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PLUTONIUM IN THE LAURENTIAN GREAT LAKES:
FOOD-CHAIN RELATIONSHIPS

by

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The radioisotope ^{239}Pu, an alpha emitter with a half-life of 24 000 yr, is a small component of fallout from atmospheric weapons testing and at present can be measured in environmental samples by using large samples and performing a rigorous radiochemical separation procedure. The toxicity of plutonium has been of concern since its production was initiated in 1943, with the result that more is known about the toxicology of plutonium than about that of most other hazardous elements (Bair and Thompson, 1974). However, its biogeochemical behavior, especially in aquatic ecosystems, remains very poorly known. A recent review (Noshkin, 1972) of plutonium dissemination in aquatic environments emphasizes the relatively limited knowledge of plutonium behavior in the oceans and the virtual absence of data for freshwater ecosystems. Because of projected increasing production of plutonium and its use in present-day reactors, future breeder reactors, and other applications, we initiated studies of the behavior of fallout ^{239}Pu in a large freshwater ecosystem, Lake Michigan, in 1972. These studies were intensified in 1973 and expanded to obtain comparative data on the other Great Lakes. The purpose of this paper is to present a preliminary assessment of the role of organisms in the removal of plutonium from Great Lakes waters and the potential for food-chain transfer of plutonium to man.

Samples of water, net plankton, and benthos were collected in June 1972 at 25 stations throughout Lake Michigan, and fish were collected in the spring and fall from areas near Milwaukee, Waukegan, South Haven, Saugatuck, Grand Haven, Frankfort, and Manistique. Additional samples of water, plankton, and fish were collected in the spring of 1973 from all five of the Great Lakes. Detailed descriptions of the sample locations, sampling procedures, and methods used for the analyses of plutonium and radiocesium are available (Marshall et al., 1974; Nelson et al., 1974). Samples of whole adult fish, each consisting of one or two individuals of a large species or as many as 120 individuals of a small species, were analyzed for ^{239}Pu and ^{137}Cs.

The results are summarized in Table 1. The relatively high average ^{239}Pu concentration observed in mixed plankton samples (compared with zooplankton) suggests that the higher value may represent the contribution by phytoplankton (primarily diatoms) which dominate "mixed" samples. The data do not preclude the possibility that the high concentrations in mixed plankton are due to the extremely minor amount of inorganic detritus in these samples. However, the sorptive properties of algal cells (Vaughn and Strand, 1972) and the dominance of phytoplankton in the mixed plankton samples seem adequate to account for the observed concentrations. The similar relatively high average concentration in Cladophora suggests the importance of the ratio of surface area to biomass rather than a specific association with the siliceous frustules of the diatoms in the mixed plankton samples. The nonspecific nature of the association with diatoms was borne out by results obtained by the Analytical Chemistry Section of the Illinois State Geological Survey, who analyzed our plankton samples for Si. Similarly, a detailed study of ^{239}Pu distribution in a giant marine alga indicated that some ^{239}Pu was on the inside, but by far the most was apparently on the outside (Wong et al., 1972).

The ^{239}Pu concentration in zooplankton is roughly an order of magnitude lower than that in mixed plankton; therefore a large fraction of the total ^{239}Pu in zooplankton could be accounted for by ^{239}Pu associated with phytoplankton in the digestive tracts. The higher concentration of ^{239}Pu in Mysis and Pontoporeia than in other crustaceans that dominate the zooplankton samples also suggests the importance of gut contents because, during daytime at least, both Mysis and Pontoporeia feed within or near the surficial layer of sediment, which preliminary analyses in our laboratory have shown to have a relatively high ^{239}Pu content.

The average $^{239}Pu/^{137}Cs$ activity ratios for mixed plankton samples are about twice as high as those for surface waters (Table 1), and those for Lake Michigan mixed plankton samples taken during July and August 1973 when the rapid decline of ^{239}Pu in the epilimnion was observed (Wahlgren and Nelson, 1974) were about ten times as high. These data, together with the apparent high concentration of ^{239}Pu in phytoplankton, are consistent with the hypothesis that biological processes are of major importance in removing ^{239}Pu from Great Lakes waters, as Bowen, et al. (1971) suggest that they are in its sedimentation in the ocean. The settling of zooplankton fecal pellets has been shown to be a major mechanism of diatom sedimentation in the sea (Schrader, 1971), and it may also be significant in removing plutonium and other elements associated with diatoms from the surface waters of the Great Lakes.

Comparison of ^{239}Pu concentrations in plankton from all five Great Lakes is facilitated by the consideration of concentration factors (Table 2). The term "concentration factor," as used in this paper, is the ratio of the concentration of ^{239}Pu in the sample (on a wet-weight basis) to that in the water. The relationship between ^{239}Pu concentration factor (CF) and ash content in Great Lakes plankton samples (including mixed plankton, zooplankton, and Mysis) is shown in Figure 1. The empirical equation of the curve determined by computer least-squares analysis is $CF = 200\ (\%\ ash)^{1.4}$. Spearman's rank correlation coefficient ($r' = 0.92$) shows a strong and highly significant ($P < 0.01$) correlation between CF and ash content in these samples. The samples having the higher ash content are mixed plankton samples dominated by diatoms, as determined by microscopic observation and confirmed by the analyses for Si mentioned above. The observation that plankton samples from all five of the Great Lakes have such a consistent relationship between plutonium and ash content suggests a rapid equilibrium between aqueous and sorbed plutonium species. If further study substantiates this, it will greatly facilitate the development of predictive models for the behavior of plutonium in the Great Lakes—including models for predicting its transfer to higher trophic levels in food chains leading to man.

The highest concentrations of ^{239}Pu in fish were found in Cottus cognatus (slimy sculpin), a bottom-dwelling species that feeds on benthic invertebrates (Anderson and Smith, 1971). C. cognatus has a mean concentration factor of 250, roughly an order of magnitude lower than that of its primary food, Pontoporeia affinis (Table 2). Intermediate concentrations are found in Coregonus hoyi (chub), Alosa pseudoharengus (alewife), Osmerus mordax (smelt), and Coregonus clupeaformis (whitefish), species that feed primarily upon zooplankton or a mixture of zooplankton and benthic invertebrates (Anderson and Smith, 1971; Wells, 1970; Wells and Beeton, 1963). These species in Lake Michigan have mean concentration factors ranging from 14 to 37, one or two orders of magnitude lower than those of the invertebrates upon which they feed (Table 2). C. hoyi feeds more frequently upon benthic invertebrates than do the other three species, and this may explain its higher concentrations of ^{239}Pu. The relatively high concentration factors for A. pseudoharengus in Lake Huron and Lake Ontario and for O. mordax in Lake Erie are unexplained at present, but they may be insignificant because of the small number of samples. Intermediate concentrations of ^{239}Pu are also found in Perca flavescens (perch), a species that feeds on a mixture of invertebrates and fish. Concentration factors for ^{239}Pu in the four samples of P. flavescens range from 4 to 29 (Table 2). The lowest concentrations of ^{239}Pu measured were found in Oncorhynchus kisutch (coho salmon), O. tschawytscha (chinook salmon), and Salvelinus namaycush (lake trout), species whose adults feed almost exclusively on smaller fish. The concentration factors for these piscivorous fish range from 1 to 7, about an order of magnitude lower than those of their prey (Table 2). Figure 2 shows the relationship between the ^{239}Pu concentration factor CF and the ash content in Lake Michigan fish. The equation of the curve computed by least squares analysis is $CF = 1.3\ (\%\ ash)^{3.3}$. The fact that the exponent in this equation is larger than in that for plankton indicates that the ^{239}Pu concentration varies more rapidly with ash content in fish than in plankton. Although there is considerable scatter in the data, Spearman's rank correlation coefficient ($r' = 0.49$) shows a weak but significant ($P < 0.01$) correlation between ash content and ^{239}Pu

concentration factors in these fish. This was expected because in marine fish the skeleton is known to be a major respository of plutonium (Noshkin, 1972).

In conclusion, the data presented in this paper are consistent with the hypothesis that sorption of plutonium by phytoplankton and the subsequent settling of phytodetritus or zooplankton fecal pellets is a major mechanism for removing plutonium from Great Lakes waters. The results clearly indicate that although the concentration of plutonium in phytoplankton is several thousand times that in the water, it decreases by an order of magnitude in each successive link in the food-chains leading to man.

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Table 1. Mean ^{239}Pu Concentrations and $^{239}Pu/^{137}Cs$ Activity Ratios in Great Lakes Water and Biota, June 1972 to November 1973.

Lake	Sample	Number analyzed	fCi ^{239}Pu/kg wet weight*	$^{239}Pu/^{137}Cs$* (10^{-3})
Superior	Water	3	0.57	7.9
	Mixed plankton	3	2520 ± 600	15.0 ± 1.1
	Zooplankton	1	400	2.1
	Osmerus mordax (smelt)	1	4	0.02
Michigan	Water	14	0.76 ± 0.03	13.2 ± 0.6
	Mixed plankton	22	4300 ± 600	34.2 ± 4.4
	Cladophora sp.	16	2800 ± 400	65.1 ± 9.9
	Zooplankton	9	260 ± 50	11.1 ± 2.3
	Mysis relicta	7	570 ± 50	2.7 ± 0.4
	Pontoporeia affinis	2	1230	7.1
	Cottus cognatus (slimy sculpin)	7	180 ± 40	1.1 ± 0.2
	Coregonus hoyi (chub)	8	28 ± 3	0.11 ± 0.01
	Alosa pseudoharengus (alewife)	7	19 ± 2	0.13 ± 0.01
	Osmerus mordax (smelt)	6	15 ± 3	0.10 ± 0.03
	Perca flavescens (perch)	2	13	0.04
	Coregonus clupeaformis (whitefish)	2	10	0.04
	Oncorhynchus kisutch (coho)	1	5	0.03
	Oncorhynchus tschawytscha (chinook)	1	3	0.009
	Salvelinus namaycush (lake trout)	2	1	0.003
Huron	Water	1	0.63	15.0
	Mixed plankton	2	2810	33.0
	Alosa pseudoharengus (alewife)	2	104	0.81
	Osmerus mordax (smelt)	1	8	0.05
	Perca flavescens (perch)	1	15	0.06
Erie	Water	3	0.21	11.0
	Zooplankton	3	85 ± 25	6.3 ± 1.1
	Osmerus mordax (smelt)	1	40	2.7
	Perca flavescens (perch)	1	2	0.07
Ontario	Water	3	0.26	10.4
	Mixed plankton	3	605 ± 50	18.0
	Alosa pseudoharengus (alewife)	1	44	0.96

*Mean ± standard error.

Table 2. Concentration Factors for ^{239}Pu in Great Lakes Biota, June 1972 to November 1973

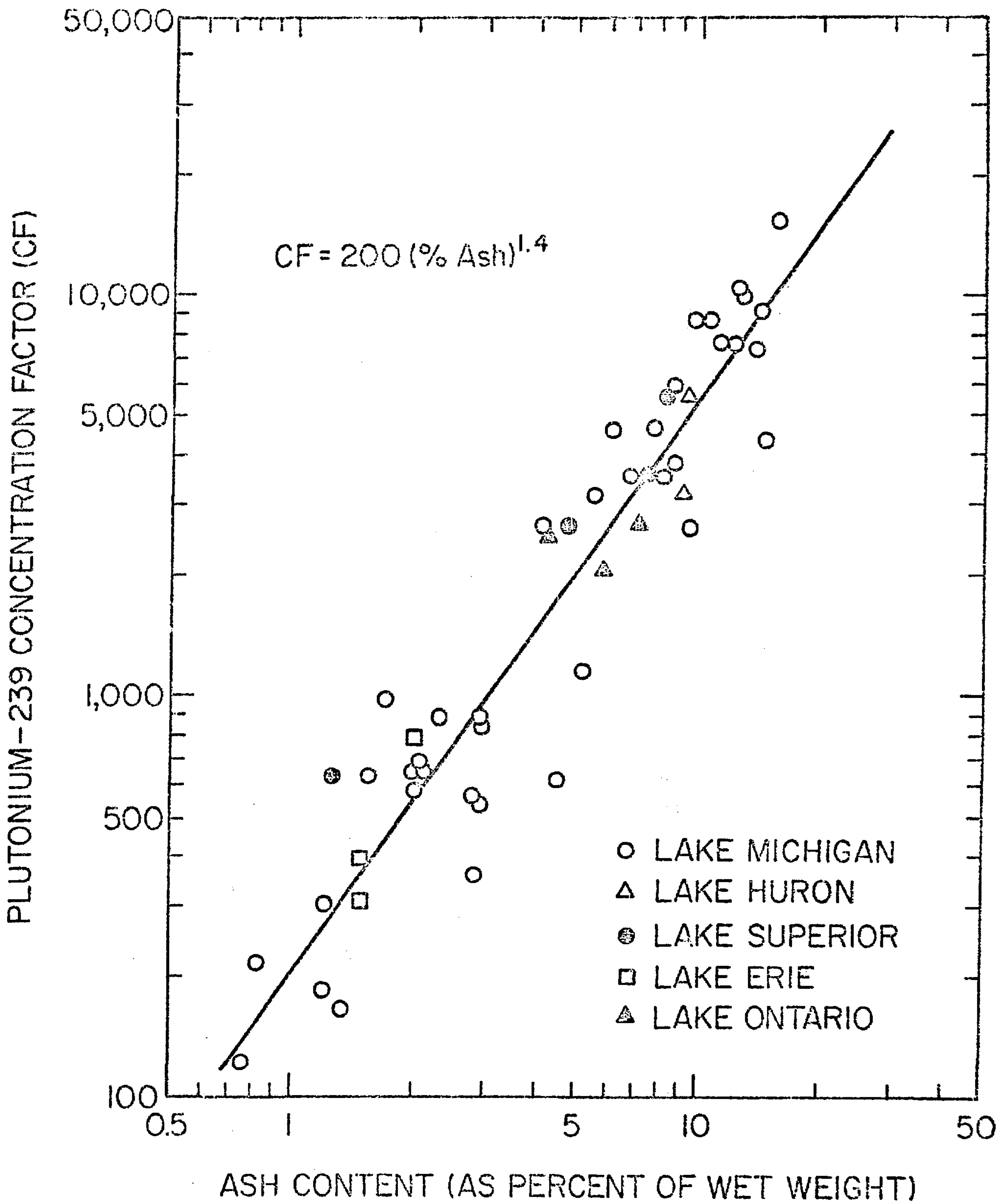
Lake	Sample	Number	Mean*	Range
Superior	Mixed plankton	3	4000 ± 900	2680 - 5730
	Zooplankton	1	630	
	Osmerus mordax (smelt)	1	6	
Michigan	Mixed plankton	22	5700 ± 800	620 - 15 300
	Cladophora sp.	16	3800 ± 500	1060 - 6930
	Zooplankton	9	350 ± 60	122 - 653
	Mysis relicta	7	760 ± 60	587 - 989
	Pontoporeia affinis	2	1600	1450 - 1830
	Cottus cognatus (slimy sculpin)	7	250 ± 60	128 - 560
	Coregonus hoyi (chub)	8	37 ± 3	21 - 50
	Alosa pseudoharengus (alewife)	7	25 ± 2	17 - 30
	Osmerus mordax (smelt)	6	20 ± 4	6 - 33
	Perca flavescens (perch)	2	16	4 - 29
	Coregonus clupeaformis (whitefish)	2	14	5 - 23
	Oncorhynchus kisutch (coho)	1	7	
	Oncorhynchus tschawytscha (chinook)	1	4	
	Salvelinus namaycush (lake trout)	2	1	1 - 2
Huron	Mixed plankton	2	4460	3240 - 5680
	Alosa pseudoharengus (alewife)	2	165	25 - 305
	Osmerus mordax (smelt)	1	13	
	Perca flavescens (perch)	1	24	
Eri	Zooplankton	3	500 ± 150	316 - 788
	Osmerus mordax (smelt)	1	235	
	Perca flavescens (perch)	1	10	
Ontario	Mixed plankton	3	2420 ± 200	2030 - 2670
	Alosa pseudoharengus (alewife)	1	176	

*Mean ± standard error.

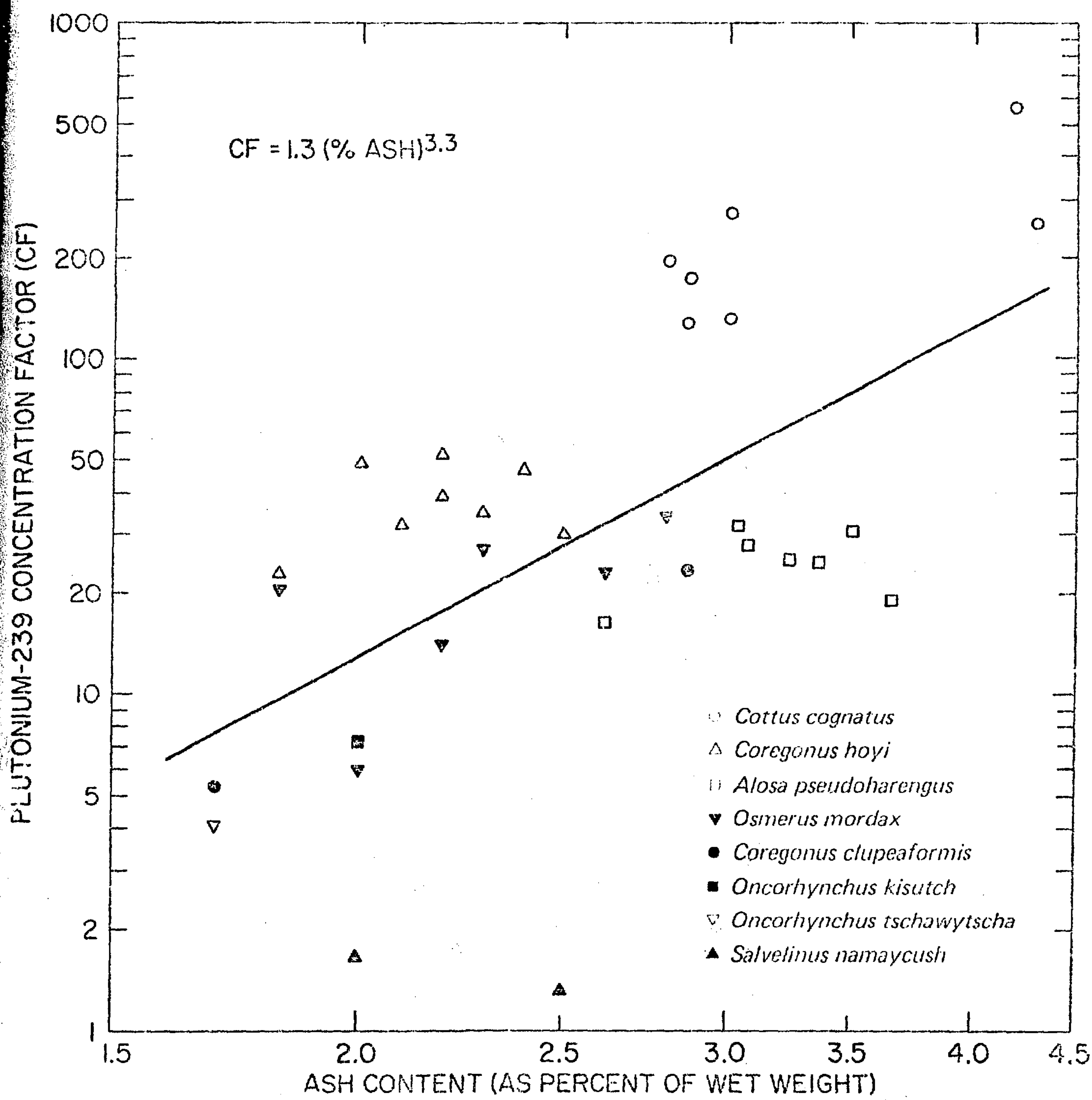
Figure Captions

Figure 1. Relationship between ^{239}Pu concentration factor and ash content in net plankton samples from the Great Lakes.

Figure 2. Relationship between ^{239}Pu concentration factor and ash content in samples of eight species of fish from Lake Michigan.



50,000
10,000
5,000
1,000
500
100
0.5
1
5
10
50
PLUTONIUM-239 CONCENTRATION FACTOR (CF)
ASH CONTENT (AS PERCENT OF WET WEIGHT)
CF = 200 (% Ash)^1.4
LAKE MICHIGAN
LAKE HURON
LAKE SUPERIOR
LAKE ERIE
LAKE ONTARIO


CF = 1.3 (% ASH)$^{3.3}$
PLUTONIUM-239 CONCENTRATION FACTOR (CF)
1000
500
200
100
50
20
10
5
2
1
1.5
2.0
2.5
3.0
3.5
4.0
4.5
ASH CONTENT (AS PERCENT OF WET WEIGHT)
Cottus cognatus
Coregonus hoyi
Alosa pseudoharengus
Osmerus mordax
Coregonus clupeaformis
Oncorhynchus kisutch
Oncorhynchus tschawytscha
Salvelinus namaycush