

EFFECT OF LONG-TERM RELEASE OF PLUTONIUM AND AMERICIUM
INTO AN ESTUARINE AND COASTAL SEA ECOSYSTEM.

III. COEFFICIENTS OF DISTRIBUTION AND CRITICAL PATHWAY
ANALYSIS; PRELIMINARY REPORT

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Resumé

Les résultats d'une étude préliminaire sur l'importance des coefficients de distribution de l'americium entre eau, sédiments et matériaux biologiques sont présentés.

L'utilisation d'un coefficient qui représente la fraction biologique disponible dans le cadre d'une analyse critique des voies de transfert pour le calcul des doses à l'homme est proposé comme alternative aux facteurs de concentration pour les éléments transuraniens.

Abstract

The concept of coefficients of distribution and their calculation for sediments and biota are discussed in relation to the assessment of the distribution of americium in the aquatic environment.

In the assessment of the effects of radioactive contamination of the environment, the use of concentration factors in critical pathway analysis has led to the identification of the radioelements representing the greatest risk, the route by which the radioactivity can reach man and the critical group most exposed.

The assumption of constant concentration factors is reasonably valid in the case of radioisotopes having stable isotope counterparts naturally occurring in the environment at concentrations of 10^{-3} to 10^{-6} g.l⁻¹. The application of these factors to transuranic elements, however, poses some special problems: they are unique in having no stable counterparts in the environment and they are all artificially introduced within the last 30-40 years by man. Specially in the case of plutonium it has the unusual ability of existing in several oxidation states at the same time, these being strongly affected by small changes in such factors as pH, Eh, complexing agents, etc. Moreover concentrations of transuranics in the environment generally vary between 10^{-12} to 10^{-17} g.l⁻¹ that is at levels where atom concentrations are extremely low so that the presence of even minor components of the system may effect their chemical behaviour.

The authors believe, therefore that the concept of a global distribution coefficient for transuranic elements may have serious drawbacks if based on measurements of the total concentration of the element in water and that fraction adsorbed to either bottom or suspended sedimentary material.

In order to illustrate this hypothesis, the following example has been taken from Avogadro et al. (1979).

Bottom sediments appear to act at least in the short-term as the major sink of actinides. The sediment over the long-term, however, may be able to act as a source of

soluble species through a series of thermodynamic reactions resulting in a continuous release of very small quantities of soluble material. In fact this is what appears to happen in our column experiments: when the contaminated sub-soils are eluted with uncontaminated groundwater there is always a continuous release of about $2 \cdot 10^{-13}$ M activity from the column not explainable by a chromatographic process. These soluble species can be interpreted by the formation of an anionic carbonate complex not retained by the soil.

Parallel to the problem of sediment distribution coefficients and their use in the assessment of the long-term behaviour of actinides in the environment, is the understanding of the availability of these elements to biota and their transfer through food chains and eventually to man. In order to study the possible variations in uptake due to different source terms and to try to relate these to the chemical speciation of the element involved, methods developed at the Joint Research Centre, Ispra, to characterize oxidation states and complex forms, were tested on aquatic microcosms. These were used as model ecosystems to study the behaviour and fate of plutonium and americium isotopes in freshwater. The experimental set-up and the variation of distribution of activity with time as well as details of the separation method have been discussed by Murray et al. (1979). Two input sources were investigated: a direct solution input (simulating discharge of low-level liquid waste by a nuclear facility) and a contaminated borosilicate glass leached in-situ (simulating accidental release from a nuclear disposal installation for high-level waste). Table 1 shows the distribution of water activity and concentration factors based on a total water concentration for americium after 3 months. A comparison of the differences between solution and glass source terms can be seen to produce variations in the

in the concentration factors for the same element of up to two orders of magnitude. The tables also give the ratio of the concentration factors between solution and glass source term (s/g). Interesting to note is that this ratio apparently varies between different types of biota as well as the sediment. It is suggested that the interaction of the biota with the elements depends upon the chemical species in solution and that only a certain fraction is biologically available for uptake. This fraction appears to be strongly influenced by the source term of the contamination and once released into the microcosm by such factors as major ion concentrations, pH and Eh; these parameters governing the further chemical species distribution in the system. It is thus proposed that concentration factors for transuranics should be replaced by a bioavailable fraction ratio (BFR) being defined as the total concentration in the biota to the concentration of the bioavailable fraction in solution or sediment.

An attempt was made to see if calculation of a constant factor could be obtained when the ratio was related to only certain fractions of the element in solution. An example of this approach is given to show the possible validity of the concept of a bioavailable fraction ratio. Referring to Table 1, the A_m uptake factor for the snail Physa acuta for solution (s) and glass (g) source term can in fact be shown to be constant if the activity in the snail is due to the particles ranging between 0.01 μm - 0.5 μm and the cation fraction. The calculation would be as follows:

1. A_m (solution):

$$\begin{array}{rcl}
 \text{snail activity} & = 500 \times 2.93 \text{ dpm.g}^{-1} & = 1465 \text{ dpm.g}^{-1} \\
 \text{0.01 } \mu\text{m particles} - \text{0.5 } \mu\text{m} & & \\
 \text{cation fraction} & = 0.26 \times 2.93 \text{ dpm.g}^{-1} & = 0.76 \text{ dpm.g}^{-1} \\
 & = 0.17 \times 2.93 \text{ dpm.g}^{-1} & = \underline{0.50 \text{ dpm.g}^{-1}} \\
 \text{water activity} & = & 1.26 \text{ dpm.g}^{-1}
 \end{array}$$

two simulated sources.

Component	Solution (s)	Glass (g)	Ratio (s/g)
Sediment	300	10	30
<u>Submerged plant:</u>			
Lagarosiphon major	200	22	9
<u>Invertebrates (snails):</u>			
Physa acuta	500	30	17
Biomphalaria glabrata	400	29	14
<u>Vertebrates (fish):</u>			
Lebistes reticulatus	33	11	3
Xiphophorus helleri	76	47	2

Distribution of chemical forms in the water.

% distribution	Solution (s)	Glass (g)
Particulate > 0.5 μm	26	33
0.01 μm < particulate < 0.5 μm	26	1
Cation fraction	17	1
Anion fraction	17	17
Neutral fraction	14	50
Total activity in $\text{dpm}\cdot\text{g}^{-1}$	2.93	1.28

The bioavailable fraction ratio (BFR) is thus:

$$\text{BFR} = \frac{1465 \text{ dpm.g}^{-1}}{1.26 \text{ dpm.g}^{-1}} = 1163$$

2. Am (glass):

$$\begin{aligned} \text{snail activity} &= 30 \times 1.28 \text{ dpm.g}^{-1} &&= 38.4 \text{ dpm.g}^{-1} \\ 0.01 \mu\text{m particles} & && 0.5 \mu\text{m} \\ &= 0.01 \times 1.28 \text{ dpm.g}^{-1} &&= 0.0128 \text{ dpm.g}^{-1} \\ \text{cation fraction} & && \\ &= 0.01 \times 1.28 \text{ dpm.g}^{-1} &&= 0.0128 \text{ dpm.g}^{-1} \\ &&& \underline{\hspace{10em}} \\ &&& \text{water activity} = 0.0256 \text{ dpm.g}^{-1} \end{aligned}$$

The bioavailable fraction ratio (BFR) is thus:

$$\text{BFR} = \frac{38.4 \text{ dpm.g}^{-1}}{0.0256 \text{ dpm.g}^{-1}} = 1500$$

The two calculations lead to a reasonable agreement in the uptake factor for americium even though the distribution in the two solutions was very different. Further the calculated BFR is at least twice that previously calculated on the basis of total water activity.

The concept of a constant bioavailable fraction ratio may be a more realistic factor for use in critical pathway analysis as it more precisely represents the fraction of the transuranics actively available for biota. For a better understanding of the concentration processes in sub-soil, sediments and biota there is a clear need to determine the role of environmental and thermodynamic parameters which govern the aqueous chemistry of the transuranic elements. Although some information on the behaviour of transuranics may be obtained from classical work under conditions of high acidity or basicity etc., little information is available from experimental studies at very low concentrations, Bondietti et al. (1976).

Theoretical work by Polzer and Miner (1976), Fried and Friedman (1977) and Ames et al. (1976) can give extremely useful indications for these studies. Initially required is a thermodynamic description of the distribution between various oxidation states of the transuranics. Further the major complexation reactions, both inorganic and organic, must be known as well as their stability constants and solubility products. This information must be supplemented by kinetic data that show the rate of formation of different oxidation states so that their distribution can be calculated with time under various conditions found in the environment.

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MURRAY, C.N., AVOGADRO, A.

"Effect of long-term release of plutonium and americium into an estuarine and coastal sea ecosystem. III. Coefficients of distribution and critical pathway analysis; preliminary report."

Paper presented by C.N. Murray (Italy)

Discussion

W.L. TEMPLETON: I have only a comment to make. While I do not disagree with your hypothesis, I think that it may be very difficult to establish the chemical parameters at a chemical reprocessing plant where various treatments may not allow a single value for the establishment of the bioavailable fraction (BFR).

Lj. MUSANI-MARAZOVIC: 1. What was the pH and Eh of the water (referring to Table 1. - the distribution of chemical forms)?

2. How did you predict the chemical forms of Pu and Am in sea water at the same pH (referring to Table 1)?

3. Can you tell us something about the concentration of dissolved organic matter in Lago Maggiore?

C.N. MURRAY: 1. The pH of the lake Maggiore water used in our experimental system was about 7.8 and the Eh 350 mV.

2. In our system we determined the distribution of the different forms using filters of 0.5 μm and 0.01 μm and by sorption on cation and anion Dowex resins. The neutral fraction was considered to be that which passed through the analysis train.

3. The organic fractions in the systems were probably higher than normally found in the natural environment which was determined to be less than 0.01 mg/l. No values in this experiment, however, were measured above the detection limits of the methods employed.

