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INTERIM REPORT

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Progress Report
1 November 1978 - 31 January

Distribution Coefficients for Radionuclides in Aquatic Environments
Laboratory of Radiation Ecology WH-10
University of Washington

Introduction: This project was initiated in August 1976 to obtain new and better information for predicting the fate of radionuclides in aquatic environments. This is the second progress report for the third year of the program which is progressing approximately on schedule as outlined in the research proposal for the 1978-1979 fiscal year. During the past quarter we have:

1. Completed all the necessary experiments on adsorption K_d values for ^{85}Sr, ^{106}Ru, ^{137}Cs, ^{237}Pu, and ^{241}Am.

2. Determined the desorption K_d values for ^{85}Sr, ^{137}Cs, ^{237}Pu and ^{241}Am for several different sediment-water systems.

3. Analyzed experiments on the effect of sediment concentration on K_d values of ^{60}Co, ^{106}Ru, ^{137}Cs, and ^{237}Pu in Lake Michigan sediment-water systems.

4. Conducted experiments on the effect of pH on K_d values.

5. Completed the analysis of the Lake Michigan dialysis experiment with ^{85}Sr and ^{237}Pu.

6. Begun experiments to investigate the effects of organic ligands on K_d values.

7. Developed a technique to obtain distribution coefficients for ^{244}Cm by measuring the characteristic L_β x-rays.

We have also begun a series of investigations to better characterize the proporties of sediments and waters that have been used in our experiments. This includes analyses for carbon, hydrogen, and nitrogen in sediments and water, x-ray diffraction studies on sediments to determine which clay minerals are present, determination of sediment-surface area and ion exchange capacity. Annual reports that were submitted for 1976-1977 and 1977-1978 fiscal years have been revised in the appropriate format for publication as NRC topical reports and will be submitted under a separate cover. Separate topical reports describing the marine dialysis experiments and the determination of distribution coefficients in marine sediment-water systems are also being prepared for publication as topical reports.

During the next quarter our experimental program will continue but our major effort will be the preparation of the 1978-1979 Annual Report summarizing our results for FY1979 and a proposal for 1979-1980 to complete this project.

Adsorption K_d Values: Constant shaking experiments have been completed to determine the adsorption K_d values of ^{85}Sr, ^{106}Ru, ^{137}Cs, ^{237}Pu and ^{241}Am in sediment-water systems from Lake Michigan, Clinch River, Cattaraugus Creek and the Hudson River Estuary. A summary of the adsorption K_d values is presented in Table 1. Many of these values have been presented in previous reports but they have not been summarized in a single table. Data are presented in Table 1 so that K_d values of different radionuclides can be easily compared within a given system; K_d values of selected radionuclides can also be compared among the different sediment-water systems.

For all of the sediment-water systems ^{85}Sr has the lowest K_d value, generally less than 100, and ^{241}Am has the highest value, greater than 10^5. The order of increasing K_d values is $^{85}Sr < ^{137}Cs$ [^{106}Ru or ^{237}Pu] $< ^{241}Am$. The radionuclides, ^{106}Ru and ^{237}Pu, are coupled in this sequence because the K_d value of ^{106}Ru is higher than ^{237}Pu for sediment-water systems from the Clinch River and Hudson River Estuary systems but in the other systems K_d values for ^{237}Pu are higher than for ^{106}Ru. The K_d values for ^{85}Sr and ^{137}Cs are greater in the freshwater systems than in the marine sediment-water systems but no similar trends were observed for ^{106}Ru, ^{137}Cs or ^{241}Am. For all three of these latter radionuclides both the greatest and the lowest K_d values were found in sediment-freshwater systems.

Desorption K_d Values: Experiments have been completed to determine the desorption K_d values ^{85}Sr, ^{106}Ru, ^{137}Cs, ^{237}Pu and ^{241}Am in sediment-water systems from Lake Michigan, Clinch River, 3 locations in the Hudson River estuary and Sinclair Inlet in Puget Sound. Desorption studies were conducted by sorbing radionuclides to sediments, centrifuging and then resuspending the sediments in unspiked water from the same sampling location. Results of these experiments are shown in Table 2 and compared to adsorption K_d values for the same sediment-water systems in Table 3. For all radionuclides the K_d values for desorption were higher than the adsorption K_d values by at least a factor of 3. More than an order of magnitude increase in K_d values for desorption, compared to adsorption, was observed for some radionuclides. These results suggest that under these experimental conditions sorption is not completely reversible. Radionuclides are strongly bound to the sediments and may be unavailable for release. This suggests that K_d values obtained in adsorption experiments may not be applicable to modeling the release of sediments from suspended or bed sediments.

Effect of pH on K_d Values: The adsorption of radionuclides to suspended particulates is dependent upon the physico-chemical species of radionuclides and the surface characteristics of the sediments. Both of these may change as a function of pH. Thus, the K_d value of some radionuclides may be affected by changes in pH. Previous experiments in our laboratory have shown some effects of pH variation for both freshwater and anoxic systems [1977-1978 Annual Report, June 1978] for ^{241}Am. We are currently conducting experiments on the effect of pH on sediment-water systems from the Cattaraugus Creek watershed in western New York and from the Hudson River Estuary. The results presented below are from experiments with water and sediments from Clinch River, Tennessee.

The K_d values obtained, for ^{106}Ru and ^{137}Cs in the Clinch River sediment-water system are shown in Figures 1 and 2, respectively. The K_d value of ^{106}Ru increases by a factor of approximately 5 between pH 4 and 6. At pH values above 6 there is considerable scatter in the data with no obvious trends. The apparent decrease in K_d values between pH 8 and 10 is believed to be an experimental artifact but will be evaluated in future experiments. Unlike ^{106}Ru which exhibits an increase in K_d values at relatively low pH, there appears to be no effect on the K_d values of ^{137}Cs at pH < 9. There is, however, a slight increase in K_d between pH 9 and 10. Consideration of the Clinch River sediment-water suggests that the K_d values of ^{106}Ru and ^{137}Cs are not affected by pH changes that are commonly observed in natural waters.

Another radionuclide that was included in the Clinch River experiments was ^{60}Co. Although we do not generally report on ^{60}Co, these results are presented here (Fig. 3) to indicate the effect that changes in pH may have on some radionuclides. Between pH 6.0 and 7.5 the K_d value of ^{60}Co increases more than two orders of magnitude. Not only is this a significantly larger effect than was noted for ^{106}Ru or ^{137}Cs, it also concurs within the pH range of most natural waters. Thus, hydrologic models for ^{60}Co must be much more pH dependent than models for ^{106}Ru or ^{137}Cs.

Effect of Sediment Concentration: As for pH, some experiments have been reported previously [1976-1977 Annual Report] on the effects of sediment concentration on the K_d values of ^{241}Am in sterile and unsterilized systems from Lake Washington. More recently we have completed and analyzed an experiment on the effects of sediment concentration in the Lake Michigan sediment-water system. The sediment concentrations ranged from 16 mg/l to 340 mg/l and the radionuclides ^{237}Pu, ^{137}Cs, ^{106}Ru and ^{60}Co were included. Results of this experiment are shown in Figure 4. For all of these radionuclides there is a significant increase in K_d value at lower sediment concentrations. This corresponds to the data reported previously for ^{241}Am. The apparently sharp increase in K_d values of ^{106}Ru and ^{137}Cs at sediment concentrations below ≈ 50 mg/l is thought to be an experimental artifact resulting from sorption of these radionuclides to the filters. Additional experiments are needed at these lowest sediment concentrations.

Effect of Organic Ligands: Dissolved organic ligands could significantly alter the K_d values of radionuclides in our experiments by forming organometallic complexes, and thus increasing the concentration of radionuclides in solution. There is, however, very little information on the complexation of radionuclides by organic ligands. This study was initiated to evalute the effects of selected ligands on the K_d values of ^{106}Ru, ^{137}Cs and ^{241}Am. Initially, a variety of organic ligands will be tested at a relatively high concentration, approximately 10^{-4}M, to identify organic molecules which affect the K_d values. In order to be compared with our previous results, experiments will be conducted at pH = 8.0 and a sediment concentration of 200 mg/l. For those ligands which alter the K_d values, additional experiments will be conducted at lower ligand concentrations to determine the minimum concentration that produces any significant effect.

Preliminary experiments with EDTA, a strong chelator of transition metals, suggest that EDTA can significantly lower the K_d value of ^{241}Am. However, no measurable effects were observed for ^{106}Ru or ^{137}Cs.

Lake Michigan Dialysis Experiment: In our last progress report we presented the results from a Lake Michigan dialysis experiment with the radionuclides ^{106}Ru, ^{137}Cs and ^{241}Am. A second experiment investigated the behavior of ^{85}Sr and ^{237}Pu during a 15-day dialysis experiment. Those results are reported here.

Strontium-85 occurs almost entirely in the soluble phase and rapidly, within 10 hours, reaches equilibrium among all the dialysis chambers (Figure 5). This is very similar to the behavior observed previously for ^{137}Cs in marine dialysis experiments. There was no significant uptake of ^{85}Sr by any of the particulates in this experiment.

Both detrital particles and the suspended sediments take up significant amounts of ^{237}Pu, but there is no apparent accumulation by phytoplankton [Figure 6]. In constant shaking experiments phytoplankton have accumulated large concentrations of ^{237}Pu. We cannot be certain what causes the differences between the constant shaking experiments and the dialysis experiment. One possible explanation, however, is that phytoplankton in the dialysis experiments produced an exometabolite which effectively complexed ^{237}Pu to keep it in the soluble phase. This interpretation is supported by the high concentrations of soluble ^{237}Pu in the phytoplankton chamber after 1 day [Figure 7]. The decreased values of particulate ^{237}Pu in the detritus and sediment chambers after 8 and 15 days could also result from exometabolites. As these compounds diffuse from the phytoplankton chamber into the other chambers it may solubilize some ^{237}Pu that had been adsorbed. The experiments we have started on the effects of organic ligands should provide valuable information on the feasibility of the above explanation. When ^{237}Pu is again available it will be interesting to conduct dialysis experiments for additional systems.

Curium-244: Analysis of ^{244}Cm by alpha spectroscopy requires a considerable amount of chemical separation. We have developed a method for determining distribution coefficients by counting the characteristic L_β x-rays [18.3 Kev] with an intrinsic germanium detector and pulse height analyzer. Particulate ^{244}Cm is counted directly while soluble ^{244}Cm is coprecipitated with $Fe_2O_3 \cdot xH_2O$ and ^{244}Cm in the precipitate is measured. The preliminary data that have been obtained to date indicate that the K_d's for ^{244}Cm in the freshwater-sediment systems are approximately 10^5.

446 326

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Table 1. Adsorption K_d values for ^{85}Sr, ^{106}Ru, ^{137}Cs, ^{237}Pu and ^{241}Am in selected sediment-water systems.

Sediment-Water System	n*	^{85}Sr K_d**	n	^{106}Ru $K_d \times 10^{-4}$	n	^{137}Cs $K_d \times 10^{-2}$	n	^{237}Pu $K_d \times 10^{-4}$	n	^{241}Am $K_d \times 10^{-5}$
Lake Michigan	7	82.2 (7.0)	12	5.23 (1.68)	17	5.09 (0.31)	7	14.1 (1.8)	12	5.48 (3.73)
Clinch River	6	124.4 (7.5)	12	6.72 (0.52)	9	13.6 (0.40)	6	4.7[illegible](0.40)	8	7.33 (3.64)
Cattaraugus Creek	7	62.3 (6.2)	9	1.40		#	7	2.09(0.65)	12	2.26 (1.47)
Hudson River										
mp 43	6	7[illegible].7(10.5)	12	3.92 (0.40)	9	4.01 (0.20)	6	0.93(0.14)	9	1.[illegible]6 (0.13)
mp 18	6	[illegible]4.8 (5.3)	11	5.15 (1.03)	9	[illegible] (0.71)	6	3.12(0.22)	9	2.37 (0.88)
mp 0		##	11	4.53 (0.37)	8	3.56 (0.21)	4	3.87(0.11)	6	2.96 (0.88)
Skagit Estuary										
Core #1		##	21	3.61 (0.63)	9	1.87 (0.15)	9	10.3 (0.8)	15	2.68 (0.74)
Core #4		-	12	4.51 (0.76)	5	2.42 (0.07)		-	10	3.80 (1.06)
Saanich Inlet		-	17	4.4[illegible] (0.52)		#		-	14	3.71 (0.8[illegible])
Sinclair Inlet		##	12	5.42 (0.43)	9	1.24 (0.09)	9	7.40(1.21)	9	4.54 (1.20)

* n is the total number of K_d calculations made for a radionuclide in a given sediment-water system.

** $\bar{K}_d$ is average value for all determinations. Number in parentheses is one standard deviation from mean of replicate determinations.

Did not reach equilibrium.

Concentration in particulate phase was below detection limits.

Table 2. Desorption distribution coefficients for ^{85}Sr, ^{137}Cs, ^{237}Pu and ^{241}Am in different sediment-water systems

Sediment-Water System	Radionuclides	n*	Average K_d**	Distribution Coefficient, ml/g Range in K_d***
Lake Michigan	^{85}Sr	10	$(1.41 \pm 0.51) \times 10^3$	$(0.57 \pm 0.13) \times 10^3$ to $(2.33 \pm 0.46) \times 10^3$
	^{237}Pu	10	$(4.79 \pm 1.19) \times 10^5$	$(3.10 \pm 0.35) \times 10^5$ to $(6.47 \pm 1.95) \times 10^5$
	^{137}Cs (A)#	6	$(3.67 \pm 0.53) \times 10^3$	$(3.03 \pm 0.48) \times 10^3$ to $(4.27 \pm 0.38) \times 10^3$
	(B)#	4	$(5.50 \pm 0.51) \times 10^3$	$(4.98 \pm 0.75) \times 10^3$ to $(6.17 \pm 0.81) \times 10^3$
	(C)#	6	$(5.62 \pm 0.73) \times 10^3$	$(4.56 \pm 0.61) \times 10^3$ to $(6.73 \pm 0.91) \times 10^3$
	^{241}Am (A)#			([illegible] ± 0.77) × 10^5 to $(12.20 \pm 1.93) \times 10^5$
	(B)#		See Text	$(6.66 \pm 2.23) \times 10^5$ to $(15.34 \pm 4.64) \times 10^5$
	(C)#			$(7.94 \pm 5.22) \times 10^5$ to $(22.34 \pm 12.00) \times 10^5$
Clinch River	^{85}Sr	8	$(4.55 \pm 0.89) \times 10^2$	$(3.57 \pm 3.34) \times 10^2$ to $(6.38 \pm 3.30) \times 10^2$
	^{237}Pu	9	$(1.54 \pm 0.09) \times 10^5$	$(1.38 \pm 0.11) \times 10^5$ to $(1.66 \pm 0.15) \times 10^5$
Hudson River SLOSH III mp 43	^{85}Sr	9	$(4.86 \pm 1.35) \times 10^2$	(3.07 ± [illegible]) × 10^2 to $(7.02 \pm 2.89) \times 10^2$
	^{237}Pu	6	$(3.60 \pm 0.37) \times 10^5$	$(3.10 \pm 0.56) \times 10^5$ to $(3.91 \pm 0.99) \times 10^5$
	^{137}Cs	5	$(3.65 \pm 0.52) \times 10^3$	$(3.08 \pm 0.37) \times 10^3$ to $(4.43 \pm 0.78) \times 10^3$
	^{241}Am	4	$(5.39 \pm 0.84) \times 10^5$	$(4.36 \pm 1.48) \times 10^5$ to $(6.21 \pm 2.41) \times 10^5$
Hudson River SLOSH II mp 18	^{85}Sr	-	-	-
	^{237}Pu	9	$(2.98 \pm 0.22) \times 10^5$	$(2.69 \pm 0.35) \times 10^5$ to $(3.39 \pm 0.51) \times 10^5$
	^{137}Cs	2	$(3.34 \pm 0.69) \times 10^3$	$(2.85 \pm 0.19) \times 10^3$ to $(3.82 \pm 0.41) \times 10^3$
	^{241}Am	5	$(8.47 \pm 1.52) \times 10^5$	$(6.52 \pm 0.61) \times 10^5$ to $(10.20 \pm 2.46) \times 10^5$
Hudson River SLOSH V mpo	^{85}Sr	-	-	-
	^{237}Pu	12	$(3.21 \pm 1.35) \times 10^5$	$(1.09 \pm 0.09) \times 10^5$ to $(5.26 \pm 0.97) \times 10^5$
	^{137}Cs	5	$(1.79 \pm 0.47) \times 10^3$	$(1.29 \pm 0.19) \times 10^3$ to $(2.48 \pm 0.39) \times 10^3$
	^{241}Am	4	$(21.73 \pm 5.12) \times 10^5$	$(16.78 \pm 5.71) \times 10^5$ to $(26.46 \pm 12.83) \times 10^5$
Sinclair Inlet	^{85}Sr	-	-	-
	^{237}Pu	9	$(3.59 \pm 1.32) \times 10^5$	$(1.87 \pm 0.19) \times 10^5$ to $(5.63 \pm 0.48) \times 10^5$

* n is the total number of K_d values obtained for each radionuclide.

** Average K_d represents the average value and one standard deviation from this average for the n number of K_d measurements.

*** Range in K_d represents the lowest and the highest values of the distribution coefficient obtained in the experiments. The error term represents 2σ propagated counting error for each isotope.

\# For ^{137}Cs and ^{241}Am in Lake Michigan, three sets of experiments were performed. The details of these three experiments will be discussed in a later report.

446 328

Table 3. Comparison of adsorption and desorption distribution coefficients in selected sediment-water systems

Sediment-Water System	Strontium-85 Adsorption n*	Strontium-85 Adsorption K_d**	Strontium-85 Desorption n	Strontium-85 Desorption $K_d \times 10^{-3}$	Plutonium-237 Adsorption n	Plutonium-237 Adsorption $K_d \times 10^{-4}$	Plutonium-237 Desorption n	Plutonium-237 Desorption $K_d \times 10^{-5}$
Lake Michigan	7	82.2 (7.0)	10	1.41 (0.51)	7	14.1 (1.8)	10	4.79 (1.19)
Clinch River	6	124.4 (7.5)	8	0.46 (0.09)	6	4.71 (.40)	9	1.54 (0.09)
Hudson River Estuary								
SLOSH III	6	73.7 (10.5)	[illegible]	0.48 (0.14)	6	0.93 (0.14)	6	3.60 (0.37)
SLOSH II	6	34.8 (5.3)		#	6	3.12 (0.22)	9	2.98 (0.22)
SLOSH V		#		#	4	3.87 (0.11)	12	3.21 (1.35)
Sinclair Inlet		#		#	9	7.40 (1.21)	9	3.59 (1.32)

Sediment-Water System	Cesium-137 Adsorption n	Cesium-137 Adsorption $K_d \times 10^{-2}$	Cesium-137 Desorption n	Cesium-137 Desorption $K_d \times 10^{-3}$	Americium-241 n	Americium-241 $K_d \times 10^{-5}$	Americium-241 n	Americium-241 $K_d \times 10^{-5}$
Lake Michigan	17	5.09 (0.31)	16	5.57 (0.64)	12	5.48 (3.73)		##
Hudson River Estuary								
SLOSH III	9	4.01 (0.20)	5	3.65 (0.52)	9	1.26 (0.13)	4	5.39 (0.84)
SLOSH II	9	8.78 (0.71)	2	3.34 (0.69)	9	2.37 (0.88)	5	8.47 (1.52)
SLOSH V	8	3.56 (0.21)	5	1.79 (0.47)	6	2.96 (0.88)	4	21.73 (5.12)

* n is the total number of K_d calculations made for a radionuclide in a given sediment-water system.

** K_d is average value for all determinations. Number in paretheses is one standard deviation from mean o. replicates.

Concentration in the particulate phase was below detection limits.

Did not reach equilibrium.

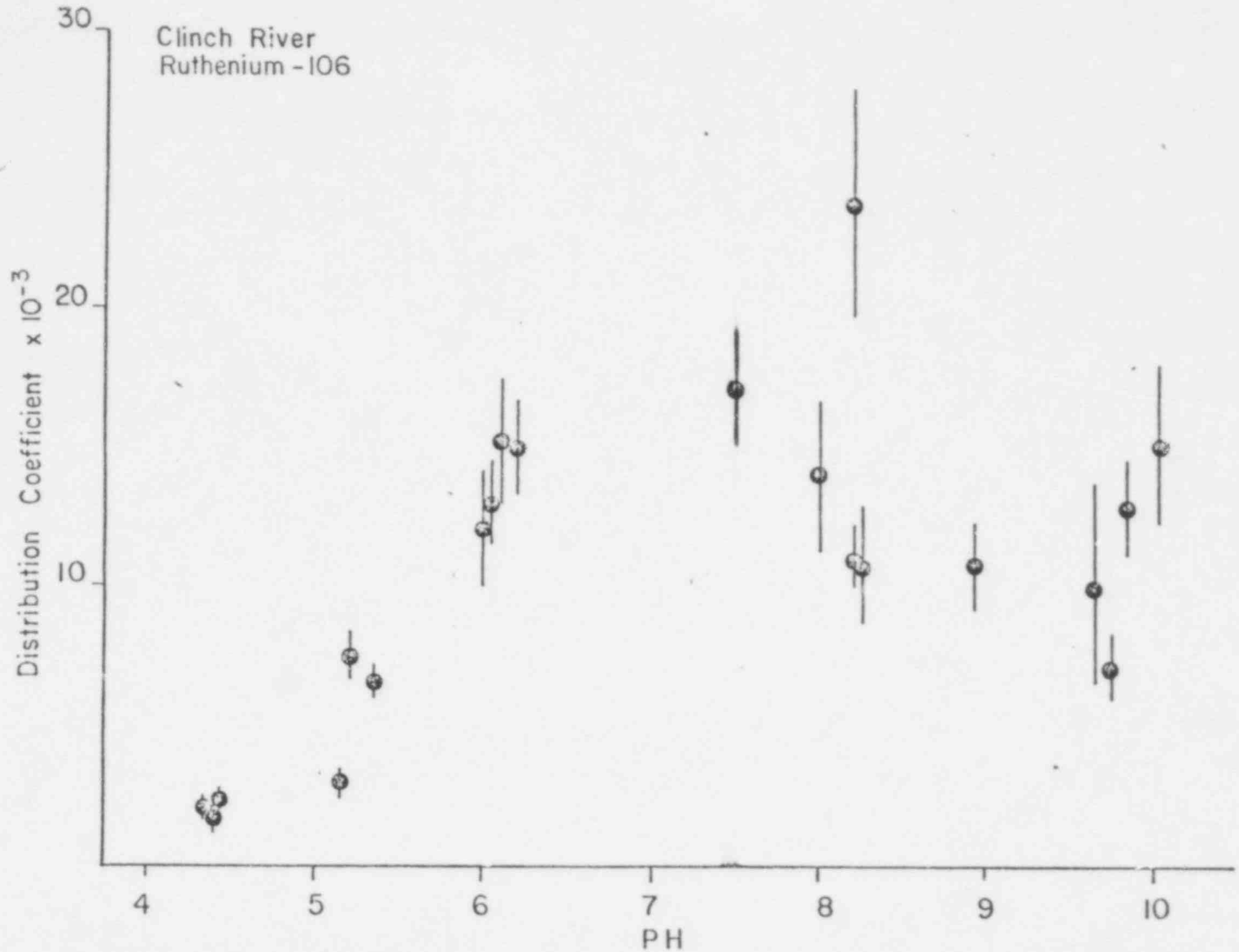

Figure 1. Distribution coefficients as a function of pH for ^{106}Ru in sediment-water systems from Clinch River.

446 330

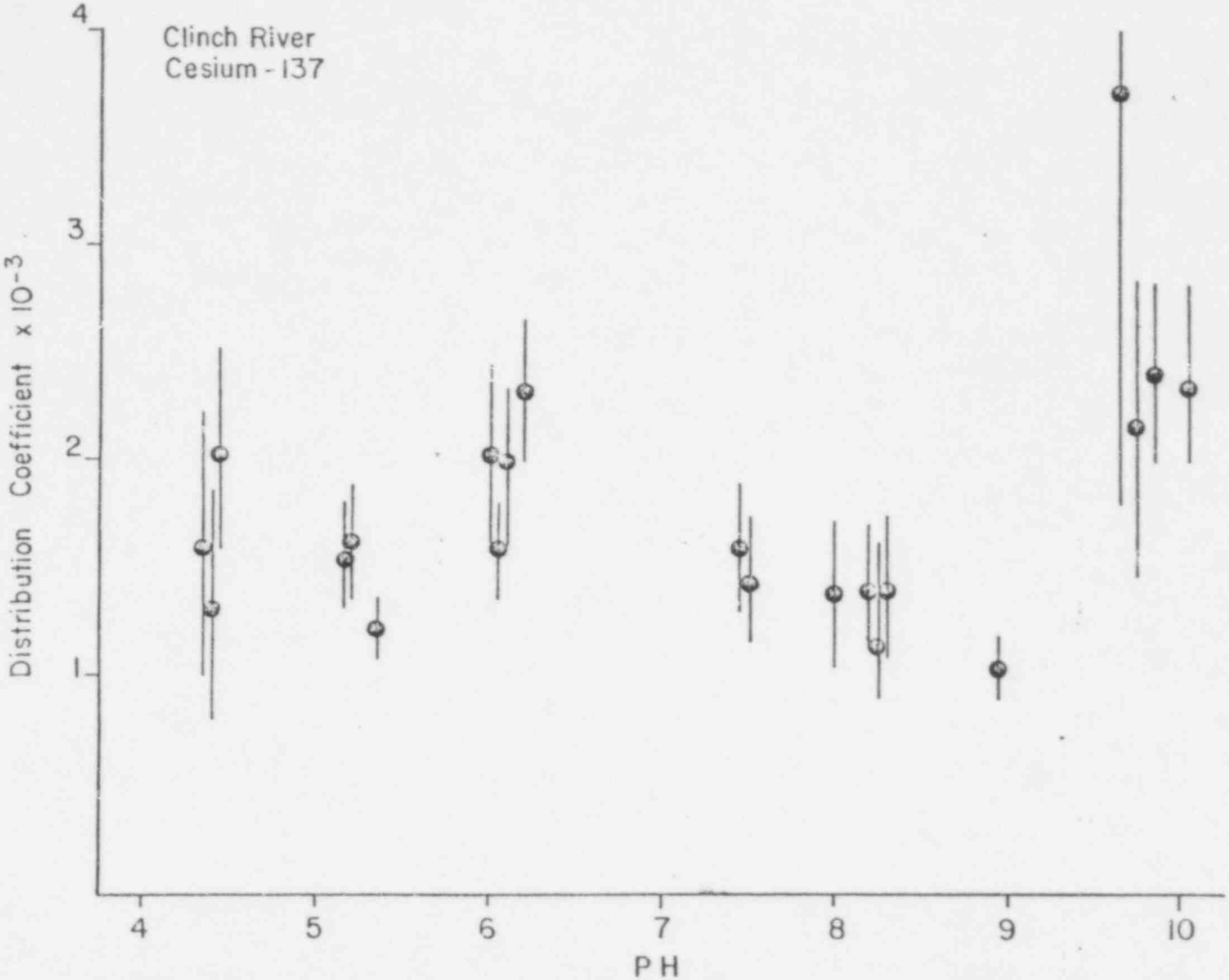

Figure 2. Distribution coefficients as a function of pH for ^{137}Cs in sediment-water systems from Clinch River.

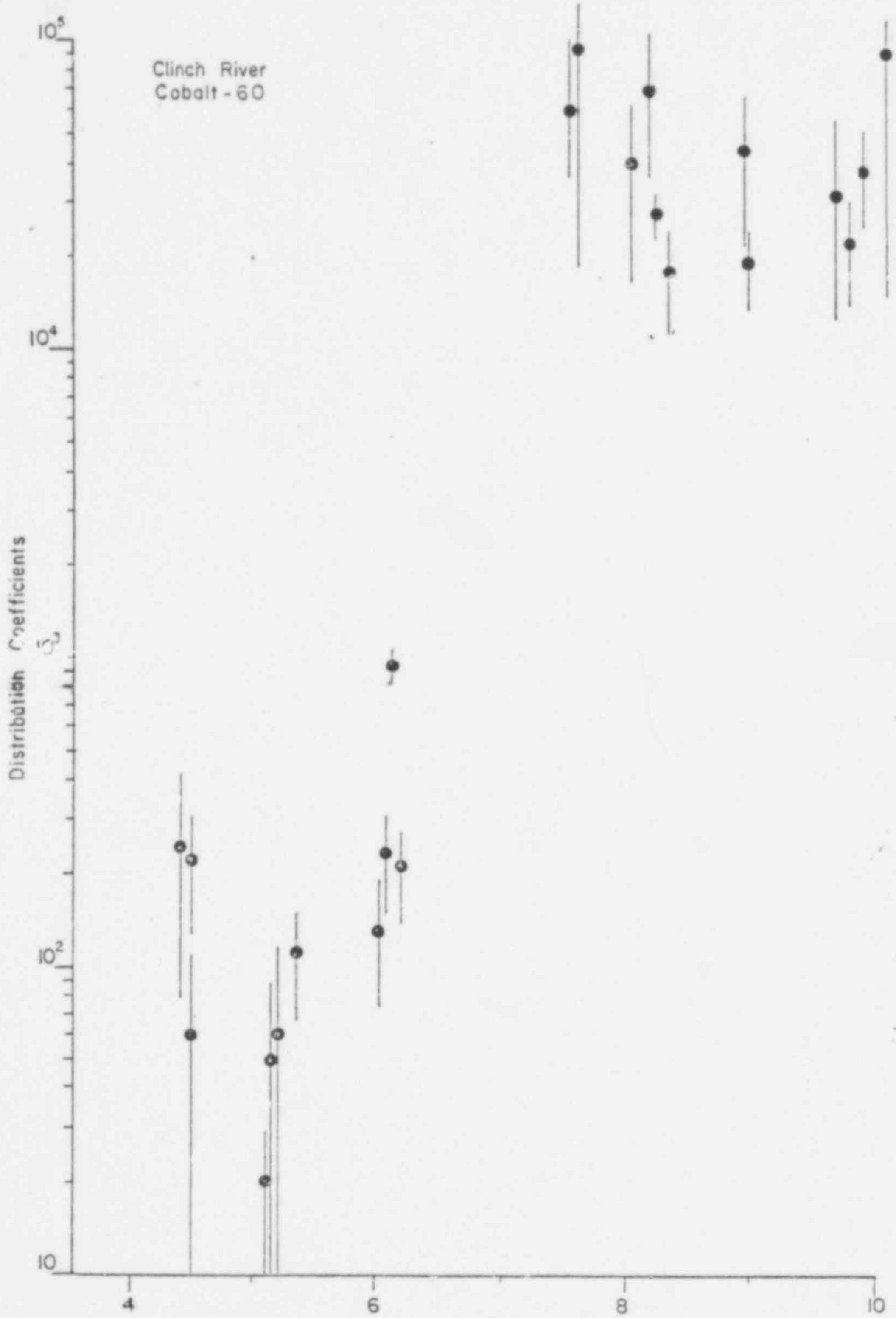

Figure 3. Distribution coefficients as a function of pH for ^{60}Co in sediment-water systems from Clinch River

446 332

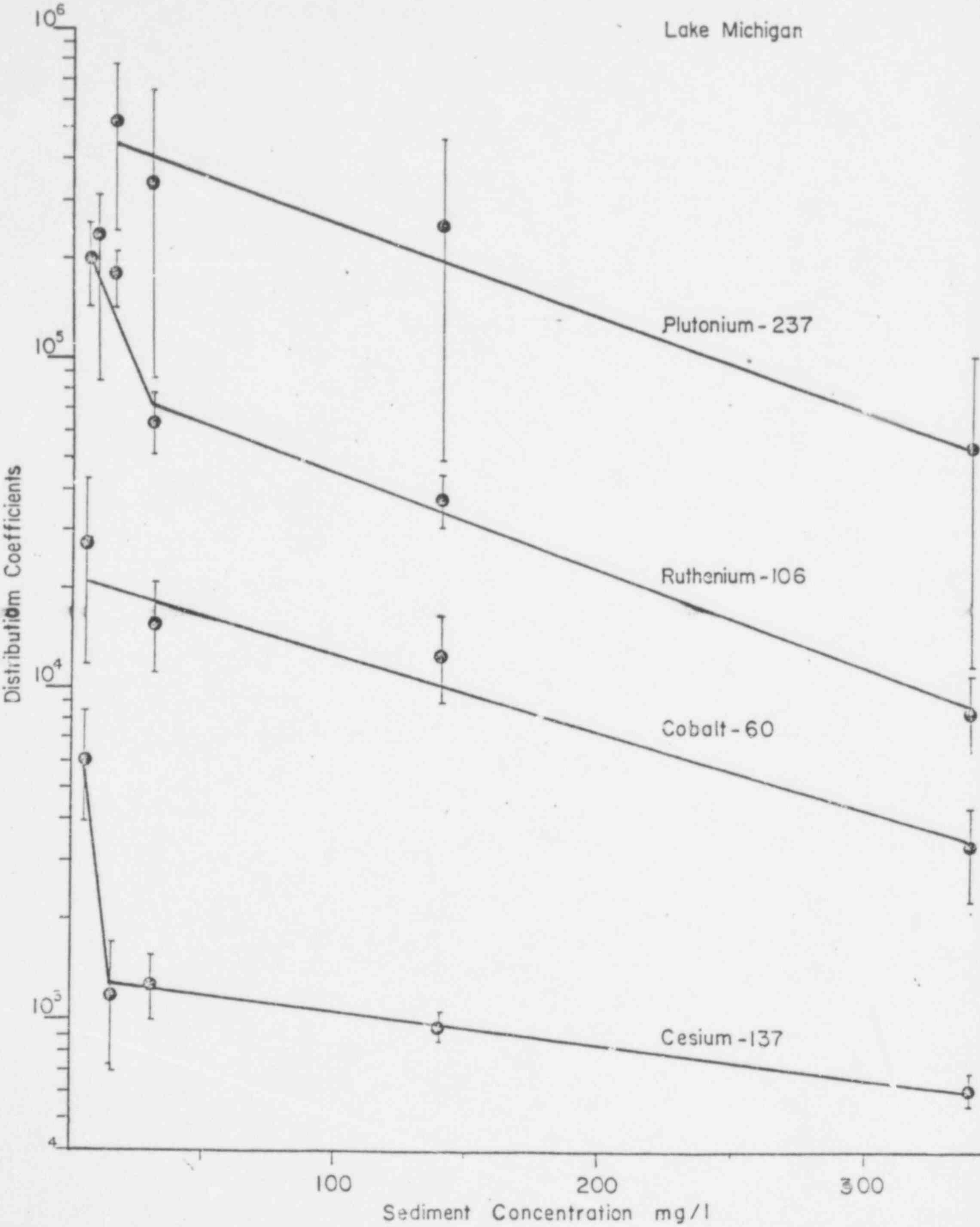

Figure 4. Distribution coefficients as a function of sediment concentration for ^{60}Co, ^{106}Ru, ^{137}Cs and ^{237}Pu in sediment-water systems from Lake Michigan.

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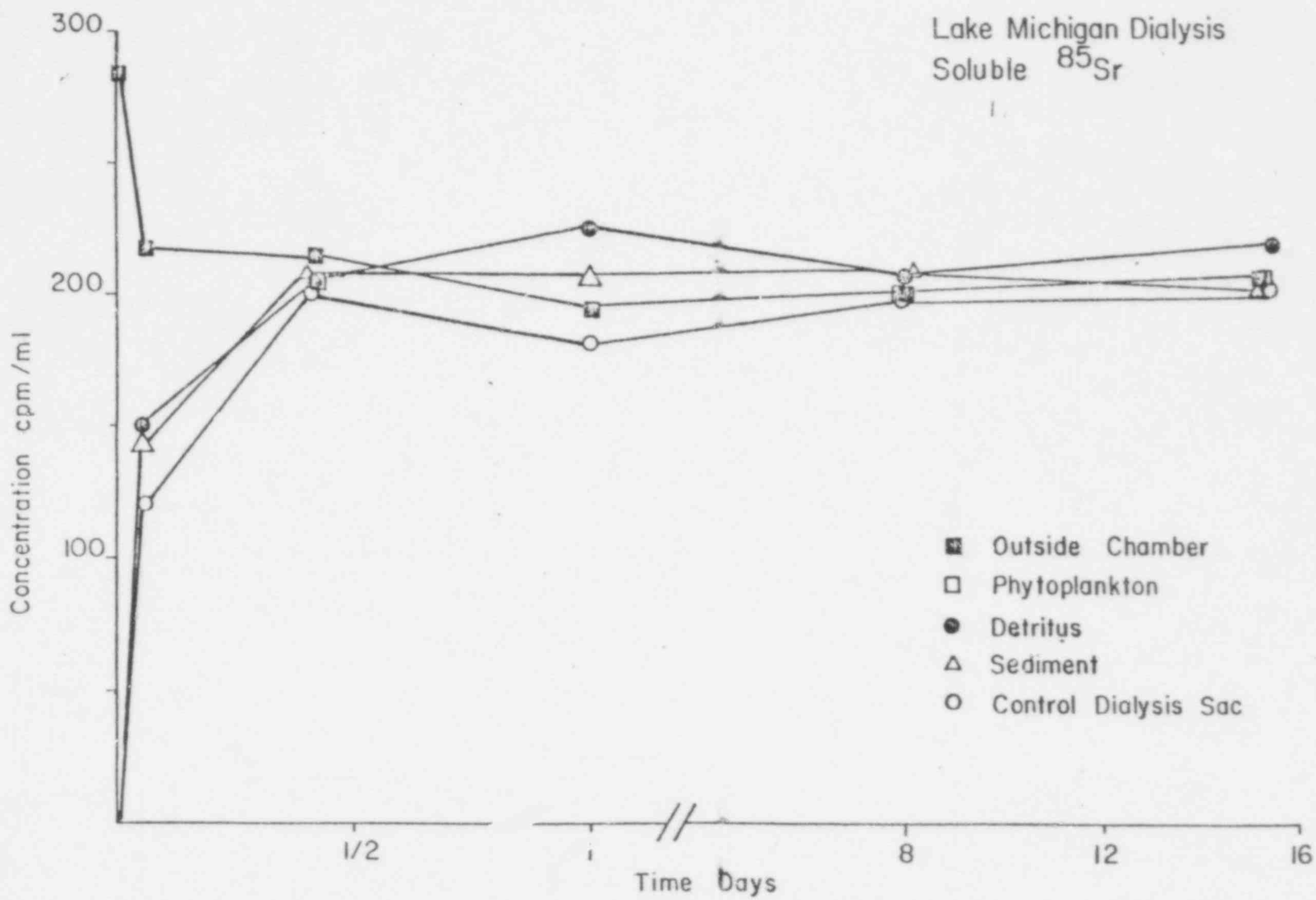

Figure 5. Concentration of soluble ^{85}Sr during a Lake Michigan dialysis experiment.

446 334

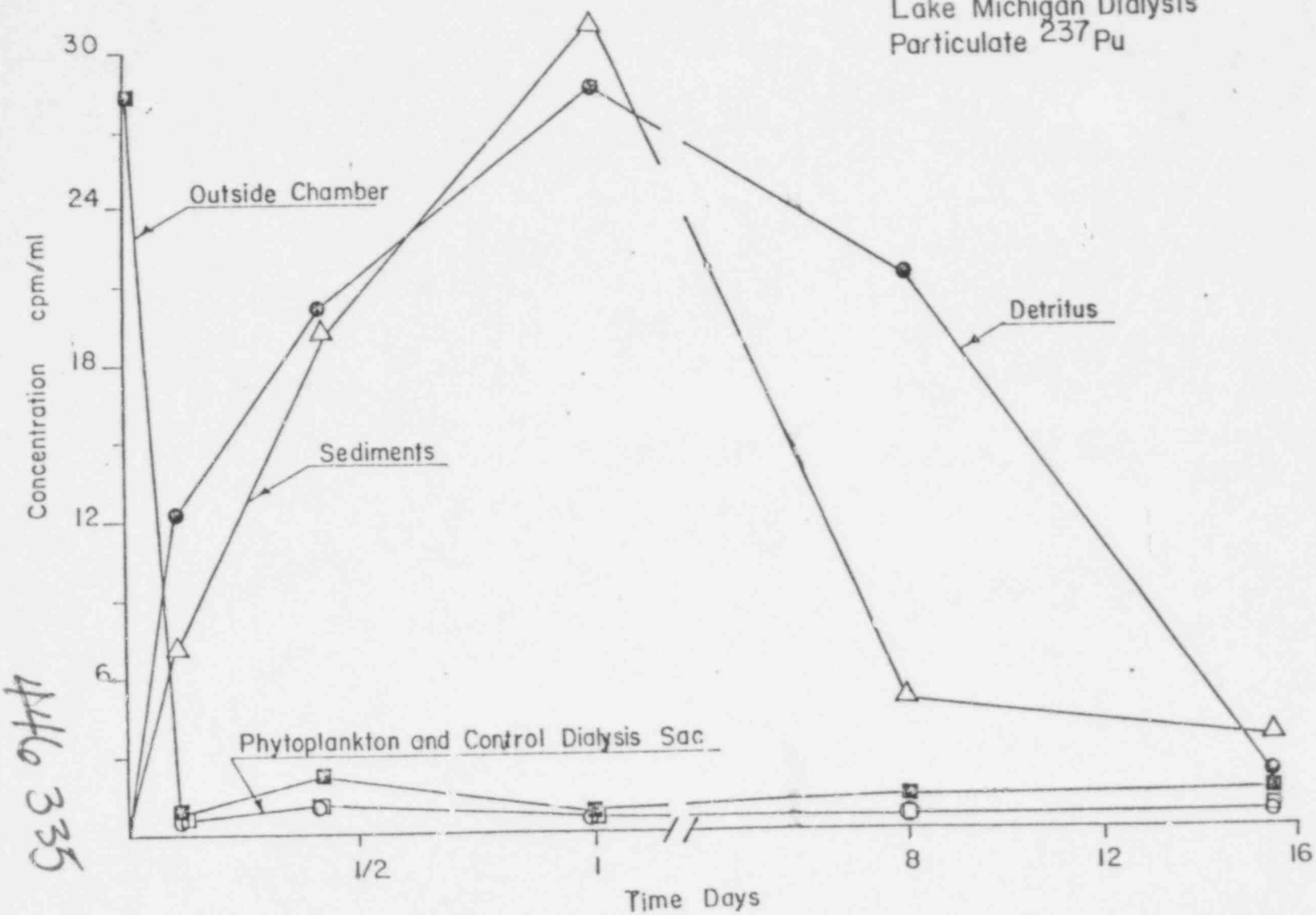

Figure 6. Concentration of particulate ^{237}Pu during a Lake Michigan dialysis experiment.

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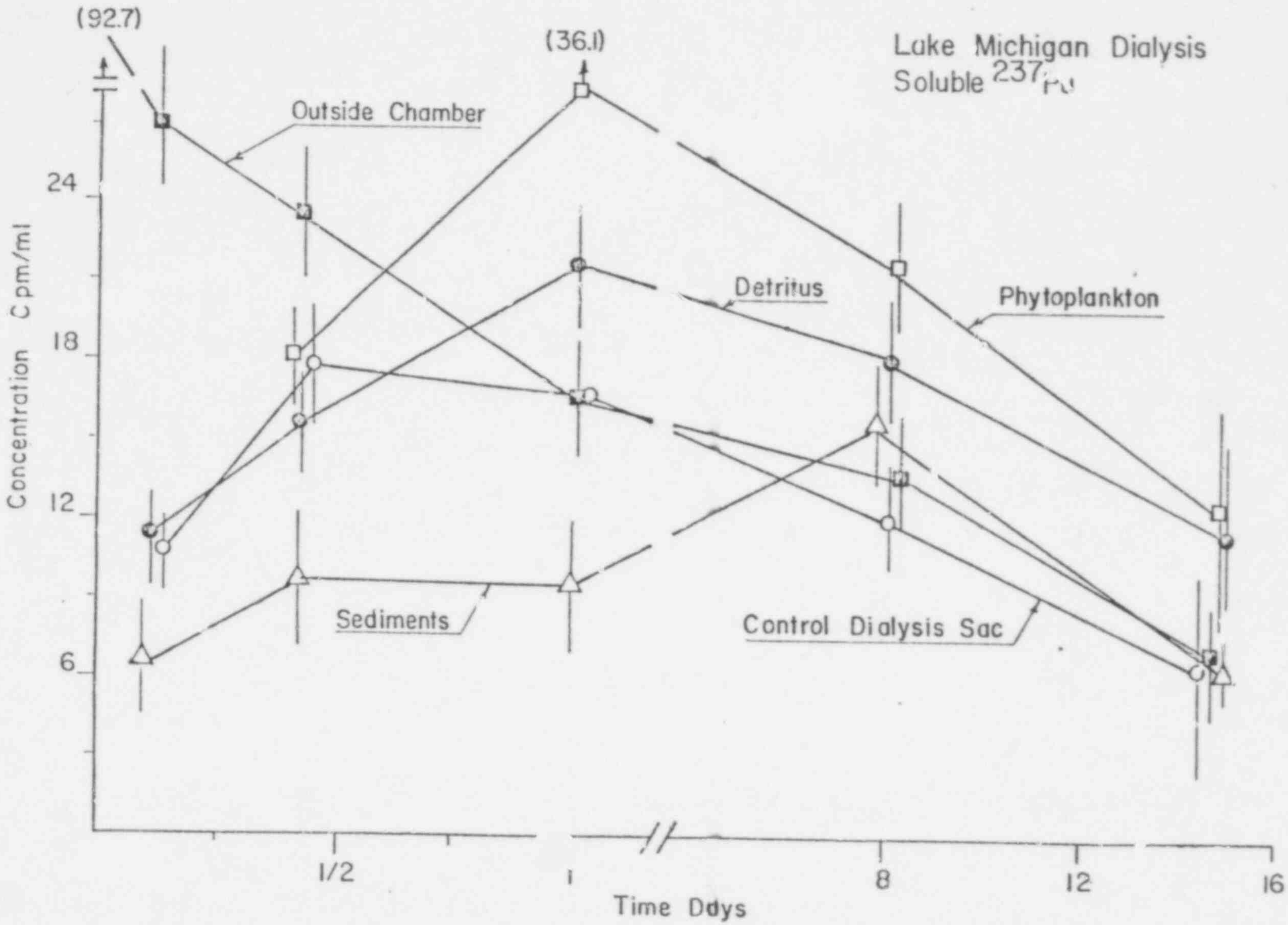

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Figure 7. Concentration of soluble ^{237}Pu during a Lake Michigan dialysis experiment.