

On rearrangement of equation 4 we obtain

$$\left(\frac{D_o}{D} - 1 \right) = Q_x = x\beta_x[M]^{x-1}[\text{HA}] \quad (6)$$

where each distribution experiment at a given [HA] and [M] yields an apparent formation constant

$$\beta_{x,M} = x\beta_x[M]^{x-1}. \quad (7)$$

But the desired quantity is β_x not $x\beta_x[M]^{x-1}$. To overcome this difficulty experiments must be done with [HA] constant and varying [M]. Now consider two experiments done with different metal ion concentrations, then let

$$R = \frac{Q_{x,M1}}{Q_{x,M2}} = \frac{x[M]_1^{x-1}[HA]}{x[M]_2^{x-1}[HA]} \quad (8)$$

$$= \left(\frac{[M]_1}{[M]_2} \right)^{x-1} \quad (9)$$

Thus distribution experiments done at two different metal ion concentrations should yield information about the number of metal cations bound to the humic acid polymer.

To the experiments described above we are measuring the distribution of Eu between an aqueous phase containing humic acid and a xylene phase containing the extractant TTA (thenoyltrifluoroacetone). The justifications for this approach are 1) There are considerable data for the extraction of Am(III) by TTA; 2) Many investigators have used this method to determine formation constants of Am, Np, Pu, Th, etc.; 3) It is conceptually simpler than the clay and soil distribution experiments described above.

As mentioned above, we are using Eu. This is done for several reasons. First, as mentioned above, the delivery of ^{241}Am has taken almost a year to come from Richland to Pullman, a distance of less than 150 miles. Second, to vary the Am(III) concentration in the aqueous phase would create potential safety problems that most universities are not equipped to handle; consequently, we are using ^{152}Eu and non radioactive Eu as stand-ins for Am. We believe that, in spite of the use of Eu, quite acceptable results will be obtained and that they will be applicable to Am(III).

These experiments are now in progress and we do not have sufficient data for analysis; however, we plan to submit a report covering these experiments in late July.

REFERENCES

1. G. A. O'Conner, W. L. Lindsay, and S. R. Olsen, Soil Sci. Soc. Amer. Proc. 35, 407 (1971).
2. E. L. Bertha and G. R. Choppin, J. Inorg. Nucl. Chem. 40, 655 (1978).
3. M. Schnitzer and S. I. M. Skinner, Soil. Sci. 96, 87 (1963).
4. J. C. Sheppard, M. J. Campbell, T. Cheng, and J. A. Kittrick, Env. Sci. Tech. 14, 1349 (1980).