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Effects of Selected Organic Compounds on Radionuclide Adsorption to Sediments in Freshwater Systems

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During the past several decades considerable effort has been directed to describing the distributions of several radionuclides in aquatic environments. A major incentive for this work has been to determine the potential of radionuclides to be ultimately transferred to man. Concern regarding the health hazards associated with radionuclides results from the continued introduction of artificially produced radionuclides from sources related to military applications and power generating facilities. A major limitation of the available data is that the physical, chemical and biological mechanisms actually producing the observed distributions have seldom been investigated. Such information is essential for understanding and predicting the environmental fates and biological availabilities of radionuclides.

One approach to the problem of predicting the behavior of many radionuclides in aquatic systems utilizes the fact that their ultimate distributions and fates are influenced significantly by associations with sediments or suspended particles (DUURSMA & GROSS 1971). These associations can be described quantitatively by a distribution coefficient defined as:

$$K_d = \frac{\text{activity of radionuclide / g of sediment or particles}}{\text{activity of radionuclide / mL of solution}} .$$

The distribution coefficients (K_d) of a given radionuclide may be influenced by a variety of variables including salinity, temperature, pH, quantity and chemistry of the sediments or suspended particles and the concentrations and specific types of inorganic or organic compounds occurring in solution. This paper presents information obtained from preliminary studies evaluating the roles of selected organic compounds on K_d values of radionuclides in laboratory sediment-water systems.

MATERIALS AND METHODS

The radionuclides ^{57}Co, ^{106}Ru, ^{137}Cs and ^{241}Am were used as tracers in these experiments. Five organic compounds: 1) 1-nitroso-2-naphthol, 2) 1,10-phenanthroline, 3) acetic acid, 4) salicylic acid and 5) EDTA were evaluated for their effects on the distribution coefficients of the four radionuclides. These compounds were selected primarily for the variety of functional groups which would be available to interact with the radionuclides and sediment particles.

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Experiments were conducted with natural sediments and water from two freshwater environments, Lake Washington (Washington State) and the mouth of Cattaraugus Creek where it enters Lake Erie (New York State). To minimize microbial effects, all experimental vessels were either autoclaved or rinsed with 95% ethanol before use. Water was filter-sterilized by passage through a 0.20 um Nucleopore polycarbonate membrane filter. All sediments were initially passed through a No. 230 U.S. Standard Testing geological sieve. The fraction passing through the sieve, less than 63 um, was used for the experiments. Sediments from Lake Washington were treated by ^{60}Co irradiation to sterilize them.

Adsorption K_d values were determined using a constant shaking technique similar to that of DUURSMA & BOSCH (1970) and MURRAY & MURRAY (1973). Briefly, the method was the following:

1) Measured quantities of the radionuclides, a stock sediment suspension and a stock organic compound solution were added to a known volume of the appropriate water sample. The pH values of the resulting solutions were then readjusted to the initial values of the natural water samples with NaOH and/or HCl. The resulting radionuclide concentrations in all experiments were between 2-8 X 10^{-11} Ci/mL solution for each radionuclide and the sediment concentration was 40 mg/L.
2) The experimental sediment-water solution was shaken at 200 rpm in a constant temperature (4-8°C) room.
3) Subsamples were collected at designated time intervals during an experiment and filtered to obtain separate particulate and dissolved radionuclide fractions. The filter and 3.00 mL of the filtrate were placed in separate 5 mL polyethylene vials for counting by gamma spectroscopy with a germanium-lithium drifted detector system. To assure a constant geometry for counting of particulate and dissolved samples, the filter was dissolved in the counting vial in 3.00 mL of 8 N HNO_3 prior to counting.

After sampling the pH in the experimental bottles was measured. If it had changed, it was readjusted to the initial pH of the experiment.

Radionuclide concentrations in individual experimental samples were recorded as (cpm/mL of solution ± 2 standard deviation units counting error). Distribution coefficients were calculated as:

$$K_d = \frac{(\text{cpm in filter/mL of solution})}{(\text{cpm in filtrate/mL of solution})} \times \frac{(\text{mL of suspension})}{(\text{g of particulates})}$$

Error terms for individual K_d determinations are based on propagated counting errors only.

RESULTS

In order to estimate the time required for sediment-water-organic systems to achieve stable K_d values, an initial experiment was conducted to measure adsorption as a function of time. The distribution coefficients of ^{106}Ru, ^{137}Cs and ^{241}Am were determined in sediment-water systems from Cattaraugus Creek for varying concentrations of EDTA (10^{-4} to 10^{-10} M) and for a control containing no EDTA. Samples were collected at five time periods between 4 hours and 480 hours following the start of the experiment. Table 1 summarizes the results obtained after 4 and 480 hours for EDTA concentrations of 10^{-6} and 10^{-10} M.

TABLE 1

Distribution coefficients (mL/g) for ^{106}Ru, ^{137}Cs and ^{241}Am in sediment-water systems from Cattaraugus Creek. Values are mean ± 1 standard deviation unit calculated for replicate samples.

Time (h)	n*	^{106}Ru $K_d X10^{-5}$	^{137}Cs $K_d X10^{-3}$	^{241}Am $K_d X10^{-5}$
		10^{-6} M EDTA		
4	3	1.6 ± 0.4	1.4 ± 0.1	5.1 ± 1.4
480	3	1.2 ± 0.3	1.4 ± 0.3	11.2 ± 4.9
		10^{-10} M EDTA		
4	2	1.6 ± 0.2	1.6 ± 0.1	5.3 ± 1.6
480	2	1.4 ± 0.5	1.3 ± 0.4	20.5 ± 14.6

*n = number of replicates

Although the mean K_d value for ^{241}Am increased during the experiment, no statistically significant differences were obtained between the two time periods for any of the radionuclides at either concentration of EDTA (student "t" test, a=0.05). The increased K_d values for ^{241}Am with time during the experiment result from decreased concentrations of soluble ^{241}Am. This may result from adsorption onto the container walls rather than interactions with the suspended sediments. Although most adsorption onto sediments occurred quite rapidly, subsequent experiments were sampled after approximately 150 hours of shaking to insure an approach to equilibrium.

To evaluate the effect of EDTA, K_d values were calculated for each radionuclide over the range of EDTA concentrations. There were no apparent differences in K_d values of ^{106}Ru or ^{137}Cs associated with increased concentrations of EDTA used in these experiments. However, for ^{241}Am a marked decrease in the K_d value occurred between EDTA concentrations of 10^{-4} M and 10^{-6} M. This trend is illustrated in Figure 1, which plots K_d values against EDTA concentrations for sediment-water systems from Cattaraugus Creek. The decreased K_d values of ^{241}Am at the higher EDTA concentrations are undoubtedly due to the formation of soluble EDTA-^{241}Am complexes. The major effect is produced at EDTA

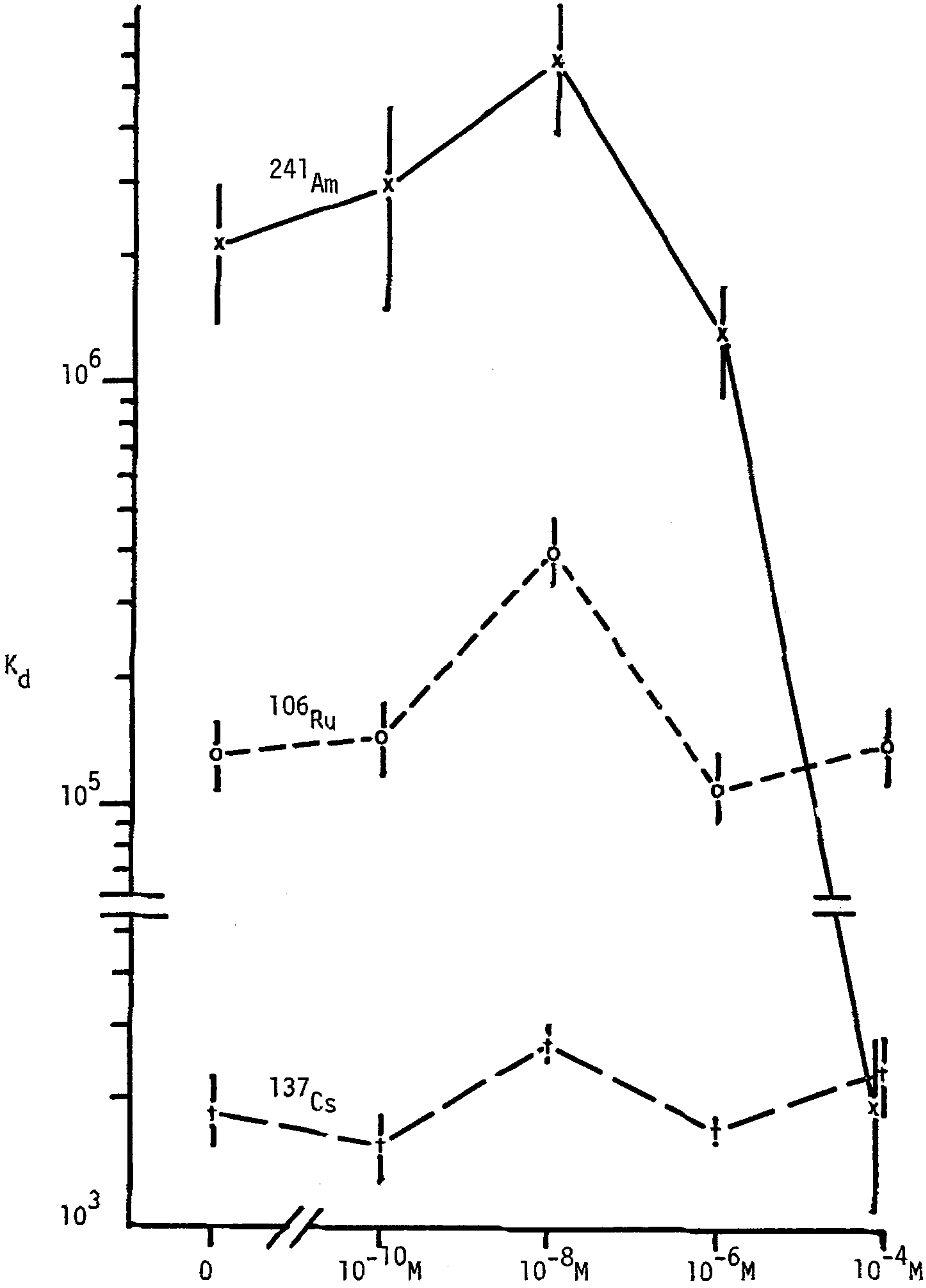

Fig. 1. Distribution coefficients of ^{106}Ru, ^{137}Cs and ^{241}Am as a function of EDTA concentration for sediment-water systems from Cattaraugus Creek. *Error bars are 2s propagated* counting error for a single sample collected after 480 hours of constant shaking.

concentrations which are considerably higher than are expected to occur in natural systems. Nevertheless, they do indicate the significant effects that can result from high concentrations of some organic compounds.

Sediments and water from Lake Washington were utilized to evaluate the effects of five different organic compounds (acetic acid, salicylic acid, 1-nitroso-2-naphthol, 1,10-phenanthroline and EDTA) upon K_d values of ^{57}Co, ^{106}Ru, ^{137}Cs and ^{241}Am. An experimental concentration of 10^{-4} M was used for all organic compounds except 1-nitroso-2-naphthol which was run at 10^{-5} M because of its low water solubility. For the purpose of statistical analyses, triplicate experiments were run for each organic compound tested and for the control containing no organic addition. All samples for radioactivity measurements were collected after 165 hours of shaking. Results of this experiment are summarized in Table 2.

TABLE 2

Distribution coefficients (mL/g) for sediment-water systems from Lake Washington. Values are means ± 1 standard deviation unit for triplicate samples.

Organic Compound*	^{57}Co $K_d X10^{-4}$	^{106}Ru $K_d X10^{-4}$	^{137}Cs $K_d X10^{-2}$	^{241}Am $K_d X10^{-4}$
None	0.32 ± 0.03	1.1 ± 0.4	4.2 ± 1.0	2.3 ± 0.7
1-nitroso-2-naphthol	35.8 ± 18.1	2.6 ± 1.0	5.0 ± 0.7	7.8 ± 3.0
1,10-phenanthroline	16.8 ± 4.2	3.8 ± 0.1	3.2 ± 0.4	25.3 ± 2.4
acetic acid	0.44 ± 0.04	2.3 ± 0.8	2.7 ± 0.8	5.6 ± 2.4
salicylic acid	0.30 ± 0.07	1.2 ± 0.5	3.8 ± 0.6	2.9 ± 1.0
EDTA	0.01 ± 0.01	3.5 ± 0.5	3.5 ± 0.8	0.05 ± 0.01

*Concentrations of organic compounds were all 10^{-4} M except for 1-nitroso-2-naphthol which was 10^{-5} M.

The data were analyzed using Kruskal-Wallis statistical tests (SOKAL & ROHLF 1969) to determine if K_d values for the organic compounds and the controls were significantly different. Statistically significant differences (a = 0.05 level) were obtained for the K_d values of ^{241}Am, ^{57}Co and ^{106}Ru, but not for ^{137}Cs. For both ^{57}Co and ^{241}Am, values of K_d relative to the controls were higher with 1-nitroso-2-naphthol, 1,10-phenanthroline and, possibly, acetic acid, whereas much lower values were observed with EDTA. For ^{106}Ru, 1-nitroso-2-naphthol, 1,10-phenanthroline, acetic acid and EDTA all appeared to produce higher K_d values. It is interesting to note that 10^{-4} M EDTA produced higher ^{106}Ru K_d values in the Lake Washington systems but no apparent effect in sediment-water systems from Cattaraugus Creek. Salicylic acid did not significantly alter the K_d values for any radionuclide that was tested.

DISCUSSION

These results confirm that organic compounds can affect sediment-water distribution coefficients of radionuclides. However, the magnitudes and directions of these K_d effects are functions of both the physico-chemical properties of the radionuclide and the specific interactions of the radionuclide and organic compounds within a given sediment-water system. For example, EDTA was able to dramatically increase the soluble concentrations of ^{241}Am, but only at concentrations between 10^{-4} M and 10^{-6} M. One hypothesis that might explain this concentration-dependent behavior is that at EDTA concentrations of 10^{-6} M and lower, the EDTA is selectively complexed to cations other than ^{241}Am. Such an explanation emphasizes the need to chemically characterize each environmental system before the distributional behavior of a given radionuclide can be fully understood and predicted.

Organic ligands such as 1-nitroso-2-naphthol and 1,10-phenanthroline can also increase the adsorption of certain radionuclides (^{57}Co, ^{106}Ru and ^{241}Am) to the particulate phase. This implies that these ligands are involved in at least two concurrent reactions: 1) complexing the radionuclides and 2) actively sorbing to the sediment particles. At concentrations lower than 10^{-5} M these ligands may still complex the radionuclides but no longer be associated with the sediments. The result would be a "solubilizing" effect upon the radionuclides analagous to that brought about by EDTA. Hence, depending upon 1) the relative affinity of an organic ligand molecule for radionuclides and sediment particles and 2) the actual concentration of such a ligand molecule, some organic compounds either increase or decrease K_d values. Such phenomena have been observed for certain trace metal-organic combinations by DAVIS & LECKIE (1978a and b).

These results emphasize the complex variety of interacting factors that can effect sediment-water distributions of radionuclides. Therefore, it is necessary in any adsorption study, whether in the laboratory or in the field, to characterize as fully as possible the chemical parameters of water and sediment that can contribute to the eventual results in any given system. The environmental relevance of many of our test compounds has not been determined. Consequently, further studies should make an attempt to use "natural" organic compounds such as humic acids. It is clear that much research remains to be done in this interesting and complicated area before we can hope to understand the environmental behavior of anthropogenic radionuclides.

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