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Distribution Coefficients for Radionuclides in Aquatic Environments

I. Development of Methods and Results for Plutonium and Americium in Fresh and Marine Water-Sediment Systems

Annual Report: August 1976 - July 1977

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I. Development of Methods and Results for Plutonium and Americium in Fresh and Marine Water-Sediment Systems.

First Annual Research Progress Report

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ABSTRACT

A study has been initiated on the processes which control removal and remobilization of radionuclides by inorganic and organic suspended particulate matter in natural aquatic systems. The initial development and testing of procedures and preliminary results have been made using americium and plutonium. An evaluation of the methods used for measuring distribution coefficients was made for different sediment-water systems by the thin layer and constant shaking techniques. The constant shaking technique was found to be the most reproducible. A comparison of sterile (by 10^6 rads gamma radiation) and natural sediments was made. The distribution coefficients of ^{237}Pu in freshwater-sediment systems for desorption was three times greater than for sorption and was also three times greater for unsterilized than for sterilized sediment. In marine sediment-water systems the distribution coefficients for ^{237}Pu gave a range of values between 10^4 and 10^5. For ^{241}Am, the distribution coefficients for desorption was three times greater than that measured for sorption and the sterilized sediment gave the highest distribution coefficient values for both sorption and desorption. Dialysis bags were utilized in experiments designed to separate the soluble from the colloidal or particulate form of the radionuclide. The results showed that both plutonium and americium diffuse through the dialysis bags in marine water systems and are then concentrated on the growing plankton Phaeodactylum tricornutium, and on the suspended sediment contained inside the bags. Further studies are essential to evaluate these early results.

TABLE OF CONTENTS

	Page
Abstract	iii
Table of Contents	v
List of Figures	vi
List of Tables	vii
1.0 INTRODUCTION	1
1.1 Background	1
1.2 Objectives	2
1.3 Personnel	2
2.0 METHODS AND MATERIALS	2
2.1 Sources and Types of Samples	2
2.2 Sterilization of Samples	6
2.3 Counting Techniques	6
2.4 Evaluation of Methods	8
3.0 RESULTS AND DISCUSSION	10
3.1 Summary of Current Literature	10
3.2 Distribution Coefficients for Water and Sediments	15
3.2.1 Fresh water-sediment system	23
3.2.2 Marine water-sediment system	23
3.2.3 Anoxic marine sediment-water system	27
3.2.4 Summary of K_d experiments	27
3.3 Dialysis Studies	29
3.3.1 Phytoplankton uptake	32
4.0 SUMMARY	34
REFERENCES	35
APPENDIX I	37

LIST OF FIGURES

Figure		Page
1	Literature values of concentration factors for $^{239,240}Pu$ in marine biota	16
2	Literature values of concentration factors for $^{239,240}Pu$ in freshwater biota	17
3	Literature values of concentration factors for ^{241}Am in freshwater biota	18
4	Comparison of literature values for concentration factors of $^{239,240}Pu$ and ^{241}Am for selective trophic levels in marine and freshwater	19
5	Distribution coefficients for ^{241}Am as a function of sediment concentration in a sterilized freshwater-sediment system	21
6	Distribution coefficients for ^{241}Am as a function of sediment concentration in an unsterilized freshwater-sediment system	22
7	Schematic drawing of experimental setup for dialysis experiments	31

LIST OF TABLES

Table		Page
1	Particle size, density, carbon and nitrogen content of sediments used in the experiments . . .	4
2	Chemical properties of water samples used in the experiments	5
3	Results of bacterial culture experiments	7
4	Distribution coefficients for ^{137}Cs and ^{65}Zn in the water-sediment systems	9
5	Distribution coefficient values for plutonium as reported in the literature and determined in this study	12
6	Distribution coefficients for ^{237}Pu and ^{241}Am in fresh-water-sediment systems	24
7	Distribution coefficients for ^{237}Pu and ^{241}Am in marine water-sediment systems	25
8	(a) Ratios of ^{237}Pu and ^{241}Am distribution coefficients to sorption distribution coefficients in unsterilized systems	28
9	Measurements of radionuclides in the three compartments of the dialysis system after 10 days' equilibrium time	30
10	Radionuclide distribution coefficients for sediments and concentration factors for phytoplankton in dialysis experiments	33

DISTRIBUTION COEFFICIENTS FOR RADIONUCLIDES IN AQUATIC ENVIRONMENTS.

I. Development of Methods and Results for Plutonium and Americium in Fresh and Marine Water-Sediment Systems.

1.0 INTRODUCTION

This is a report of progress for the first 9 months of a proposed three-year program to obtain new information and to supplement current information about the behavior of transuranic elements in water-sediment systems. The information in the report is the foundation upon which the proposal for the second year's program is built. The principal sections are: Introduction; Methods and Materials; Results and Discussion; and Conclusions and Recommendations.

The program has been supported by Contract AT(49-1)-0352 with the Nuclear Regulatory Commission in the amount of $64,114 for the period 1 August 1976 to 31 July 1977.

1.1 Background

The original proposal stated that the transuranic elements are removed from water by sorption to organic and inorganic sediments and materials and, to a lesser extent, by adsorption to and uptake by living organisms, but the physical, chemical, and biological factors that govern the removal processes are numerous and many are not well understood. An understanding of these processes is further complicated by the fact that the physico-chemical states of the radionuclides may be altered from one time or place to another by environmental factors. The single, most important key to understanding the behavior of any radionuclide in aquatic environments, or nuclides of any chemical element for that matter, is knowledge of the physico-chemical state of the nuclide. Therefore, although our interests are in transuranic elements, this is not a unique problem for these elements.

There are many facets to the problem, but in our work attention is focused, primarily, upon distribution coefficients. The term is defined as the ratio of the amount of transuranic radionuclide bound to the sediment to the amount present in water. Conventionally, the calculation is based on dry sediments and the volumes of sediment and of water. The distribution coefficients is a measure of the binding property of the sediment for the radionuclide, and hence, the larger the coefficient, the stronger the sorption.

1.2 Objectives

The objectives of the first year's program were to establish what is known about the behavior of transuranic elements in aquatic environments by a review of the pertinent literature and to conduct laboratory experiments to determine distribution coefficients for five parameters: radionuclides; direction of movement of the radionuclides; physical state of the media; sediment sample type; and bacterial effect. The specific parameters selected were: ^{237}Pu and ^{241}Am; adsorption from water to sediment and desorption from sediment to water and, also, movement through a semi-permeable membrane; "at rest" and "in motion" states for the media with temperature selection for some experiments; three sediment types including freshwater, marine, and anoxic marine; and non-sterilization or sterilization of the samples by irradiation to evaluate bacterial effect. For all experiments, the distribution coefficients, K_d, was the variable.

1.3 Personnel

The Principal Investigator, Professor A. H. Seymour, served as administrator and scientific advisor for the program at no cost to the funding agency. The senior scientists were Drs. W. R. Schell and A. Nevissi, radiochemists, and the principal researcher under their supervision was graduate student, Arthur Sanchez. A Predoctoral Associate, Michael Brown, joined the program in January, 1977. In addition, the program has had support, as required for preparation and analyses of samples and reduction of data, from the Scientific Programmer, the Engineering Technician, and Research and Laboratory Assistants. The total effort is predicted to be 2.0 man years for the contract (1.4 man years for the period of this report).

2.0 METHODS AND MATERIALS

The methods which have been used to determine the distribution coefficients were methods described in the literature but modified to accommodate our special needs. In particular, the methods developed by Duursma and his co-workers at the International Atomic Energy Agency (IAEA) Marine Laboratory, Monaco, have been used extensively.

2.1 Sources and Types of Samples

For the initial laboratory studies, large quantities of "standard" sediment and water samples have been prepared. Three local samples have been collected--one of anoxic marine sediments from Lake Nitinat (a fjord), Vancouver Island, British Columbia; one of marine sediments collected from off the mouth of the Columbia River; and one of the freshwater sediments from the deepest part (62 m) of Lake Washington, Seattle. All water samples were filtered through 0.3 μm Millipore filters. Both water and sediment samples were frozen after collection, and kept frozen until they were used in the experiments. By having a large quantity of sediment and water available, replicate experiments can be conducted. Samples from Lake Michigan and Chesapeake Bay have not yet been obtained.

Particle size measurements and carbon and nitrogen determinations of the sediment were made and the results are shown in Table 1. It was observed that the clay fraction is predominant (75%-80%) in both the Lake Washington and Lake Nitinat (saltwater) samples. The marine sediment is composed of sand (40%), silt (21%), and clay (39%). Knowledge of the physical and chemical characteristics of the sediments and water is necessary for proper interpretation of the distribution coefficient values for various water-sediment systems.

The chemical and physical properties of the water samples used in the experiments are given in Table 2. The chemical analyses of the marine water samples were made shortly after collection and then again after freezing and storage for about 1 year. The freshwater samples (Lake Washington) were frozen and stored for 1 month after collection before they were used in the experiments and analyzed for nutrients. The chemical analysis of anoxic marine water (Lake Nitinat) showed large differences in the nutrients following filtration and/or sterilization. Similar treatment produced only small differences for most nutrients in the marine and freshwater samples. These differences are due to both removal of particulates (filtration) and to irradiation. The effects of the irradiation alone on the water have not been identified. However, the changes in chemical properties of the water illustrate that the laboratory experimental conditions may not necessarily represent chemical and biological conditions found in the field.

Table 1. Particle size, density, carbon and nitrogen content of sediments used in the experiments.

Particle		Percentage in sediments		
ϕ Size	Diameter, mm	Lake Washington	Lake Nitinat	Marine
-1	2	0	0.11	0.17
0	1	0.17	0.42	0.33
1	0.5	0.43	1.18	0.67
2	0.25	1.20	1.10	1.84
3	0.125	0.47	0.48	13.40
4	0.0625	0.21	0.49	24.00
Sand (0.4)		2.48	3.67	40.24
6	0.0156	3.31	3.90	12.58
7	0.008	3.31	5.61	2.58
9	0.002	8.97	11.88	5.67
Silt (5-9)		15.99	21.39	20.83
Clays(>9)		81.93	74.93	38.7
Density g/cm^3		2.38	2.55*	2.56*
Carbon and nitrogen contents				
Total carbon %		5.25	2.77	1.81
Total nitrogen %		0.41	0.26	0.08
C/N ratio		11.9	10.5	21.7

*Corrected for 5% salt content.

Table 2. Chemical properties of water samples used in the experiments

Sample Type	Temp °C	Salinity °/oo	Reactive Phosphate µM	Reactive Silicate µM	Reactive Nitrate µM	Reactive Nitrate µM	Reactive Ammonia µM	Hydrogen Sulfide µM	Remarks
Lake Nitinat 48° 44.6′ N 124° 45.3′ W	10.11	31.267	8.30	104.43	0.00	0.06	76.86	166	Unfiltered
			2.14	43.2	26.7	0.23	2.0	--	Filtered
			3.58	67.1	14.9	0.72	49.3	--	Filtered Sterilized
Marine Water 48° 38.0′N 124° 53.0′W	8.29	32.566	2.37	44.96	26.83	0.16	0.61	--	Unfiltered
			2.24	45.9	28.5	0.23	0.4	--	Filtered
			1.37	24.2	23.6	1.01	3.4	--	Filtered Sterilized
Lake Washington 47° 37.5′N 122° 16′ W			0.06	14.2	3.4	0.00	2.0	--	Filtered
			0.09	15.3	5.7	0.00	2.2	--	Filtered Sterilized

*Filtered samples were passed through 0.3µm Millipore filters.

2.2 Sterilization of Samples

As a means of eliminating bacteria as a factor in the distribution of the radionuclides in the water-sediment system, both water and sediment samples were sterilized with the expectation that the sterilization process would not significantly change the physical and/or chemical characteristics of the systems. There are three practical methods for deactivating bacteria in sediments: heat, addition of an anti-bacterial agent, or irradiation. However, each of these treatments may cause changes in the sediment and water properties. It was decided that sterilization by irradiation would be more appropriate than the other methods. Sediment and water samples were sterilized with a dose of 10^6 rads of gamma radiation from the ^{60}Co food irradiator at the College of Fisheries.

Culture experiments were conducted to test for the presence of bacteria in the sterilized and unsterilized samples. Both aerobic and anaerobic culture midea were prepared for each sample and were incubated at 22°C. The results in Table 3 show that the filtered water samples do not contain bacteria. However, the unsterilized samples of the three types of sediments showed positive indications of both aerobic and anaerobic bacteria after 4 days of incubation. Anaerobic bacteria were absent in both marine and Lake Nitinat sediments after 90 days. The sterilized freshwater sediments (Lake Washington) showed positive indications of anaerobic and aerobic bacteria after only 13 days of incubation. Thus, the indications are that 10^6 rads were effective in sterilizing sediment from Lake Nitinat, partly effective in sterilizing marine sediments (off the Columbia River), and much less effective in sterilizing freshwater sediments. Considering that the distribution coefficient experiments were conducted at a lower temperature (4-10°C) than the temperature for the bacteria growth experiments, less effect would be expected and perhaps the experiments with sterilized sediment can be considered as not affected by bacteria.

2.3 Counting Techniques

Initial counting methods included the use of the sensitive energy resolution characteristic of a Ge(Li) system to measure the low energy X- and gamma rays of ^{237}Pu and ^{241}Am, but for this system, the counting efficiency is only about 2%. We also used a system with a 2" NaI (Tl) well crystal and two single-channel analyzers to improve the detection efficiency. Calibration tests have shown that with this system the efficiency for ^{237}Pu and ^{241}Am is 65%-70%, and hence the counting time and/or the amount of tracer radio nuclides required for the experiments have been reduced. Because of the differences in energies of the ^{237}Pu (97-101 Kev) and ^{241}Am (60 Kev), the NaI (Tl) can be used to resolve the energies of these two isotopes in dual-labeled experiments. However, a 5% correction must be made for the fraction of the ^{237}Pu gamma rays which occur in the 60 Kev channel of ^{241}Am.

Table 3. Results of bacterial culture experiments

	Growth	Days of incubation	Remarks
I. Water			
Seawater, sterilized (1)	-	90	
" " (2)	-	"	
" unsterilized (1)	-	"	
" " (2)	-	"	
Lk. Nitinat, sterilized (1)	-	"	
" " (2)	-	"	
" unsterilized (1)	-	"	
" " (2)	-	"	
Lk. Wash., sterilized (1)	-	"	
" "	-	"	
" unsterilized (1)	-	"	
" " (2)	-	"	
II. Sediments			
Marine, sterilized (1)	+	39	Slight turbidity change
" " (2)	-	90	
" unsterilized (1)	+	4	meat turned black
" " (2)	+	4	after 20 days
Lk. Nitinat, sterilized (1)	-	90	
" " (2)	-	90	
" unsterilized (1)	+	4	meat turned black after 4 days of incubation indicating high anaerobic content of H_2S-producing bacteria
" " (2)	+	4	
Lk. Wash., sterilized (1)	+	13	meat turned slightly black
" " (2)	+	13	after 40 days of incubation
" unsterilized (1)	+	4	meat medium black after 20
" " (2)	+	4	days of incubation

(1) aerobic culture
(2) anaerobic culture

2.4 Evaluation of Methods

The thin layer techniques of Duursma and Bosch (1) were used for the initial experiments. This technique exposes a known amount of sediment on a filter to the radionuclides in solution. Sampling, by removing the filter, is made when equilibrium between sediment and water is reached (see Section 3.2 for more details). The purpose of duplicating Duursma's experiment in our laboratory was to evaluate our ability to conduct distribution coefficient experiments. If our results are comparable to Duursma's, then it is reasonable to compare results of other experiments in our laboratory with the results of Duursma and others.

The results in Table 4 present the distribution coefficients for ^{137}Cs and ^{65}Zn in the three standard sediments which have been sterilized. The 48-hour interval required for equilibrium to be reached, as reported by Duursma and Eisma (2) has been verified by our experiments with three types of sediments. However, the range of distribution coefficients for our sediments is somewhat less than those reported by Duursma, but probably is within the expected range of values if the different types of sediments measured are considered. To more accurately evaluate the methods of the two laboratories, an exchange of samples should be made.

Table 4. Distribution coefficients for ^{137}Cs and ^{65}Zn in the water-sediment systems: Freshwater (Lake Washington), marine (off Columbia River mouth), anoxic marine (Lake Nitinat), using the thin layer technique.

	Radionuclide	Time Hours	Distribution Coefficient, K_d
Anoxic marine water-sediment (sterilized)	^{137}Cs	49	53.82 ± 3.88
		95	49.40 ± 3.47
		146.5	54.97 ± 3.62
		216.5	54.57 ± 3.44
		288	47.95 ± 2.11
		379.4	49.02 ± 3.09
	Average K_d	=	51.62 ± 3.14
	^{65}Zn	95	(2.26 ± 0.15) x 10^3
		146.5	(2.19 ± 0.15) x 10^3
		216.5	(1.42 ± 0.09) x 10^3
	Average K_d	=	(1.96 ± 0.47) x 10^3
Marine water-sediment (sterilized)	^{137}Cs	95	15.68 ± 1.72
		216.5	18.31 ± 4.78
		288	18.18 ± 1.73
	Average K_d	=	17.39 ± 1.48
	^{65}Zn	95	(2.22 ± 0.13) x 10^2
		216.5	(7.48 ± 0.46) x 10^2
Fresh water-sediment (sterilized)	^{137}Cs	49	55.60 ± 4.24
		95	48.46 ± 3.47
		146.5	50.77 ± 3.70
		216.5	45.28 ± 2.96
	Average K_d	=	50.03 ± 4.34
	^{65}Zn	49	(5.96 ± 0.30) x 10^3
		95	(5.11 ± 0.15) x 10^3
		146.5	(4.42 ± 0.15) x 10^3
	Average K_d	=	(5.16 ± 0.77) x 10^3

3.0 RESULTS AND DISCUSSION

3.1 Summary of Current Literature

As stated in the original proposal (1976), the objectives are to prepare a status report of the results of research related to the dynamics of the distribution and transfer of transuranic elements in aquatic environments. The sources which were used to obtain information from the literature were: Radioactivity in the Marine Environment, 1971; Proceedings of a Symposium on the Impacts of Nuclear Releases in the Aquatic Environment, 1975; Transuranic Nuclides in the Environment, 1976; Nuclear Science Abstracts, June 1975-1976; A report of computerized literature searches on transuranic elements from Oak Ridge National Laboratory; and bibliographies in articles accompanying reports in Netherlands Journal of Sea Research, Health Physics, and a number of marine biological and geochemical journals. Pertinent data from the literature, including distribution, diffusion, transfer coefficients, and concentration and accumulation factors, have been evaluated. The definitions of the above terms, as customarily used in the scientific literature, are as follows:

Distribution coefficient,*K_d = $\frac{\text{concentrations of bound radionuclides in dry sediment (dpm/ml)}}{\text{concentration of radionuclide in water (dpm/ml)}}$

Diffusion Coefficient, D — For a medium not in motion, the transport of a radionuclide is by concentration gradients and is qualified by:

$$\frac{C(x,t)}{C_o} = \text{erfc}\ \frac{x}{2/D,t}$$

---

*This definition is adopted by Duursma and Gross (3) and is also used in the present study. However, the ratio of $\frac{\text{dpm/g sediment}}{\text{dpm/ml water}}$ is also used by some authors as distribution coefficients. Indication of wet or dry sediment is not always given.

C_0 = concentration of the source
D = diffusion coefficient cm^2/sec.
x = distance in cm
t = time in sec.
erfc = error function

Transfer coefficient = $\frac{\text{concentration of radionuclide in organism of higher trophic level (dpm/g)}}{\text{concentration of radionuclide in organism of lower trophic level (dpm/g)}}$

Concentration factor = $\frac{\text{concentration of radionuclide in organism (dpm/g wet)}}{\text{concentration of radionuclide in water (dpm/ml)}}$

Accumulation factor = the sum of the sorption processes, both physical and biological

Sorption = the term used whenever both adsorption and absorption are involved

Unfortunately, the terms as defined above are not always used by all authors. However, we have tabulated the literature values as much as possible in accordance with the above definitions.

A summary of the distribution coefficient (K_d) values of plutonium for laboratory experiments and for field studies is presented in Table 5. For comparison, our experimental values of the distribution coefficients for plutonium are also included in Table 5. Although the literature search has not been exhaustive (the survey of the non-English literature is not complete) we did not find reports on the distribution coefficient values for americium. We have concluded that literature on the distribution coefficients of transuranics is limited mainly to plutonium.

Reports in English on diffusion coefficients are few. Duursma and Bosch (1) propose a method for measuring diffusion coefficients which compares a "non adsorbed" radionuclide (^{36}Cl) with a strongly sorbed radionuclide. The ^{36}Cl diffuses rapidly into the sediment which permits differences in the diffusion rates to be measured as a function of physical and chemical parameters (temperature, salinity, sediment type, etc.) In determining the diffusion of a radionuclide in sediments where strong sorption occurs, the distribution coefficient is measured and calculations are made which relate this distribution coefficient to the measured diffusion coefficient of ^{36}Cl under particular conditions. This method is applicable to these combinations of elements and sediments where diffusion coefficients are lower than 10^{-8} cm^2/sec. No data

Table 5. Distribution coefficient values for plutonium as reported in the literature and determined in this study.

Sediment Type	Type of Experiment	Isotope (Valance)	$K_d x10^4$	Reference
Mediterranean	Sedimentation-oxic	^{237}Pu (III)	1.6	Duursma and Parsi (12)
"	"	^{237}Pu (IV)	1.8	
"	"	^{237}Pu (VI)	1.3	
"	Sedimentation-anoxic	^{237}Pu (III)	1.9	"
"	"	^{237}Pu (IV)	1.3	
"	"	^{237}Pu (VI)	2.2	
"	Thin-layer-oxic	^{237}Pu (III)	2.1	"
"	"	^{237}Pu (VI)	1.9 1.5	
"	"	^{237}Pu (VI)	5.7	
"	Thin-layer-anoxic	^{237}Pu (IV)	>9.4	"
Carbonate deposit (Pacific Ocean)	Adsorption	^{239}Pu	1.1	Gromov (13)
"	Desorption	^{239}Pu	7.0	"
Diatomaceous ooze (Pacific)	Adsorption	^{239}Pu	0.87	"
"	Desorption	^{239}Pu	0.65	"
Red Clay (Pacific)	Adsorption	^{239}Pu	0.98	"
"	Desorption	^{239}Pu	1.5	"
Hydrogenic Sediment (Pac.)	Adsorption	^{239}Pu	0.00	"
Silt (Bombay Bay Harbour)	Field Studies	^{239}Pu	4.84 to 13.1 (average 9.0)	Pillai and Mathew (14)

Table 5 (Cont) Distribution coefficient values for plutonium as reported in the literature and determined in this study.

Sediment Type	Type of Experiment	Isotope (Valance)	$K_d x10^4$	Reference
Lake Michigan	Field Studies	$^{239,240}Pu$	∿30	Wahlgren et al. (15)
Miami silt loam	Sorption experiments	^{237}Pu (IV)	10.4	Bondietti et al. (16)
"	"	^{238}Pu (IV)	16.8	
"	"	^{239}Pu (VI)	7.5	"
Montmorillonite (pure clay)	Sorption experiments	^{239}Pu (IV)	2.1	"
"	"	^{239}Pu (VI)	0.025	"
Contaminated calcareous sediments from Bikini Atoll	Desorption - oxic	$^{239,240}Pu$	1.64	Mo and Lowman (17)
		$^{239,240}Pu$	38.5	
Irish Sea (off Windscale) (various stations)	Field Studies	^{237}Pu	0.1 to	Hetherington et al. (18)
"		"	22	"
Lake Washington (sterilized)	Sorption (constant-mixing)	^{237}Pu	1.05 to	This study
"	"	"	3.94	"
"	"	^{237}Pu	8.46	"
"	Desorption (constant-mixing)	^{237}Pu	6.87 to	"
"	"	"	14.3	"
		^{237}Pu	26.7	"
Lake Washington (Unsterilized)	Sorption (constant-mixing)	"	28.5	"
"	Desorption (constant-mixing)	^{237}Pu	71.2	"
Columbia River mouth, marine (sterilized)	Sorption (constant-mixing)	^{237}Pu	28.4 to	"
"	"	"	80.4	"

Table 5. (Cont.) Distribution coefficient values for plutonium as reported in the literature and determined in this study.

Sediment Type	Type of Experiment	Isotope (Valance)	$K_d x10^4$	Reference
Columbia River mouth,marine (sterilized)	Sorption (constant-mixing)	^{237}Pu	27.9 to	This study
"	"	"	140	"
"	Desorption (constant mixing)	^{237}Pu	16.3 to	"
"	"	"	82.9	"
"	"	"	2.98 to	"
"	"	"	113	"
Columbia River mouth,marine (unsterilized)	Sorption (constant-mixing)	^{237}Pu	3.86 to	"
"	"	"	11.10	"
"	Desorption (constant-mixing)	^{237}Pu	5.41 to	"
"	"	"	113	"
Lake Nitinat (anoxic marine) (sterilized)	Sorption (constant-mixing)	^{237}Pu	21 to	This study
"	"	"	85.3	"
"	"	"	9.81	"
"	Desorption (constant-mixing)	^{237}Pu	2.90 to	"
"	"	"	17.9	"
"	"	"	28.3	"
Lake Nitinat, anoxic-marine (unsterilized)	Sorption (constant-mixing)	^{237}Pu	14	"
	Desorption (constant-mixing)	^{237}Pu	44.2	"

for transuranic elements in sediment are available. However, some data on the diffusion coefficient for plutonium in soils are available.

We could not find data on the transfer coefficient for organisms which were in accordance with the above definition. The available literature gives ratios of radioactivity in organisms to that of sediment or water. However, by dividing the concentration factors for trophic level organisms as given in Figs. 1, 2, and 3, an average value for transfer coefficient can be obtained.

A summary of concentration factors is presented in Figs. 1, 2, and 3, which represent field measurements only. For ease of presentation, the biological data in the figures have been grouped according to their radionuclide content. References from previous reports and from our search for new information were used to compile these histograms (see Appendix).

By inspection of Figs. 1, 2, and 3, it can be seen, except for marine seaweed and benthic invertebrates, that there is a gradual decrease in concentration factors from lower to higher trophic levels. Figure 4 compares $^{239,240}Pu$ and ^{241}Am in three trophic levels: phytoplankton, zooplankton, and fish for freshwater, and marine environments. There does not appear to be any dramatic difference in concentration factors between $^{239,240}Pu$ and ^{241}Am in freshwater and between marine and freshwater for $^{239,240}Pu$.

3.2 Distribution Coefficients for Water and Sediments

Transuranic elements are removed from water by adsorption onto detritus and suspended sediments and by uptake and/or adsorption by organisms. There are, however, numerous physical, chemical, and biological factors that govern the removal processes, some of which are not well understood. To obtain new information and to confirm the K_d values which have been reported on the magnitude of removal and remobilization of transuranic elements in aquatic environments, and on the different factors affecting this removal and remobilization, a series of controlled laboratory experiments has been undertaken.

The information on distribution coefficients is more abundant for fission products and induced radionuclides than for transuranic radionuclides. The experimental techniques used by Duursma and others have been applied in our study of the transuranic elements, plutonium and americium. The two techniques most applicable to our studies are: thin layer "at rest" method (1), and constant shaking "in motion" method (4, 5).

Thin Layer Technique: Six duplicate sediment samples of 10 mg were deposited on filter papers and with six blank filter papers were submerged into the radioactive solution. The sorption rate of the radionuclide to the sediment was determined by the differences in the

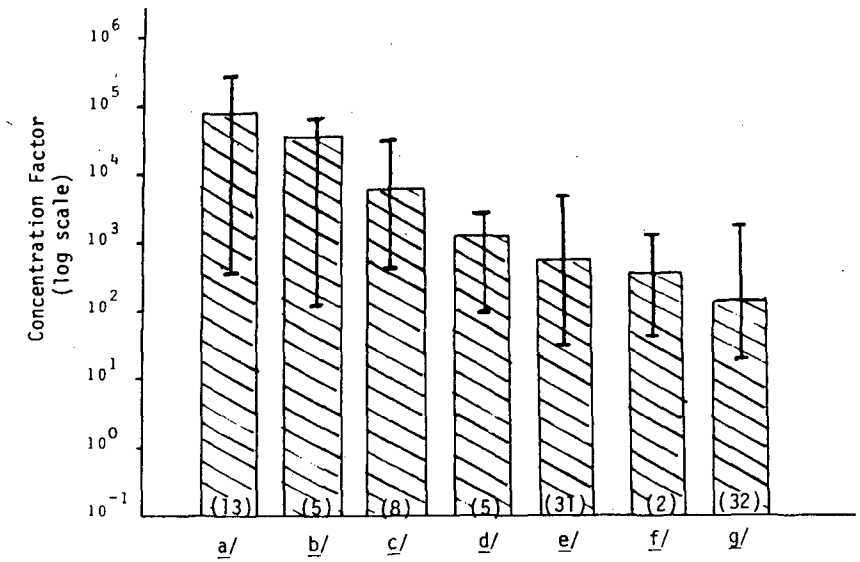

Figure 1. Literature values of concentration factors for $^{239,240}Pu$ in marine biota; a/ algae (Ref. A1, A5, A6, A7, A13); b/ phytoplankton (Ref. A1, A4, A7, A8); c/ zooplankton (Ref. A6, A7, A8, A12); d/ invertebrates, other than molluscs and crustacean (Ref. A6, A8); e/ molluscs, soft parts and shell (Ref. A2, A4, A6); f/ crustacean, soft and hard parts (Ref. A4, A5); g/ fish, entire and fish parts (Ref. A2, A3, A4, A6, A7, A12, A13). Histograms represent the mean, and bars the range of the values. Numbers in ( ) show the number of specimens or samples. The data were compiled from 1957-1974 literature.

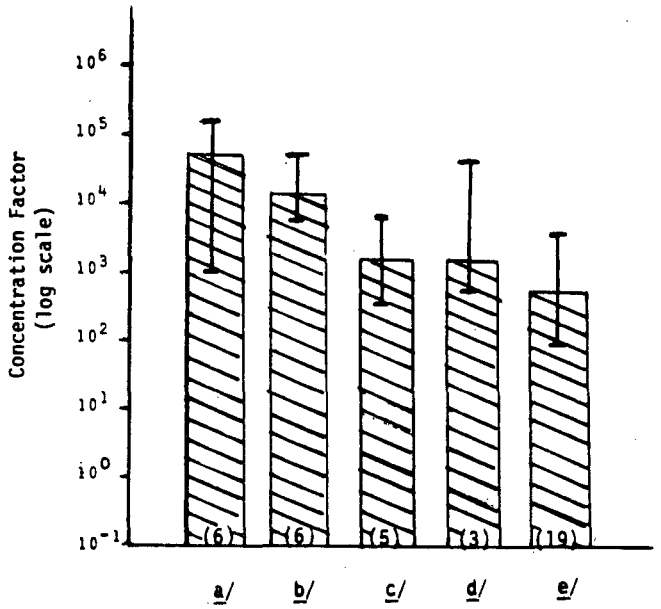

Figure 2. Literature values of concentration factors for $^{239,240}Pu$ in freshwater biota; a/ littoral organisms (Ref. A9, A10, A11); b/ phytoplankton (Ref. A9, A10, A11); c/ zooplankton (Ref. A9, A10, A11); d/ benthic invertebrates (Ref. A10); e/ fish, entire (Ref. A9. A10, A11). Histograms represent the mean and bars the range of the values. Numbers in ( ) show the number of specimens or samples. The data were reported for Rocky Flats, Great Lakes and Hanford's U Pond.

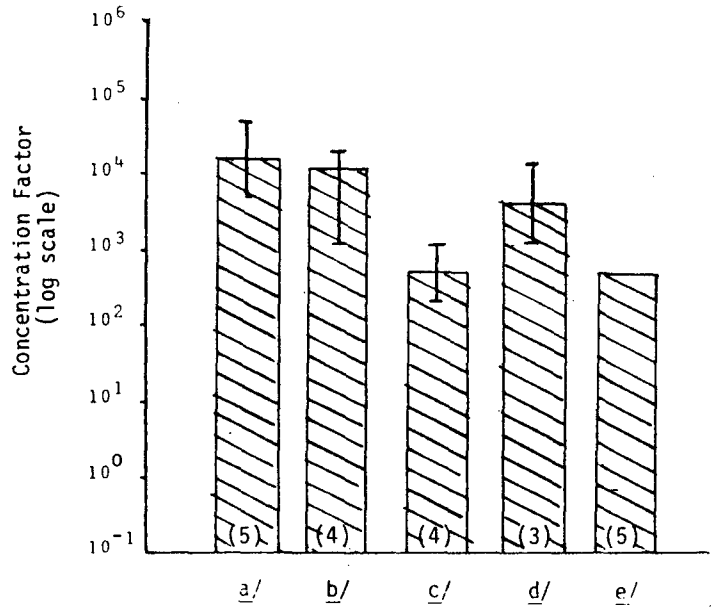

Figure 3. Literature values of concentration factors for ^{241}Am in freshwater biota; a/ littoral organisms; b/ phytoplankton; c/ zooplankton; d/ benthic invertebrates; c/ fish (upper value). Histograms represent the mean and bars the range of values. Numbers in ( ) show the number of specimens or samples (Ref. A10).

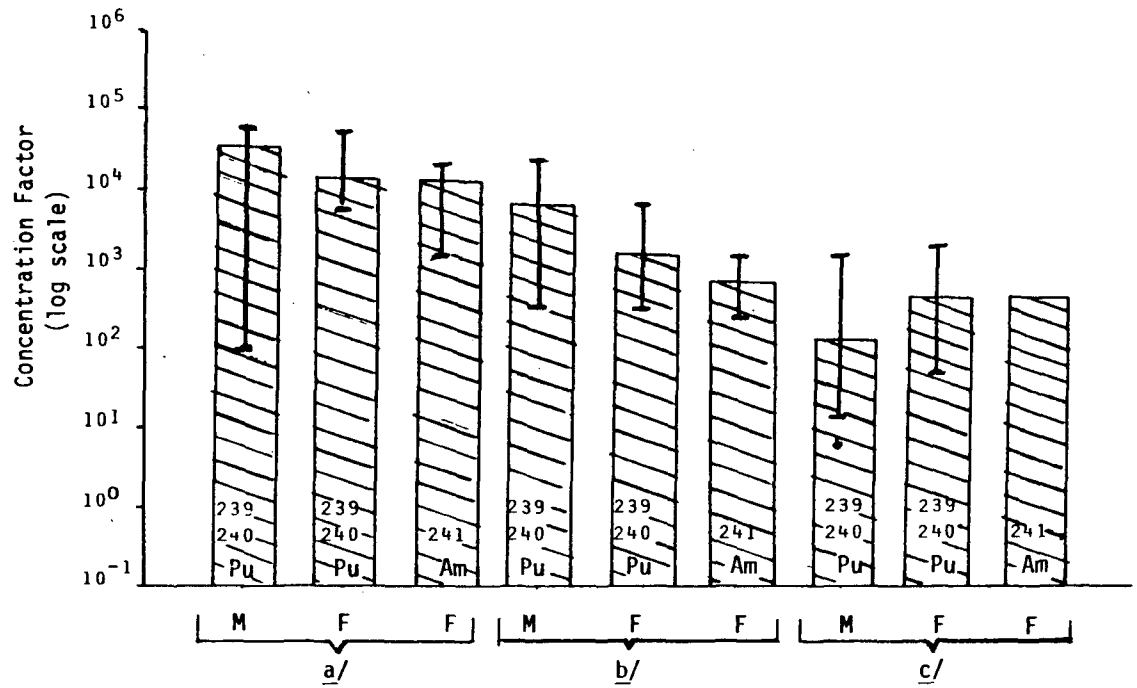

Figure 4. Comparison of literature values for concentration factors of $^{239,240}Pu$ and ^{241}Am for selective trophic levels in marine and freshwater. Histograms for the species are the same as in Figures 1-3.

accumulation of the radionuclides by the sediment and the blank filters after various exposure periods.

Problems found with this technique are agitation of the water in the container during the sorption phase and loss of sediment during removal of the sample from the solution and in subsequent treatment of the samples. We have found that the sediments will not adhere to the filters unless the size of the particles is similar to the particle size of silty-clay. It has been found by Duursma and Eisma (2) and subsequently verified in our experiments that the rate of sorption to sediments is rapid for the first 48 hours and then decreases after this time.

Constant Shaking Technique: For the sorption experiments, known amounts of sediment were suspended in water and then the mixture was spiked with radionuclides. The suspension was maintained with constant shaking under controlled temperature conditions. At different time intervals, subsamples were taken from the suspension and filtered through 0.45 μm Millipore filters. Both filters and filtrates were measured for radionuclides, and the activity of radionuclides in sediment (cpm/g) and in water (cpm/ml) was calculated. The particulates on the filters were weighed (g/ml) to correct for the units in determining the K_d value. Using this technique larger amounts of sediments can be exposed to the radionuclide solutions than in the "thin layer" method and the effects of sediment concentration can also be measured.

For desorption studies the experiments were performed in the same manner as the sorption experiments. After the sorption experiment was completed, the sediment sample was centrifuged and the radioactive solution above the sediment was decanted off and replaced with an equal amount of unspiked water. The experiment was then continued with constant shaking in the same way as for the sorption experiment.

Effects of Sediment Concentration: The variation in the distribution coefficients for ^{241}Am with different concentrations in a freshwater-sediment system was studied. Sterilized and unsterilized samples from Lake Washington were used for adsorption and desorption constant mixing experiments. The distribution coefficient decreased with increasing sediment concentrations for both sterilized and unsterilized samples as shown in Figs. 5 and 6. The desorption of ^{241}Am from the sterilized water-sediment system was not completely reversible and residual activity remained on the sediment at higher sediment concentrations (Fig. 5). This trend was not indicated in the unsterilized samples, suggesting a different sorption mechanism which is possibly due to bacterial effects or to changes in the sediment sorption sites due to the irradiation.

The values for the distribution coefficient were slightly higher at low sediment concentrations (0.1 and 0.2 mg/ml) for sterilized samples than for unsterilized samples, but were within the same range at higher sediment concentrations (0.5 and 1.0 mg/ml).

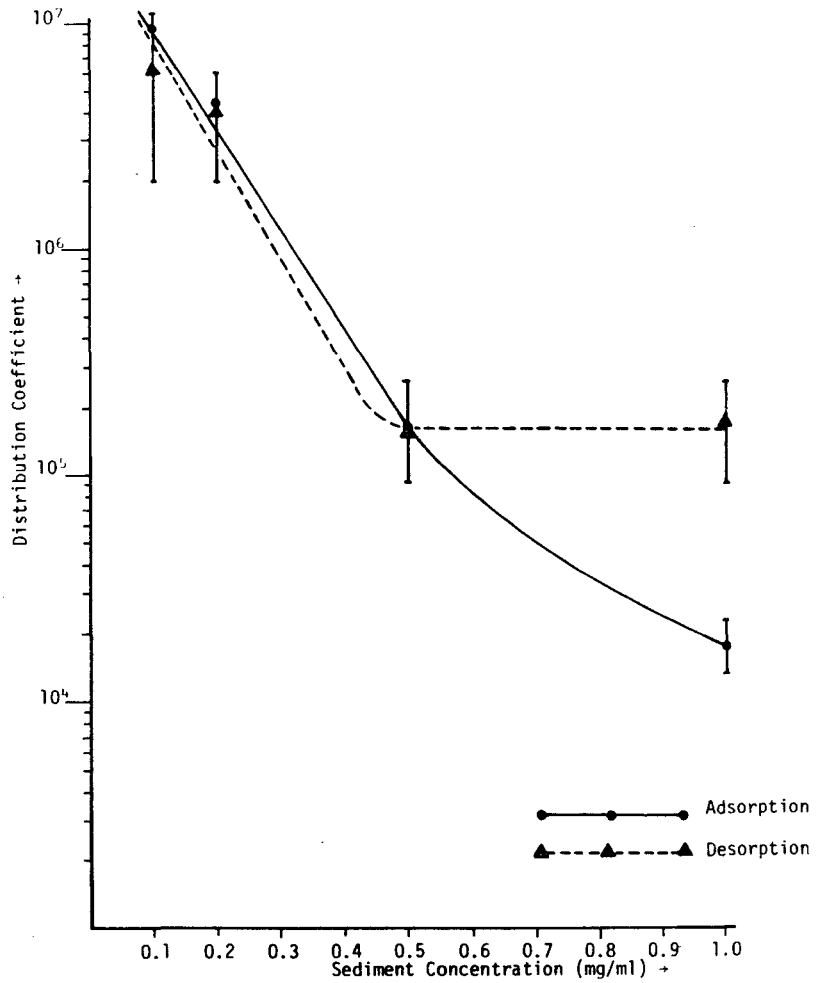

Figure 5. Distribution coefficient for ^{241}Am as a function of sediment concentration in freshwater (water and sediment, both sterilized).

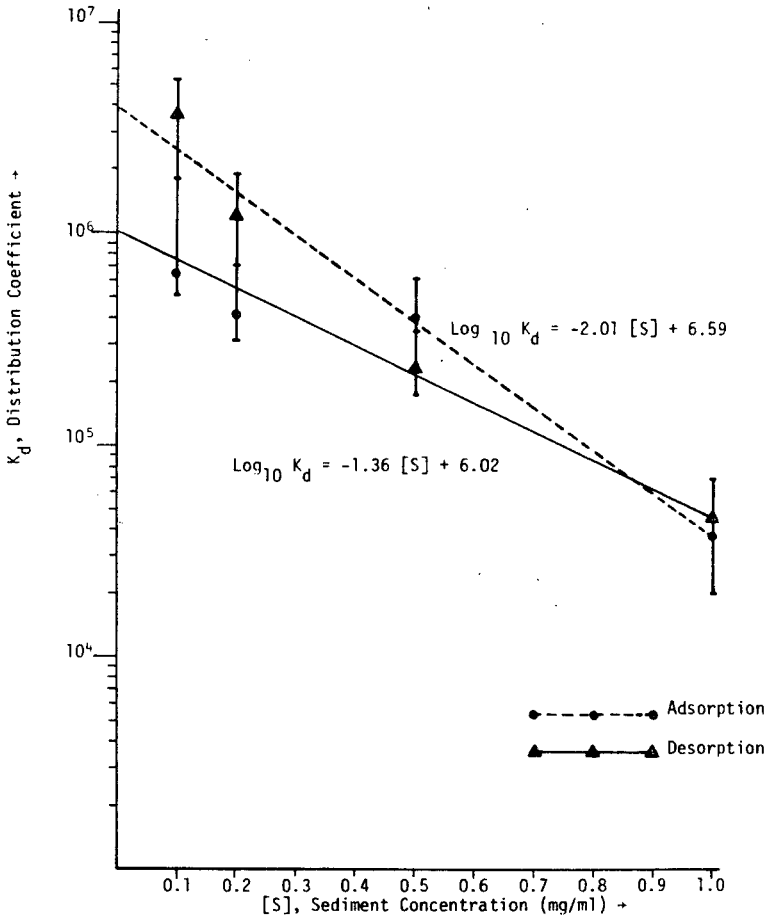

Figure 6. Distribution coefficient for ^{241}Am as a function of sediment concentration in freshwater (water and sediment, both unsterilized).

3.2.1 Fresh water-sediment system

Measurements of the distribution coefficients, K_d, for sorption and desorption of ^{237}Pu and ^{241}Am in the freshwater-sediment system (Lake Washington), are shown in Table 6. The time to reach equilibrium between sediment and transuranic radionuclides in water appears to be between 30 and 60 hours when the sediment is shaken continuously. Duursma and Eisma (2) found that most elements in marine water-sediment systems achieved equilibrium within about 40 hours, although ^{237}Pu and ^{241}Am were not among the radionuclides tested. Murray and Fukai (6) found that 50 hours was sufficient for equilibrium in their adsorption-desorption studies with ^{237}Pu and ^{241}Am.

In our determination of K_d, it has been assumed in the analysis of the data that the distribution coefficients have reached equilibrium in 40 hours and that the subsequent time series of samples represents values at equilibrium conditions. Thus, the values after 40 hours have been averaged to determine the mean and standard deviation of the distribution coefficients for the three water-sediment systems. The values in Table 6 represent duplicate experiments under identical conditions. The mean and standard deviation were calculated for data from which anomalous values had been eliminated by Chauvenet's criterion.

Data in Table 6 show that for ^{237}Pu, the K_d values for desorption are three times greater for unsterilized than for sterilized sediment. Thus, the highest K_d value for ^{237}Pu in the freshwater-sediment system is for desorption using unsterilized sediment.

For ^{241}Am, shown also in Table 6, the sterilized sediment gives the highest K_d values for both sorption and desorption where "greater than" values are observed. (This indicates the limits of detection for the water fraction since nearly all of the activity is found in the sediment fraction.) The desorption K_d value is about three times greater than the sorption K_d value for unsterilized sediments. The highest K_d values for ^{241}Am in the freshwater-sediment system are for sterilized sediments.

3.2.2 Marine water-sediment system

Measurements of the sorption and desorption K_d values for the ^{237}Pu and ^{241}Am in a marine water-sediment system are shown in Table 7. The desorption K_d values for ^{237}Pu have a wide range, indicating possible problems with the experimental method. It is expected that the "sedimentation" technique of Duursma and Bosch (1) will be better for this type of sediment.

The sorption K_d values for ^{241}Am in the marine water-sediment system show that the sterilized sediment is about 3.5 times greater than the unsterilized sediments. The desorption K_d values for the sterilized sediments have a wide range, indicating possible problems with the

Table 6. Distribution coefficients for ^{237}Pu and ^{241}Am in fresh water-sediment systems.

System	Type of Experiment	Type of Sample	Time Hours	Distribution Coefficient, ^{237}Pu	Time Hours	Distribution Coefficient, ^{241}Am
Lake Wash. Water-Sed. System	Constant-mixing (Sorption)	Sterilized	63.0	$(6.45 \pm 0.17) \times 10^4$		
		"	87.5	$(6.83 \pm 0.18) \times 10^4$	46.5	$>5.33 \pm 10^6$
			109.3	$(6.41 \pm 0.19) \times 10^4$	"	$>5.88 \pm 10^6$
			"	$(9.93 \pm 0.33) \times 10^4$	70.5	$>4.89 \pm 10^6$
			130.3	$(11.12 \pm 0.39) \times 10^4$	94.3	$>5.21 \pm 10^6$
			"	$(10.03 \pm 0.35) \times 10^4$	"	$>5.14 \pm 10^6$
		Average K_d =		$(8.46 \pm 2.13) \times 10^4$		*
	Constant-mixing (Sorption)	Unsterilized	63.0	$(2.47 \pm 0.10) \times 10^5$	46.5	$(3.67 \pm 0.46) \times 10^5$
			87.5	$(2.98 \pm 0.13) \times 10^5$	"	$(3.55 \pm 0.40) \times 10^5$
			109.3	$(2.52 \pm 0.13) \times 10^5$	70.5	$(4.85 \pm 0.62) \times 10^5$
			"	$(3.01 \pm 0.14) \times 10^5$	"	$(3.79 \pm 0.45) \times 10^5$
			130.3	$(3.25 \pm 0.12) \times 10^5$	94.5	$(3.46 \pm 0.37) \times 10^5$
		Average K_d =		$(2.85 \pm 0.34) \times 10^5$	=	$(3.86 \pm 0.57) \times 10^5$
	Constant-mixing (Desorption)	Sterilized	71.5	$(2.73 \pm 0.08) \times 10^5$		
			"	$(2.53 \pm 0.07) \times 10^5$	64.5	$>5.07 \times 10^6$
			90.0	$(2.95 \pm 0.13) \times 10^5$	"	$>4.93 \times 10^6$
			"	$(2.65 \pm 0.07) \times 10^5$	113.5	$>5.17 \times 10^6$
			116.0	$(2.70 \pm 0.07) \times 10^5$	144.0	$>5.77 \times 10^6$
			"	$(2.48 \pm 0.10) \times 10^5$	"	$>4.80 \times 10^6$
		Average K_d =		$(2.67 \pm 0.17) \times 10^5$	=	*
	Constant-mixing (Desorption)	Unsterilized	46	$(7.00 \pm 0.23) \times 10^5$		
			71.5	$(7.14 \pm 0.37) \times 10^5$	64.5	$(1.37 \pm 0.75) \times 10^6$
			"	$(6.85 \pm 0.47) \times 10^5$		$(1.68 \pm 0.10) \times 10^6$
			90.0	$(7.40 \pm 0.28) \times 10^5$	113.5	$(0.70 \pm 0.18) \times 10^6$
			"	$(7.16 \pm 0.50) \times 10^5$	"	$(0.78 \pm 0.27) \times 10^6$
			116.0	$(6.81 \pm 0.22) \times 10^5$	144.0	$(1.92 \pm 1.61) \times 10^6$
			"	$(7.48 \pm 0.48) \times 10^5$	"	$(0.96 \pm 0.31) \times 10^6$
		Average K_d =		$(7.12 \pm 0.26) \times 10^5$	=	$(1.24 \pm 0.50) \times 10^6$

*Duplicate experiments did not give reproducible K_d's. See text for discussion.

Table 7. Distribution coefficients for ^{237}Pu and ^{241}Am in marine water-sediment systems.

System	Type of Experiment	Type of Sample	Time Hours	Distribution Coefficient, ^{237}Pu	Time Hours	Distribution Coefficent, ^{241}Am
Marine-Water Sed. System	Constant-mixing (Sorption)	Sterilized	44.5	$(2.79 \pm 0.08) \times 10^4$	44.5	$(9.33 \pm 0.72) \times 10^5$
			65.0	$(3.65 \pm 0.08) \times 10^4$	65.0	$(9.57 \pm 0.63) \times 10^5$
			88.0	$(3.06 \pm 0.07) \times 10^4$	88.0	$(8.22 \pm 0.65) \times 10^5$
			"	$(6.50 \pm 0.31) \times 10^5$	"	$(9.35 \pm 0.54) \times 10^5$
			113.5	$(3.34 \pm 0.08) \times 10^4$	113.5	$(9.85 \pm 0.88) \times 10^5$
			"	$(1.40 \pm 0.08) \times 10^6$		
			136.5	$(7.90 \pm 0.26) \times 10^5$		
		Average K_d =		*	=	$(9.26 \pm 0.62) \times 10^5$
	Constant-mixing (Sorption)	Unsterilized	44.0	$(3.93 \pm 0.09) \times 10^4$	44	$(2.20 \pm 0.08) \times 10^5$
			64.5	$(3.86 \pm 0.08) \times 10^4$	64.5	$(2.27 \pm 0.07) \times 10^5$
			87.5	$(3.92 \pm 0.09) \times 10^4$	87.5	$(2.21 \pm 0.09) \times 10^5$
				$(9.43 \pm 0.26) \times 10^4$	"	$(3.10 \pm 0.14) \times 10^5$
			113.0	$(4.84 \pm 0.12) \times 10^4$	113	$(2.89 \pm 0.12) \times 10^5$
			113.5	$(9.87 \pm 0.20) \times 10^4$	113.5	$(3.11 \pm 0.09) \times 10^5$
			136.0	$(11.10 \pm 0.78) \times 10^4$		
		Average K_d =		*	=	$(2.63 \pm 0.45) \times 10^5$
	Constant-mixing (Desorption)	Sterlized	70.5	$(11.34 \pm 0.45) \times 10^5$	70.5	$(6.16 \quad 0.54) \times 10^6$
			"	$(3.97 \pm 0.13) \times 10^4$	"	$(3.14 \quad 0.27) \times 10^5$
			119.5	$(8.36 \pm 0.38) \times 10^5$	119.5	$(4.11 \quad 0.39) \times 10^6$
				$(2.98 \pm 0.07) \times 10^4$	"	$(5.15 \quad 0.37) \times 10^5$
			149.5	$(5.18 \pm 0.21) \times 10^5$	149.5	$(0.90 \quad 0.05) \times 10^6$
				$(3.68 \pm 0.11) \times 10^4$	"	$(4.96 \quad 0.43) \times 10^5$
		Average K_d =		*	=	*
	Constant-mixing (Desorption)		70.5	$(1.30 \pm 0.05) \times 10^5$	70.5	$(2.09 \pm 0.09) \times 10^5$
			"	$(7.50 \pm 0.27) \times 10^4$	"	$(1.66 \pm 0.08) \times 10^5$
			119.5	$(1.08 \pm 0.04) \times 10^5$	119.5	$(1.83 \pm 0.08) \times 10^5$
			"	$(5.41 \pm 0.16) \times 10^4$		
			149.5	$(7.14 \pm 0.30) \times 10^4$	149.5	$(1.82 \pm 0.08) \times 10^5$
			"	$(5.44 \pm 0.20) \times 10^4$	"	$(1.53 \pm 0.08) \times 10^5$
		Average K_d =		*		$(1.79 \quad 0.21) \times 10$

*Duplicate experiments did not give reproducible K_d's. See text for discussion.

Table 7. (Cont.) Distribution coefficients for ^{237}Pu and ^{241}Am in marine water-sediment systems.

System	Type of Experiment	Type of Sample	Time Hours	Distribution Coefficient, ^{237}Pu	Time Hours	Distribution Coefficient, ^{241}Am
Anoxic Marine Water-Sediment System	Constant-mixing (Sorption)	Sterilized			68.5	$(7.46 \pm 0.39) \times 10^5$
					89.0	$(7.98 \pm 0.43) \times 10^5$
			112	$(9.69 \pm 0.21) \times 10^4$	112.0	$(6.91 \pm 0.29) \times 10^5$
				$(9.78 \pm 0.22) \times 10^4$		$(9.37 \pm 0.53) \times 10^5$
			137.5	$(9.88 \pm 0.22) \times 10^4$	137.5	$(6.10 \pm 0.29) \times 10^5$
				$(9.80 \pm 0.22) \times 10^4$		$(7.59 \pm 0.41) \times 10^5$
			160.5	$(9.89 \pm 0.22) \times 10^4$	160.5	$(5.88 \pm 0.29) \times 10^5$
				$(9.84 \pm 0.22) \times 10^4$		$(8.66 \pm 0.50) \times 10^5$
			Average K_d =	$(9.81 \pm 0.07) \times 10^4$	=	$(7.49 \pm 1.20) \times 10^5$
	Constant-mixing (Sorption)	Unsterilized	68.0	$(1.12 \pm 0.03) \times 10^5$	68.0	$(7.42 \pm 0.31) \times 10^5$
			88.5	$(1.29 \pm 0.04) \times 10^5$	88.5	$(5.77 \pm 0.28) \times 10^5$
			111.5	$(1.42 \pm 0.04) \times 10^5$	111.5	$(6.26 \pm 0.26) \times 10^5$
				$(1.68 \pm 0.06) \times 10^5$		$(6.25 \pm 0.33) \times 10^5$
			137.0	$(1.37 \pm 0.04) \times 10^5$	137.0	$(6.79 \pm 0.35) \times 10^5$
				$(1.53 \pm 0.04) \times 10^5$		$(7.44 \pm 0.32) \times 10^5$
			160	$(1.36 \pm 0.04) \times 10^5$	160	$(5.35 \pm 0.21) \times 10^5$
			Average K_d =	$(1.40 \pm 0.18) \times 10^5$	=	$(6.47 \pm 0.79) \times 10^5$
	Constant-mixing (Desorption)	Sterilized	71.0	$(3.39 \pm 0.08) \times 10^5$	71.0	$>1.27 \times 10^7$
						$(7.15 \quad 0.93) \times 10^6$
			120.0	$(2.07 \pm 0.07) \times 10^5$	120.0	$>1.27 \times 10^7$
				$(2.07 \pm 0.06) \times 10^5$		$(8.20 \pm 1.35) \times 10^6$
			150.0	$(3.47 \pm 0.10) \times 10^5$	150.0	$(1.02 \pm 0.15) \times 10^7$
				$(2.88 \pm 0.10) \times 10^5$		$(3.54 \pm 0.31) \times 10^6$
			Average K_d =	$(2.83 \pm 0.62) \times 10^5$	=	*
	Constant-mixing (Desorption)	Unsterilized	71.0	$(4.23 \pm 0.19) \times 10^5$	71.0	$(7.46 \pm 1.17) \times 10^6$
				$(4.85 \pm 0.24) \times 10^5$		$(2.99 \pm 0.31) \times 10^6$
			120.0	$(4.22 \pm 0.12) \times 10^5$	120.0	$>1.13 \times 10^7$
				$(4.90 \pm 0.20) \times 10^5$		$(9.25 \pm 1.35) \times 10^6$
			150.0	$(3.82 \pm 0.15) \times 10^5$	150.0	$(8.74 \pm 1.18) \times 10^6$
				$(4.47 \pm 0.22) \times 10^5$		$>1.13 \times 10^7$
			Average K_d =	$(4.42 \pm 0.41) \times 10^5$	=	*

*Duplicate experiments did not give reproducible K_d's. See text for discussion.

experimental method. The desorption K_d values for the unsterilized sediments give more constant values which are slightly lower in absolute magnitude than the sorption K_d values. The wide range of values found in the marine sediment may be due to the inhomogeneous distribution of the sediments in the suspension. The high fraction of sand compared to the other two components (40% vs. 2.5-3.7%), may have contributed to the "anomalous" values. A small inhomogeneity of the suspended sediments could give the range of values found. Additional effort is required in developing the techniques for measuring the K_d values in sediments with high sand content.

3.2.3 Anoxic marine sediment-water system

Measurements of the sorption-desorption K_d values for ^{237}Pu and ^{241}Am in the anoxic marine water-sediment system are also shown in Table 7. The time to reach equilibrium for the sorption K_d is longer than for the freshwater and marine water-sediment systems discussed previously. For ^{237}Pu, the sorption K_d value measured is slightly higher (1.4 times) in unsterilized than in the sterilized water-sediment system. The desorption K_d values are about three times higher in both the sterilized and unsterilized sediments, indicating that, once sorbed, ^{237}Pu remains strongly attached to the sediment particle.

The sorption K_d values for both sterilized and unsterilized sediments for ^{241}Am are almost the same (7×10^5). The desorption K_d values for ^{241}Am are the highest measured in our studies; measurement of the water fraction are at the limits of detection (equivalent to a K_d of about 10^7). In anoxic marine water-sediment systems the ^{241}Am, once deposited, has a great tendency to remain sorbed; the presence of bacteria does not change sorption or desorption coefficients for ^{241}Am.

3.2.4 Summary of K_d experiments

An attempt has been made to identify which of the several parameters are most important to the distribution coefficients. The summary of the ratios of K_d values of ^{237}Pu and ^{241}Am for the parameters--sterilized, unsterilized, sorption, desorption--in the three sediment types is shown in Table 8. The values are all measured K_d ratios, compared in each case to the conditions of unsterilized and sorption K_d measurements of ^{237}Pu and ^{241}Am which are taken as 1. It appears that sterilization has affected a decrease in the K_d values for ^{237}Pu in freshwater-sediment and anoxic marine water-sediment systems. The values for the marine water-sediment system were too variable to be used. Sterilization affected an increase in the K_d value for ^{241}Am in freshwater-sediment and marine water-sediment systems. No effect of sterilization was observed in the anoxic marine water-sediment system.

The significance of the differences in the measured values shown in Tables 6 and 7 due to radionuclide, sorption-desorption, sterilization-

Table 8. (a) Ratios of all ^{237}Pu and ^{241}Am distribution coefficients to sorption distribution coefficients in the unsterilized system: (b) Levels of significance for measurements of distribution coefficients.

(a)

Water-sediment	Sorption		Desorption		Sorption		Desorption	
	^{237}Pu	^{241}Pu	^{237}Pu	^{241}Am	^{237}Pu	^{241}Am	^{237}Pu	^{241}Am
Anoxic Marine water-sediment system	1	1	3	?	0.7	1	2	?
Marine water-sediment system	1	1	?	0.7	?	3.5	?	?
Freshwater-sediment system	1	1	2.5	3	0.3	>13	1	>13

(b)

System		Sterilized Unsterilized	Sorption Desorption	Interaction
Anoxic marine water-sediment system	^{237}Pu	$p \leq 0.01$	$p \leq 0.01$	$p \leq 0.01$
	^{241}Am	N.S.	$p \leq 0.01$	N.S.
Marine water-sediment system	^{237}Pu ^{241}Am	$p \leq 0.05$	$p > 0.05$	$p > 0.05$
Freshwater-sediment system	^{237}Pu	$p \leq 0.01$	$p \leq 0.01$	$p \leq 0.01$
	^{241}Am	$p \leq 0.01$	$p \leq 0.05$	$p \leq 0.01$

unsterilization was analyzed using a 2 x 2 factorial model for each of the water-sediment systems (7). The two levels for Factor A are sorption and desorption for ^{237}Pu and ^{241}Am, while the two levels for Factor B are sterilization and unsterilization for ^{237}Pu and ^{241}Am. The response variable for this analysis is the distribution coefficient, K_d. The levels of statistical significance are given in Table 8. From this analysis of the data the following observations can be made:

(a) With the exception of ^{241}Am in the anoxic marine water-sediment system, there is significant difference between the sterilized and unsterilized systems.

(b) With the exception of ^{241}Am in the marine water-sediment system, there are significant differences between the sorption and desorption experiments.

(c) For ^{237}Pu there appears to be an interaction between the sorption-desorption and sterilization for anoxic marine water-sediment and freshwater-sediment systems.

3.3 Dialysis Studies

The experimental setup shown in Fig. 7 is similar in design to the setup employed by Barsdate et al. (8) and Dawson and Duursma (9). The porosity of the dialysis membranes used in our experiments permitted passage of particles equivalent to a molecular weight of 6000-8000. With this membrane, only the low molecular weight compounds, small colloids, and ionic solutes could participate in the sorption and/or uptake processes. The membrane sacs were filled with 50 ml of unspiked seawater and were suspended in the radioactive seawater. To the phytoplankton sac, 5 ml of concentrated inoculum of *Phaeodactylum tricornutum* were added; and to the sediment sac, 5 ml of filtrate (0.4μm) from the *P. tricornutum* culture and 31.3 mg of anoxic marine sediment from Lake Nitinat were added. The contents of the sacs were kept in suspension and aerated by stirring. A light source was provided to maintain the growth of the phytoplankton. The radioactive seawater outside the dialysis sacs was kept in motion by a magnetic stirrer. The phytoplankton concentration at the end of the experiment was 7×10^6 cells/ml, and the total weight of the dry plankton was .0068g.

After ten days, 50 ml aliquots from each of the three compartments was filtered through 0.22 μm filters and the activity of the radionuclides on the filters and in the filtrates was measured using the calibrated Ge(Li) detector system. Duursma and Dawson (9) demonstrated that the equilibrium time for most radionuclides was established after 100 hours; we have assumed that the 10-day period was sufficient to reach equilibrium in our first experiments.

Table 9. Measurements of radionuclides in the three compartments of the dialysis system after 10 days' equilibrium time.

Radio-nuclide	A Sediment Sac Compartment		B Phytoplankton Sac Compartment		C Spiked Seawater Compartment	
	Filtrate dpm/ml ± 2 SD, %	Sediment on filter dpm/g ± 2 SD, %	Filtrate dpm/ml ± 2 SD, %	Phytoplankton on filter dpm/g ± 2 SD, %	Filtrate dpm/ml ± 2 SD, %	Particulate dpm/ml ± 2 SD, %
^{241}Am	27 ±5.2	2615± 2.0	29 ± 5.6	2.77×10^5± 2.2	25 ±14.2	25 ± 1.8
^{207}Bi	*	41±24.4	2 ±50	299±18	*	0.78±17.3
^{137}Cs	836 ±0.6	75±19.3	701 ± 0.7	*	827 ± 1.1	208 ± 5.3
^{65}Zn	1511 ±0.7	566±11.7	1669 ± 0.8	465± 0.6	1133 ± 1.3	27 ± 4.6
^{60}Co	1095 ±0.6	893± 6.0	1107 ± 0.7	1.73×10^4± 1.4	1108 ± 1.1	21 ± 3.6
^{238}Pu	0.32± .03	20± 5.0	0.25± .02	488 ±22.2	0.30± .02	*

* Poor counting statistics.

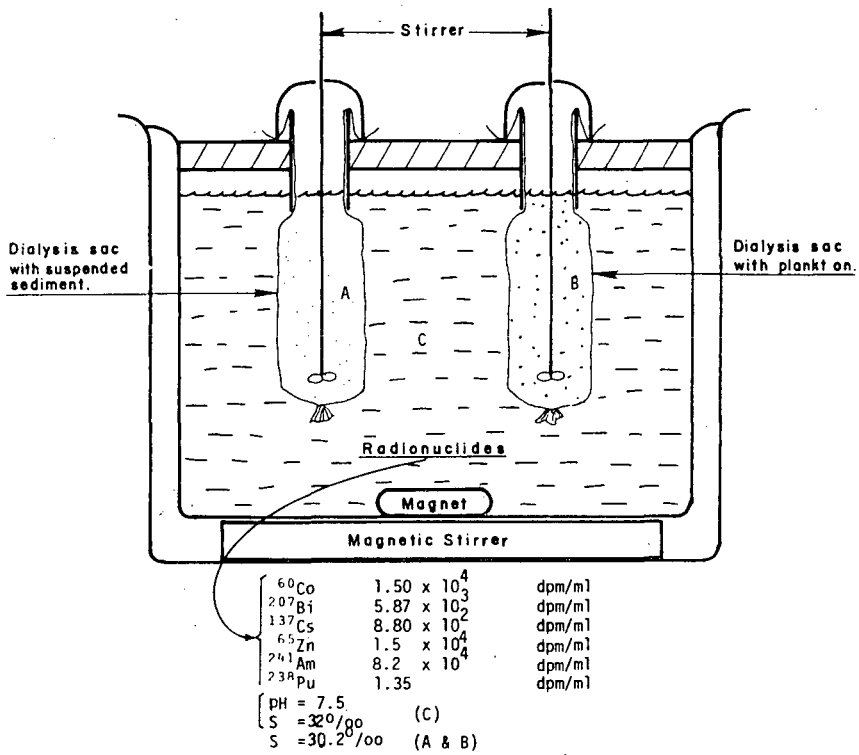

Figure 7. Dialysis experiment setup.

Following gamma counting, known amounts of a chemical yield tracer ^{242}Pu were added and the samples were wet ashed with $HNO_3/HClO_4$. The plutonium isotopes were initially separated from the bulk of the matrix material by sorption from an 8M HNO_3 solution on an ion exchange resin column (BIO-RAD-AGI-x8, 100-200 mesh). The plutonium solution was then purified, using the liquid ion exchange (triisooctylamine, TIOA) method by Butler (1968). The measurements of the ^{238}Pu and ^{242}Pu in samples which were electroplated onto stainless steel discs, was by alpha spectroscopy, using silicon surface-barrier detectors and pulse-height analyzers. The chemical yield for plutonium analysis was determined from the recovery of the ^{242}Pu tracer. The results of analysis for ^{238}Pu and other radionuclides are shown in Tables 9 and 10.

The radiochemical procedure of the separation and purification of ^{238}Pu is time-consuming and thus only one dialysis experiment has been completed. Plutonium-237 may be used for the experiments since it can be measured by gamma spectrometry rather than by alpha spectrometry which is used for ^{238}Pu. However, ^{237}Pu, which is produced at Oak Ridge, is available only periodically.

Information is lacking on the actual pore size (or pore size spectrum) of the dialysis membrane for these inorganic colloidal radionuclides in seawater, since the approximate size has been determined using organic molecules of known size. Therefore, it is not possible to determine the extent that colloids are blocked by the dialysis membrane until other pore sizes are used. The time for the radionuclides to come to equilibrium on both sides of the membrane has not been determined.

3.3.1 Phytoplankton uptake

From the experiments to date, it appears that a fraction of the ^{241}Am, ^{137}Cs, ^{65}Zn, ^{60}Co, and ^{238}Pu is "soluble" and diffuses easily through the membrane, and, except for ^{207}Bi, it is reasonable to assume that equilibrium has been achieved in the 10-day period of the experiment. However, the soluble radionuclides, after passage through the membrane, have been subsequently taken up by plankton, or they have been sorbed onto the sediment particles. It should be noted that the walls of the membrane may also adsorb a considerable fraction of the radionuclides, but the amount has not been measured. Further studies of the processes controlling the diffusion are in progress. Complexation of radionuclides by plankton metabolites, nutrients, or organic molecules from sediments may be occurring and, as a result, the solubility of the transuranic elements increased. A comparison of the concentration factors obtained in this experiment with those reported in the literature reveals that ^{65}Zn and ^{60}Co values are low by two to four orders of magnitude (Lowman et al. 1971); the two methods may not be comparable. These differences could also be explained by metabolites, or organic molecules present in the water which have stronger chemical bonds to zinc and cobalt than these elements have to plankton.

The results in Table 9 show that high concentrations of ^{238}Pu and ^{241}Am in compartment B are associated with phytoplankton. It was reported previously that the major mode of plutonium and americium accumulation in P. triconutum was a nonbiological process (1976-1977 Annual Progress Report, Assessment of Nuclear Industrial Impact on the Environment, Section IV. Confirmation of Radionuclide Pathways, Laboratory of Radiation Ecology). It was also reported that adsorption, rather than absorption, was the major mode of accumulation for both radionuclides. However, a significant fraction of the ^{237}Pu remained as a solute in the water and was not taken up by P. triconutum.

The accumulation of the radionuclides on the sediments in the dialysis sacs (dpm/g sediment) is much lower than the corresponding value for plankton as shown in Table 10. However, this comparison does not give a clear picture of the competition between suspended sediment and phytoplankton in concentrating radionuclides due to the different quantities present (mg/ml). Since the method of accumulation of plutonium and americium on both plankton and sediment is mainly a surface sorption process, a better comparison may be on the basis of surface area.

Table 10. Radionuclide distribution coefficients for sediments and concentration factors for phytoplankton in dialysis experiments.

Radionuclide	A Distribution coefficients for sediment dpm/g sediment / dpm/ml filtrate	B Concentration factor for phytoplankton dpm/g phytoplankton / dpm/ml filtrate
^{241}Am	98	9447
^{207}Bi	*	128
^{137}Cs	0.1	*
^{65}Zn	0.4	0.3
^{60}Co	0.8	16
^{238}Pu	63	1952

* poor counting statistics

4.0 SUMMARY

The major conclusions from these studies are as follows:

1) Tests of the experimental procedures have been made using ^{65}Zn and ^{137}Cs and the distribution coefficients for near-Washington sediments have been determined. The values are about the same order of magnitude as those found by Duursma and Eisma (2) for different sediment types.

2) Distribution coefficients of ^{237}Pu, ^{241}Am, ^{65}Zn, and ^{137}Cs have been measured in sorption and desorption experiments for three standard water-sediment systems--freshwater, marine, and anoxic marine. For ^{237}Pu the distribution coefficient for desorption is three times greater than for sorption.

3) Bacterial effects on distribution coefficients have been demonstrated using sterile and unsterilized water-sediment. For ^{237}Pu the distribution coefficient for the sterilized system is one-third that of the unsterilized system; for ^{241}Am the K_d value for the sterilized system is three times that of the unsterilized system.

The environmental factors which may influence the distribution coefficients in these experiments have been defined: the temperature has been chosen which represents the natural conditions at the water-sediment interface; i.e., 4°-8° C; the salinity has been chosen to represent the natural conditions of $32^o/oo$; other variables such as nutrients in the water and pH have been measured, but their effects on the K_d values have not been determined.

4) The desorption distribution coefficients have been measured. In many experiments desorption K_d values are significantly higher than the sorption K_d values for both ^{237}Pu and ^{241}Am. This finding shows that the transuranic elements are strongly sorbed to sediment particles and that ^{241}Am is more strongly sorbed than ^{237}Pu.

5) A preliminary experiment has been completed using sediment and phytoplankton in dialysis bags exposed to a reservoir of several radioclides. The results show that ^{237}Pu, ^{65}Zn, ^{137}Cs, ^{241}Am, and ^{60}Co diffuse easily through dialysis bags that have a 6000-8000 molecular weight cut-off.

In the first year of the study we have been able to define several areas in which we need more information and would recommend further work. We would like to: compare K_d values in identical samples with Duursma; compare chemical with radiation sterilization; evaluate chemical and physico-chemical state effects on K_d values; determine effects of pH and surface area on K_d values; and design field experiments to obtain data which would give a more realistic evaluation of the processes which influence remobilization of transuranic elements from sediments.

REFERENCES

1. Duursma, E. K. and C. J. Bosch. 1970. Theoretical, experimental and field studies concerning diffusion of radioisotopes in sediments and suspended particles of the sea. Part B. Methods and experiments. Neth. J. Sea Res. 4:395-469.

2. Duursma, E. K. and D. Eisma. 1973. Theoretical, experimental and field studies concerning reactions of radioisotopes with sediments and suspended particles of the sea. Part C: Applications to field studies. Neth. J. Sea Res. 6:265-324.

3. Duursma, E. K. and M. G. Gross. 1971. Marine sediments and radioactivity In: Radioactivity in the marine environment. U.S. Nat. Acad. Sci., NRC, Washington, D.C.:147-160.

4. Aston, S. R. and E. K. Duursma. 1973. Concentration effects on ^{137}Cs, ^{65}Zn, ^{60}Co and ^{106}Ru sorption by marine sediments, with geochemical implications. Neth. J. Sea Res. 6:225-240.

5. Murray, C. N. and L. Murray. 1973. Adsorption-desorption equilibria of some radionuclides in sediment-freshwater and sediment-seawater systems. In: Radioactive Contamination of the Marine Environment, Proc. Symp., Seattle, July 10-14, 1972. IAEA, Vienna.

6. Murray, C. N. and R. Fukai. 1975. Adsorption-desorption characteristics of plutonium and americium with sediment particles in the estuarine environment, studies using plutonium-237 and americium-241. In: Impacts of Nuclear Releases into the Aquatic Environment, Proc. Symp., Otaniemi, Finland, June 30-July 4, 1975. IAEA, Vienna.

7. Dixon, W. J. and F. J. Massey. 1969. Introduction to statistical analysis. McGraw-Hill Book Co., New York. Pp. 181.

8. Barsdate, R. J. 1970. Transition metal binding by large molecules in high latitude waters. In: P.W. Hood, ed. Organic matter in natural waters. Occ Publ. No. 1, Inst. Mar. Sci., Univ. Alaska:425-493.

9. Dawson, R. and Duursma, E. K. 1974. Distribution of radioisotopes between phytoplankton, sediment, and seawater via dialysis compartment system. Neth. J. Sea Res. 8:339-353.

10. Butler, F. E. 1968. Rapid bioassay methods for plutonium, neptunium, and uranium. Health Physics, 15:19-24.

11. Lowman, F. G., T. R. Rice, and F. A. Richards. 1971. Accumulation and redistribution of radionuclides by marine organisms. In: Radioactivity in the marine environment. U.S. Nat. Acad. Sci., NRC. Washington D.C.:147-160.

12. Duursma, E. K. and P. Parsi. 1974. Distribution coefficient of plutonium between sediment and seawater. In: Activities of the International Laboratory of Marine Radiactivity. 1974 Reports IAEA (SM-163) 94-96.

13. Gromov, V. V. 1974. Investigation of the behavior of microelements in ocean water by the desorption method. Soviet Radiochemistry, 16(6):742-745.

14. Pillai, K. C. and E. Mathew. 1976. Plutonium in the aquatic environment, its behaviour, distribution and significance. In: Transuranium nuclides in the environment, Proc., USERDA/IAEA Symp., San Francisco, CA, Nov. 17-21, 1975, IAEA, Vienna.

15. Wahlgren, M. A., J. J. Alberts, D. M. Nelson, and K. A. Orlandini. 1976. Study of the behaviour of transuranics and possible chemical homologues in Lake Michigan water and biota. In: Transuranium nuclides in the environment, Proc., USERDA/IAEA Symp., San Francisco, CA, Nov. 17-21, 1975. IAEA, Vienna.

16. Bondietti, E. A., S. A. Reynolds, and M. H. Shanks. 1976. Interaction of plutonium with complexing substances in soils and natural waters. In: Transuranium nuclides in the environment, Proc., USERDA/IAEA Symp., San Francisco, CA, Nov. 17-21, 1975. IAEA, Vienna.

17. Mo, T. and F. G. Lowman. 1975. Laboratory experiments on the transfer dynamics of plutonium from marine sediments to seawater and to marine organisms. 4th Nat. Symp. on Radioecology, Corvallis, OR, May 12, 1975. 35 pp.

18. Hetherington, J. A., D. F. Jefferies, and M. B. Lovett. 1975. Some investigations into the behaviour of plutonium in the marine environment. In: Impacts of nuclear releases into the aquatic environment. Proc. Symp., Otoaniemi, Finland, June 30-July 4, 1975. IAEA, Vienna.

APPENDIX I

Literature Cited in Compilation of Histograms

A1. Aarkrog, A. 1971. Radioecological investigations of plutonium in the Arctic marine environment. Health Physics 20:31-48.

A2. Hetherington, J. A., D. R. Jefferies, and M. B. Lovett. 1975. Some investigations with the behavior of plutonium in the marine environment. In: Impacts of Nuclear releases into the aquatic environment. Proc., Sympos., Otaniemi, Finland, June 30-July 4, 1975. IAEA, Vienna.

A3. Hetherington, J. A., D. F. Jefferies, N. T. Mitchell, R. J. Pentreath, and D. S. Woodhead. 1976. Environmental and public health consequences of the controlled disposal of transuranic elements to the marine environment. In: Transuranium nuclides in the environment, Proc., USERDA/IAEA Sympos., San Francisco, CA, Nov 17-21, 1975. IAEA, Vienna.

A4. Lowman, F. G., T. P. Rice, and F. A. Richards. 1971. Accumulation and redistribution of radionuclides by marine organisms in: Radioactivity in the marine environment. U.S. Nat. Acad. Sci., NRC, Washington, D. C.:147-160.

A5. Miyaki, T. and Sugimura, T. 1975. The plutonium content of Pacific ocean waters. In: Transuranium nuclides in the environment, Proc., USERDA/IAEA Sympos., San Francisco, CA, Nov. 17-21, 1975. IAEA, Vienna.

A6. Noshkin, V. B. 1972. Ecological aspects of plutonium dissemination in aquatic environments. Health Physics 22:537-549.

A7. Pillai, K. C., R. C. Smith, and T. R. Folsom. 1975. Plutonium in the marine environment. Nature 203:568-571.

A8. Schell, W. R., and R. L. Watters. 1975. Plutonium in Aqueous Systems. Health Physics 29:587-597.

A9. Thompson, M. A. 1975. Plutonium in the aquatic environment around the Rocky Flats Facility. In: Impacts of nuclear releases into the aquatic environment. Proc., Sympos., Otaniemi, Finland, June 30-July 4, 1975. IAEA, Vienna.

A10. Wahlgren, M. A., J. J. Alberts, D. M. Nelson, and K. A. Orlandini. 1976. Study of the behaviour of transuranics and possible chemical homologues in lake Michigan water and biota. In: Transuranium nuclides in the environment. Proc., USERDA/IAEA Sympos., San Francisco, CA. Nov. 17-21, 1975. IAEA, Vienna.

A11. Wahlgren, M. A., and J. S. Marshall. 1975. The behaviour of plutonium and other long-lived radionuclides in lake Michigan I.

In: Impacts nucler releases into the aquatic environment. Proc., Sympos., Otaniemi, Finland, June 30-July 4, 1975. IAEA, Vienna.

A12. Wong, K. M., J. C. Burke, and V. T. Bowen. 1970. In: Proc. 5th Annu. Health Phys. Soc. Mid-year Topical Sympos. P. 529.

A13. Wong, K. M., V. B. Hodge, and T. R. Folsom. 1971. Presented at the Environmental Plutonium Sympos., Los Alamos Scientific Lab 4-5 August 1971.

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16. ABSTRACT *(200 words or less)* A study has been initiated on the processes which control removal and remobilization of radionuclides by inorganic and organic suspended particulate matter in natural aquatic systems. The initial development and testing of procedures and preliminary results have been made using americium and plutonium. An evaluation of of the methods used for measuring distribution coefficients was made for different sediment-water systems by the thin layer and constant shaking techniques. The constant shaking technique was found to be the most reproducible. A comparison of sterile (by 10^6 rads gamma radiation) and natural sediments was made. The distribution coefficients of ^{237}Pu in freshwater-sediment systems for desorption was three times greater than for sorption and was also three times greater for unsterilized than for sterilized sediment. In marine sediment-water systems the distribution coefficients for ^{237}Pu gave a range of values between 10^4 and 10^5. For ^{241}Am, the distribution coefficients for desorption was three times greater than that measured for sorption and the sterilized sediment gave the highest distribution coefficient values for both sorption and desorption. Dialysis bags were utilized in experiments designed to separate the soluble from the colloidal or particulate form of the radionuclide. The results showed that both plutonium and americium concentrated on the growing plankton Phaeodactylum tricornutium, and on the suspended sediment contained inside the bags. Further studies are essential to evaluate these early results.

17. KEY WORDS AND DOCUMENT ANALYSIS

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