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PLUTONIUM AND AMERICIUM IN LAKE MICHIGAN SEDIMENTS*

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Abstract

The vertical distributions of ^{239,240}Pu, ^{238}Pu, and ^{137}Cs have been measured in sediment cores taken from Lake Michigan. Sections from a limited number of cores have been analyzed for ^{241}Am. In addition, grab samples from ten locations in the southern basin of the lake have been analyzed for phase distribution of ^{239,240}Pu using a sequential extraction technique.

The results indicate that the ^{239,240}Pu, ^{238}Pu, and ^{137}Cs from weapons testing, and the ^{241}Am formed <u>in situ</u> are concentrated in the sediments. A comparison of the total deposition of ^{239,240}Pu and ^{137}Cs indicates that ^{137}Cs may be valuable as a monitor for ^{239,240}Pu deposition in the sediments. Values of the ^{238}Pu/^{239,240}Pu ratio are in agreement with values reported in Lake Ontario sediments (and Lake Michigan plankton) and show little variation with depth. ^{241}Am data support the concept of in situ production with little preferential mobility after formation.

Studies of sedimentary phase distributions show that ^{239,240}Pu is associated with hydrous oxide phases which are chemically stable under the prevailing conditions in the lake sediments. Since Lake Michigan sediments remain aerobic, relatively little ^{239,240}Pu is available for chemical mobilization from the hydrous oxide or organic phases present in the sediments.

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Introduction

Plutonium, as well as many other artificial radionuclides, was first introduced into the environment as a result of weapons testing approximately thirty years ago. With the possible introduction of plutonium recycle boiling water and pressurized water reactors and an extensive breeder reactor program, it is imperative that the environmental chemistry of plutonium and other transuranic elements be fully understood. Since there have been very few documented cases of other general releases of transuranic elements to the environment and since releases from operating nuclear facilities have been negligible up to now, studies of fallout materials will provide an essential understanding of the behavior of transuranic elements in the environment.

Wahlgren and Nelson [1] have shown that approximately 97% of the plutonium that entered Lake Michigan now resides in the sediments. As a result, the concentration of plutonium in the surficial sediments in Lake Michigan varies between 140 and 400 fCi/g dry sediment, and the concentration in the water column is less than 1 fCi/l [1]. Since the surficial sediments appear to be acting as the initial sink for plutonium, a knowledge of the relative importance of remobilization versus burial for this element is a prerequisite to understanding the ultimate fate and importance of all transuranic elements in the aquatic environment.

In this paper we shall report on (1) the areal and depth distribution of plutonium and americium; and (2) the physico-chemical speciation of plutonium in sediments from Lake Michigan. These results will be discussed in relation to patterns of deposition and changes in water quality.

Methods

Sample Collection

The sediments were sampled using conventional grab and coring techniques. Sampling operations were carried out on the University of Michigan research vessels, Inland Seas, Laurentian and Mysis, during several cruises between 1972 and 1974 (Figure 1). A description of the physical nature of the cores and the methods of sectioning have been presented elsewhere [2]. The cores were sectioned immediately after core recovery, transferred to preweighed plastic bottles, and frozen for return to the laboratory. The bulk density was measured before air drying at 90° C for 48 hr before analysis so that the porosity of each section could be determined.

The samples for the chemical speciation experiments were taken with a grab in 1974 (Figure 2). These samples were stored at 4° C and were homogenized before subsampling. Aliquots were also taken to determine total plutonium and dry weight.

Radioactivity Measurements

The ^{137}Cs activity in each section was determined by gamma counting $\leq$ 20 g of the oven-dried samples in standard glass scintillation vials for up to

800 min using a 10 x 10 cm NaI detector and a multichannel-analyzer system. Standards of ^{137}Cs, uranium ore, thorium ore, and potassium having the same density and geometry as the unknowns were used and the ^{137}Cs concentrations were determined by least-squares analysis of the resulting gamma spectra [3].

Total Plutonium

Samples were analyzed for plutonium using techniques similar to those described by Golchert [4], Talavitie [5], and Wong [6]. Up to 5 g aliquots of the ground and well-mixed, air-dried material with 1—2 pCi of ^{242}Pu as an isotopic diluent, were digested first in concentrated nitric acid to destroy organic material and then in aqua regia. (If the sample is to be analyzed for ^{210}Pb, the sample is treated with concentrated hydrochloric acid until all the nitric acid has been destroyed [2].) The sample is then centrifuged and filtered to remove all solids that are resistant to this digestion procedure and the supernatant taken down almost to dryness. The residue is taken up in 20 ml of 8 M nitric acid which is then passed through an anion exchange column of Dowex 1 x 8 (100—200 mesh) which has been preconditioned with nitric acid. The column is washed with 75 ml of 8 M nitric acid to remove all traces of uranium and almost all other heavy elements. The column is then washed with 100 ml of 12 M hydrochloric acid to remove thorium. Plutonium is eluted with 50 ml of a mixture of 0.1 M hydrochloric acid and 0.01 M hydrofluoric acid.

The eluent is taken to dryness, redissolved in 5 ml of concentrated HCl, taken to dryness again. This step is repeated twice. Finally, the residue is taken up in a few drops of 6 M HCl and then 5 ml of a mixture of 1 M NH_4Cl and 0.01 M oxalic acid with warming. The plutonium is plated out of this solution onto pre-electropolished stainless steel discs as described by Talavitie [5].

The plates are finally assayed by alpha spectroscopy using silicon barrier detectors whose background in the region of interest (4.5—5.5 MeV) is $\leq$ 0.001 cpm. Activities of ^{238}Pu and ^{239,240}Pu are determined by comparing the integrated count in their respective peaks with that in the ^{242}Pu peak. The specific procedures for determination of ^{239,240}Pu in each of the extraction fractions is too lengthy for presentation in this report and has been published elsewhere [8].

Americium

1—2 pCi of ^{243}Am is added to the 8 M nitric acid eluent from the ion exchange column and the solution is evaporated to a small volume (~10 ml) to remove excess acid. The solution is diluted to ~100 ml with deionized water and concentrated ammonium hydroxide is added to precipitate iron and aluminum hydroxides, which scavenge the americium and rare earth elements from the sample. This precipitate is dissolved in a minimum volume of nitric acid and sufficient aluminum nitrate added to almost saturate the solution (2.0—2.5 M $Al(NO_3)_3$). The solution is vigorously stirred and concentrated NH_4OH added to adjust the pH to 2. The americium and rare earths are extracted with Aliquat 336-S nitrate in xylene (30% w/v) [7] (prepared by equilibrating an equal volume of 30% w/v Aliquat 336-S chloride with three equal volumes of 1 M $Al(NO_3)_3$. The two phases are thoroughly mixed for about 2 minutes and then separated by centrifugation followed by withdrawal of the aqueous phase. The organic layer containing the americium activity is then scrubbed three times with equal volumes of 10 M ammonium nitrate solution. This scrubbing serves to back-extract from the organic phase metallic ions such as iron and aluminum. The scrub solutions are discarded. The americium and rare earths are then back-extracted from the organic layer with an equal volume of 0.3 M nitric acid and the solution evaporated to dryness. The residue is then dissolved in a convenient volume (~10 ml) of 0.2 M hydrochloric acid and then an equal volume of 10 ml of 1.2 M ammonium thiocyanate is added. This solution is contacted with an equal volume of 30% (w/v) Aliquat 336-S thiocyanate in xylene. (The americium thiocyanate complex is readily extracted (> 95%) from aqueous solution by Aliquat 336-S thiocyanate but the rare earths, especially the light lanthanides, are poorly extracted (3—5%) from an acidified thiocyanate medium.) The organic layer containing the americium activity is scrubbed two times with equal portions of a solution which is 0.6 M in ammonium thiocyanate and 0.1 M in hydrochloric acid. The americium is removed from the organic layer by back-extraction with 6 M hydrochloric acid. Iron (also uranium), frequently present, remains in the organic phase. The aqueous phase containing the americium is contacted once with pure xylene in order to extract the entrained Aliquat 336-S reagent. The acid solution containing the americium activity is then evaporated. Any ammonium thiocyanate residue is destroyed by treatment with hot concentrated nitric and hydrochloric acids. The solution containing the back-extracted americium is evaporated to dryness. Any ammonium nitrate residue remaining is destroyed by heating with concentrated nitric acid to which some concentrated hydrochloric acid is added. These acids are subsequently evaporated and the sample is then evaporated once more with hydrochloric acid to remove any residual nitrates. Finally, the sample residue is taken up in 1.0 M ammonium chloride, 0.01 M oxalic acid, and electroplated onto a stainless steel counting disc using the technique given previously [5], and increasing the plating time to one hour. The ^{241}Am activity is then assayed by alpha spectroscopy making use of the added ^{243}Am as a yield monitor.

Plutonium Speciation

The chemical speciation of plutonium present in the sediments was determined by a series of sequential extractions of sedimentary material designed to differentiate material into the ion exchangeable, reductant-soluble (hydrous oxides of iron and manganese), organic and crystalline phases within the sediments [9]. It is recognized that the use of extraction techniques such as those outlined below do not absolutely define materials into the above categories. However, these techniques are useful in determining the relative mobility of various elements in the environment.

10.00 grams wet sediment were placed in a one-liter Erlenmeyer flask fitted with a plastic cap, 500 ml of 0.1 M magnesium chloride was added, and the mixture was stirred at room temperature for about 24 hours. The reaction mixture was then centrifuged (23,000 g). The solids were washed twice by shaking with distilled water and centrifugation. The washings were added to the liquid, which was filtered through paper to remove any trace or residual solid, and stored in a two-liter polyethylene bottle. The average pH of the magnesium chloride solutions was found to be 7.5.

The remaining solid was placed in a solution composed of 10 grams of sodium dithionite dissolved in 400 ml of 0.3 N sodium citrate. This mixture was heated to 80—90° C in a water bath, with constant stirring for 15 minutes. The solid was centrifuged and washed as before, and the supernate and washings were filtered through paper and stored in a one-liter polyethylene bottle. The average pH of the citrate-dithionite solutions was found to be 5.9.

The remaining solid was placed in 500 ml of 0.1 N sodium hydroxide in a one-liter Erlenmeyer flask with a plastic cap, and stirred for about 12 hours. The solid was centrifuged and washed as above, and again the liquid was filtered through paper.

The remaining material was dried in an oven at about 100° C. In a 100 ml platinum crucible, 4 grams of boric acid and 6 grams of lithium fluoride were mixed. Into a small hollow in this mixture was placed 1 gram of the material to be fused, which had previously been finely ground using a mortar and pestle. (The total weight of the dried material left after fractionation of each sample was measured and recorded, but only one gram of this material was actually used in the fusion.) 1—2 pCi of ^{242}Pu spike was added to the mixture, and the crucible was tapped on the side to cover the sediment. The crucible was then covered and heated gently for two to three minutes over a low flame. The flame was increased gradually until the contents of the crucible reached their melting point, and the mixture was heated strongly until it was entirely melted. The crucible was cooled quickly by half immersing it in a stream of cold tap water. Then, 20 ml of concentrated H_2SO_4 were added to the contents, and the covered crucible was gently heated on a wire gauze over a Bunsen burner until gas bubbles were evolved. The heating was regulated so that the reaction would not be too vigorous. When the evolution of gas ceased (after about 90 minutes), the temperature was increased until copious fumes of sulfur trioxide appeared, and this temperature was held for 10—15 minutes. The crucible was submerged in about 400 ml of deionized water in a one-liter beaker, 10 ml of concentrated HNO_3 were added, then the crucible and cover were boiled until all their contents were dissolved. The resulting solution was clear, often yellowish. This solution was evaporated to dryness on a hotplate, the residue was dissolved in 8 M HNO_3 and reserved for plutonium analysis.

In an effort to verify that no significant quantity of ^{239,240}Pu existed in a possibly mobile organic phase, between 125 and 180 grams of wet sample were shaken with 500 ml 0.1 N NaOH overnight. The liquid phase was removed from the sediment by centrifugation at 14,000 g and decanting. The liquid was acidified with 10 ml 6 N HCl and allowed to stand overnight. Again the liquid was removed by centrifugation and decantation. The liquid was spiked with ^{242}Pu and analyzed for ^{239,240}Pu in the normal manner. The solid was redissolved in 200 ml 0.1 N NaOH and analyzed for ^{239,240}Pu.

Results and Discussion

The vertical distribution of $^{239,240}Pu$ has been measured in fifteen sediment cores. A large proportion of these cores were taken from the southern basin of the lake, i.e., south of latitude 43° N (Figure 1). The data are shown in Figure 3(a—o). Since there have been only minor releases of radioactivity from nuclear power plants around the lake, effectively all the plutonium (and ^{137}Cs) found in the sediments is the result of atmospheric fallout from nuclear testing during 1952—1962 [10]. Even though the present inputs from the atmosphere are approximately two orders of magnitude lower than their maximum in 1963, analysis of the distribution of ^{137}Cs in more than 50 sediment cores from the southern half of the lake indicates that there is a negligible contribution to the input of ^{137}Cs and $^{239,240}Pu$ to the lake from runoff via tributary rivers and streams [11]. Measurements of $^{239,240}Pu$ in the water column indicate that > 97% of the plutonium that has fallen onto the lake now resides in the sediments [1].

In all of the cores studied, the $^{239,240}Pu$ activity was confined to the uppermost 6 cm of the sediments, and in many cores no activity was found below 3 cm. Since the sedimentation rate has been determined by the ^{210}Pb method, it can be shown that the depth to which plutonium (and ^{137}Cs) is found in these cores is consistent with the known history of deposition from the atmosphere. In cores taken at stations having high sedimentation rates, a maximum activity is found at a depth corresponding to the maximum input in 1963 (Figure 3(g—l)) [12].

Robbins and Edgington [2] have derived a simple steady-state model which describes the shape of the distribution of the activity of plutonium in sediment cores in terms of three variables; the sedimentation rate, a mixing depth which takes into account disturbances of the sediment/water interface by bioturbation [13] or physical mixing [14], and the flux of plutonium to the sediment/water interface. Since the residence time of $^{239,240}Pu$ (and ^{137}Cs) appears to be $\leqq 1$ year in the water column, it is assumed that there is an almost instantaneous removal of most of each annual increment. The expected deposition using a variable residence time (1—10 y) in the water column was calculated and the best least-squares fits, which reproduce a maximum at depth in the core, were obtained using the shortest residence time.

This model has been applied to all of the plutonium and cesium data accumulated for cores taken from Lake Michigan. The profiles representing the least-squares best fits to the plutonium data were calculated using the annual values of the flux of plutonium to the lake estimated from monthly fallout monitoring data for ^{90}Sr and a $^{239,240}Pu/^{90}Sr$ ratio of 0.017 [15]. These are shown as histograms in Figure 3(a—o). Similar calculations were performed with the ^{137}Cs data. The values of the sedimentation rate, mixing depth, and a flux multiplier which relates the actual concentration of plutonium in the sediment per unit area to the flux at the air/water interface from fallout, have been calculated in an earlier paper [12] and are shown in Figure 3(a—o).

It was found that the total deposition of $^{239,240}Pu$ per unit area varied between 0.02 and 0.43 pCi/cm^2 according to sampling location with a flux multiplier varying between 0.05 and 3.1 times the average flux at the air/water interface.

This multiplier has been compared with the same parameter calculated for the deposition of ^{137}Cs in the same cores. It was found that the value of the ratio of the plutonium to cesium multiplier at all fifteen stations varied between 0.54 and 1.06 with most of the values lying between 0.80 and 1.06 [12]. The constancy of this ratio suggests that plutonium and cesium are removed to sediments with the same efficiency regardless of sampling location, and are therefore being scavenged by the same particulates. This is fortunate because it means that in lakes similar to Lake Michigan, measurements of ^{137}Cs can provide the necessary information to predict those areas where plutonium will be deposited.

The distribution of plutonium (and cesium) in the sediments of southern Lake Michigan is shown in Figure 4(b). The data are presented in terms of the flux multiplier which is proportional to the total deposition. The isopleths are drawn mainly on the basis of the ^{137}Cs data, but in light of the similarity of the flux multipliers for plutonium and cesium at stations where both isotopes have been measured, this assumption is justified. By comparing the data in Figure 4(b) with the mass sedimentation rate in Figure 4(a), it is clear that the concentration of plutonium or cesium is greatest where the sedimentation rate is greatest. These data also suggest that there is a strong horizontal movement of sedimentary material in the lake which rapidly moves radioactivity from the site of impingement on the surface, through the water, to a final site of deposition in the sediments. Unfortunately, there are very few data available regarding the current structure in the lake. However, those which are available indicate that there are currents $\geqq$ 10 cm/sec [16] which are sufficient to resuspend the fine floc, clays and silt which make up the bottom sediments [14].

Evidence for aperiodic resuspension of the sediments can be seen by careful examination of the plutonium profiles and from sediment trap data. The profiles shown as histograms in Figure 3(a—o) are the calculated best least-squares fits to the data according to the model which are in reasonable agreement with the experimental data. However, in several of the profiles, Figure 3(g,i), the calculated concentrations of plutonium are significantly lower than those observed, reflecting the short residence time of plutonium in the water column and the very low input fluxes in recent years. Since the only significant source of new plutonium is from the atmosphere and the required amount of plutonium to produce a high concentration in surface sediments cannot be maintained by erosion from the watershed [11], it is clear that the additional plutonium must come from the sediment itself. As can be seen from an examination of Figure 4(a), there are large areas of the lake where no significant sedimentation occurs, but there is a layer of floc overlying the glacial till or sand which contains high concentrations of plutonium. The profile for station 72-54, Figure 3(d), is representative of these areas. Since no significant accumulations of sediment have occurred, it is likely that these 1—2 cm thick deposits are transitory and that this material is readily available for resuspension.

Recently measurements of sedimenting material have been made at one of the coring stations (ANL 74-5, Figure 1) using sediment traps. The total flux of material found in these traps, particularly in those situated within 5 m of the bottom is far greater, 200—300 mg/cm^2/yr, (~10 x) than the sedimentation rate estimated from ^{210}Pb, ^{137}Cs or ^{239,240}Pu (31 mg/cm^2/yr). The concentration of ^{239,240}Pu in the material collected in these traps has approximately the same value as that found in the 0—0.5 cm or 0—1 cm layers in sediment cores, ~0.2 pCi/g, which is not significantly lower than the maximum concentration found in many of the cores, and therefore not supported by new inputs. This evidence again tends to support the idea of a large degree of resuspension of sedimentary material in the lake and the availability for translocation by physical means.

While the plutonium profiles reported here have some similarities to those measured by Bowen and Noshkin in cores from Lake Ontario [17], no evidence has been found of significant concentrations of plutonium or cesium in sediment layers deeper than 6 cm for any core from Lake Michigan.

Measurements have been made of the vertical distribution of ^{238}Pu in these same cores. A summary of the data is presented in Table 1. The ^{239,240}Pu activity and the ratio of the ^{238}Pu to the ^{239,240}Pu ratio is given for each sediment layer. It can be seen that the values of the ^{238}Pu/^{239,240}Pu ratio are quite variable, but that the ratio tends to values of 0.03 to 0.04 where there is the greatest ^{239,240}Pu activity. As the concentration of ^{239,240}Pu decreases, the value of the ratio tends to increase. Bowen and Noshkin observe the same effect in the cores from Lake Ontario [17]. This is largely a function of counting statistics with the confidence limit of the ratio being ±15% in the most favorable cases, but tending to ±50% when the ^{239,240}Pu activity falls below ~0.1 pCi/g. Better data would require the analysis of much larger samples than those analyzed here.

However, there is some question as to whether there is any real need to expend the effort to analyze larger samples. The ^{238}Pu content in the surface air has been extremely variable. Thomas and Perkins have shown that the ^{238}Pu/^{239,240}Pu ratio decreased from 0.03 to 0.015 between 1962 and 1966 when the greatest concentration of fallout debris returned to earth. In 1966 and 1967, the ratio rapidly increased to 0.40 as a result of the large input of ^{238}Pu into the southern hemisphere due to the Snap burnup in 1964. Since then the ratio has dropped back to 0.01—0.02 [18]. Hardy <u>et</u> <u>al</u>. [19] have shown that the average ^{238}Pu/^{239,240}Pu ratio in soil for the 40° N latitude band is 0.0375. Therefore, the apparently large inputs of ^{238}Pu in 1966—1970 had very little effect on its overall ratio to the ^{239,240}Pu activity.

The large change in the ^{238}Pu/^{239,240}Pu ratio between 1966 and 1970 will only be detected in sediment cores where the sedimentation rate is of such a magnitude that the sampling interval contains one or two years of atmospheric input to the lake. This would require rates of sedimentation equivalent to 0.25 to 0.5 cm/yr. There are very few locations in Lake Michigan where such rates of sedimentation are found. However, there is another factor working against the observation of a horizon corresponding to the 1966—1970 input of ^{238}Pu and that is the effect of vertical mixing in the sediment which has been described earlier [2]. At those stations where there are the highest sedimentation rates, there is generally a deep mixing layer, e.g. station 72-29, Figure 3(c), and station 74-1, Figure 3(l), with mixed layers corresponding to 8 and 12 years of deposition, respectively. Since for Lake Michigan the average sedimentation rate is ~0.1 cm/yr and mixing depths are typically 1—2 cm, Figure 3(a—o), the ^{238}Pu/^{239,240}Pu ratio would be expected to be ~0.0375, the same as the average soil value, at all depths in these cores because of the averaging effect of the lake sediments.

Since there appears to be no a priori reason why there should be any significant variations in the ^{238}Pu/^{239,240}Pu ratios with depth in the sediment core, it is probably more sensible to take a few larger samples undifferentiated with respect to depth and obtain an accurate average value of the ratio. This average value is important as a baseline, since possible releases from the nuclear power industry can be expected to have ^{238}Pu/^{239,240}Pu ratios as high as 44.0 [18].

Although ^{241}Am is not formed directly in the detonation of nuclear weapons, its concentration in the environment will continue to increase due to the decay of ^{241}Pu and may be largely found wherever ^{241}Pu is concentrated.

Therefore, a few samples of sediment from Lake Michigan have been analyzed for ^{241}Am. The data are summarized in Table 2. Since ^{239,240}Pu is an effective tracer for ^{241}Pu and the ratio of ^{239,240}Pu to ^{241}Pu in fallout is relatively constant, differences in the value of ^{239,240}Pu/^{241}Am ratio will indicate any differences in the relative mobility of these two elements in the sediments. The ^{241}Pu in the environment has an average age of ~15 years. Based on the known relative activities of ^{239,240}Pu and ^{241}Pu at the time of introduction into the environment and provided that there has been no preferential scavenging or mobility of either element, the ^{239,240}Pu/^{241}Am activity ratio should be $\simeq$ 4. From the data shown in Table 2, it can be seen that the values of this ratio vary between 3.8 and 6.1 with a mean of 4.5. The agreement suggests that there is little preferential mobility or scavenging of plutonium or americium in this system. Since there is a lack of any significant differences in the ratio between surface and deeper sediments, it implies that in the deeper and older sediment ^{241}Am is growing in without any mobility and that ^{241}Pu and ^{241}Am are being scavenged equally from the water column to the younger sediment.

In a recent paper, Livingston et al. have presented estimates of the concentration of ^{241}Pu in marine sediment samples measured by analysis of their original plutonium counting plates for ^{241}Am several years after the initial separation of plutonium [20]. They also calculated the decrease in time of the ^{239,240}Pu/^{241}Am activity ratio in global fallout indicating a value 5.71 for January 1975 (analyzed between January and May 1975). The values reported in this paper are essentially in agreement with this value. It is intended to examine the Lake Michigan samples for ^{241}Pu by the technique described by Livingston after the plutonium plates have aged sufficiently.

As there is little apparent selective mobility of plutonium or americium within the sedimentary column, investigations were begun to determine if these nuclides could migrate as a group from the sediment to the overlying water. These studies centered around determining the sedimentary phase distribution of plutonium as defined by a series of sequential extractions. This decision was made with the realization that an extraction technique does not absolutely define sedimentary phases, but rather indicates relative solubilities of phases. Since americium is forming in situ within the sediments, plutonium distribution is likely to be a good indicator of americium distribution.

The results of the analyses are shown in Table 3. It can be seen that the concentrations of $^{239,240}Pu$ are low in all samples; and consequently, the analysis of the fractions containing low concentrations have relatively large associated counting errors. In addition, the total activity of $^{239,240}Pu$, which is usually confined to the first few centimeters of sediment, may have been diluted in some samples by mixing with sediment from a lower depth which did not contain plutonium. The results, however, are indicative of the areal distribution and phase distribution of the cumulative $^{239,240}Pu$ deposition at the sample station. The extremely low value at the 4 mile station is consistent with the sediment type in that area, which is mostly sand and coarse material [21]. The value at the 10 mile station appears to be anomalously low and cannot be explained by sediment characteristics. This value is further suspect when the rest of the data is considered and it is shown that the sum of the fractions add up to ~150% of this total value.

Examination of the data does show one extremely interesting characteristic which is evident in spite of the data scatter; that is the marked predominance of the distribution of $^{239,240}Pu$ in the citrate-dithionite fraction. This fraction was described by Chang and Jackson [22] as representing the occluded or reductant-soluble fraction. They recognized the fraction as representing that material occurring in a solid phase which required a reducing environment before dissolution could occur. This fraction contains at least 60% of the recovered $^{239,240}Pu$ in all but two cases. In both of these two exceptions, Bridge station and station 5A, the citrate-dithionite fraction represented only 47.9 and 45.7%, respectively; however, these values represent the entire recovery of plutonium in the fractionation scheme.

The question may be raised that, since the citrate-dithionite extraction preceeded the base extraction, the distribution coefficient for the citrate-plutonium complex may be much higher than that of a natural organic-plutonium complex which may have existed, and redistribution occurred in the extraction solution. Although the period of time that the sediment was exposed to the citrate-dithionite solution, 20 minutes, was very short for such an exchange to occur, an experiment was conducted in which another subsample of sediment from station 5B (chosen because of its high total $^{239,240}Pu$ concentration) was extracted as before, except that the base extraction was conducted prior to the citrate-dithionite extraction. The results of this experiment (Table 3) indicate that while there is some activity in both the $MgCl_2$ and NaOH fractions, the vast majority of the activity is still in the citrate-dithionite extractable phase.

One further question that arises from the observation that most of the sedimentary $^{239,240}Pu$ is in the citrate-dithionite extractable fraction is whether dithionite is required or if citrate alone is capable of extracting the plutonium. To investigate this possibility, additional subsamples of sediment from station 5B were extracted as before, except that in one sample citrate was used in the procedure without dithionite. Also, a third experiment was undertaken in which dithionite was added to the $MgCl_2$ extraction. The results of these experiments are also shown in Table 3.

It is apparent that the addition of a reducing agent to the $MgCl_2$

solution increases the extractable ^{239,240}Pu concentration. However, the two-fold increase in plutonium extracted in this fraction indicates that simple reduction is not sufficient to release large amounts of plutonium through ion exchange processes. Similarly, the significant reduction in the amount of ^{239,240}Pu extractable by citrate solution without a reducing agent would suggest that a complexing agent must be present in conjunction with reducing conditions to effectively remove plutonium from sedimentary phases.

Additional confirmation of the fact that plutonium in natural sediments does not exist in the base soluble or humic acid phase is shown in Table 4. These results are from sediments taken from the same grab samples as those used in Table 3. Larger samples were taken in this case in an attempt to quantify the amount of ^{239,240}Pu in the fulvic acid (FA) versus the humic acid (HA) fraction of the sediments. As can be seen from the data, less than 7% of the total sedimentary ^{239,240}Pu is found in the base soluble fraction. One interesting note regarding the data in Table 4 is the apparent consistency of the fraction of plutonium in the FA fraction as opposed to the apparent decrease in plutonium content of the HA fraction from river to lake sediments. However, although this is an interesting observation, more data are required before it can be shown whether this trend is real.

The results of this study would indicate that ^{239,240}Pu in Lake Michigan sediments is relatively immobile chemically, and that essentially none is in the form of refractory particles. However, the study does raise the question of the fate of plutonium in environments which undergo reducing conditions. These naturally occurring systems, caused by natural stratification or pollution, are characterized by highly reducing sediments and high concentrations of organic matter which has been shown to contain natural complexing agents. In these systems, the fate of plutonium is not as clear since remobilization cannot be ruled out at this time, and therefore re-entry into the hydrosphere and eventually the biosphere must be considered as a possibility.

Conclusions

The vertical distribution of ^{239,240}Pu and ^{137}Cs has been determined in fifteen sediment cores from Lake Michigan which had previously been dated by the ^{210}Pb method. These sediments showed a total deposition of ^{239,240}Pu ranging from 0.02 to 0.43 pCi/cm^2 and, in areas of high sedimentation, a maximum concentration corresponding to the maximum atmospheric input during 1963. Comparison of ^{239,240}Pu and ^{137}Cs deposition indicated that these isotopes are being removed by the same mechanism, with greatest deposition in areas of highest sedimentation rates. Data were presented to support the concept of remobilization and translocation of ^{239,240}Pu and ^{137}Cs by resuspension of the sediment.

The ^{238}Pu/^{239,240}Pu ratio in selected cores exhibited ratios in the range 0.03 to 0.04. Because of low sedimentation rates and mixing, little variation in this ratio with depth in the core is expected. Therefore, detailed examination of the ^{238}Pu/^{239,240}Pu ratio is less important than determining accurate baseline ratios which will be of value in the estimation of possible inputs from the nuclear industry.

The possible chemical mobility of $^{239,240}Pu$ has been determined by examination of the sedimentary phase distribution of plutonium in 10 grab samples from the southern basin of Lake Michigan. It is shown that most of the plutonium in the sediments is associated with the hydrous oxides of iron and manganese. Less than 7% of the total $^{239,240}Pu$ is associated with the sedimentary humic and fulvic acid fractions.

Studies of ^{241}Am with depth in sediments show that ^{241}Am is being formed in situ and shows little or no preferential mobility over $^{239,240}Pu$.

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TABLE 1. Summary of measured $^{239,240}Pu$ activity (Pu) (pCi/g dry weight) and $^{238}Pu/^{239,240}Pu$ activity ratio (R) in sediment cores taken from Lake Michigan in 1972, 1973, and 1974. The serial distribution in the cores is shown.

Sampling Depth (cm)	Pu	R	Pu	R	Pu	R	Pu	R	Pu	R	Pu	R
Station	72-11 43°01'N 86°24'W		72-17(2) 42°40'N 87°00'W		72-29(9) 42°17'N 86°38'W		72-54 42°20'N 37°32'W		72-101 44°44'N 86°44'W		72-103 44°28'N 86°42'W	
Floc	--	--	--	--	--		0.24	0.035	--	--	0.23	0.035
0—1	0.18	0.031	0.16	0.041	--	0.050	0.20	0.043	0.401	0.047	0.09	0.043
1—2	0.06	0.026	0.04	0.040	0.12		0.03	0.040	0.202	0.036	--	0.040
2—3	--	--	0.01	0.075	--	0.026	0.00	0.061	0.053	0.062	--	0.061
3—4	--	--	0.01	0.38	0.16		--	--	0.10	0.27	0.01	0.14
4—5	--	--	0.01	0.16	--	0.018	--	--	0.006	0.13	--	--
5—6	--	--	--	--	0.14		--	--	0.001	--	--	--
Station	73-5(c1) 42°30'N 86°33'W		73-6(c1) 42°33'N 86°38'W		73-6(c3) 42°33'N 86°38'W		73-7(c3) 42°36'N 86°47'W		73-8(c3) 42°40'N 86°58'W			
0.0 - 0.5	0.205	0.068	0.233	0.032	0.211	0.089	0.291	0.108	0.206	0.082		
0.5 - 1.0	0.247	0.056	0.235	0.056	--	--	0.274	0.050				
1.0 - 1.5	0.275	0.045	0.220	0.037	0.263	0.038	0.216	0.130	0.245	0.069		
1.5 - 2.0	0.305	0.024	0.265	0.048	0.259	0.030	0.239	0.047	0.222	0.089		
2.0 - 2.5	0.202	0.041	0.228	0.034	--	--	0.258	0.034	0.165	0.067		
2.5 - 3.0	0.173	0.048	0.241	0.033	0.135	0.043	0.211	0.035				
3.0 - 3.5	0.103	0.111	0.156	0.039	0.064	0.044	0.105	0.073	0.059	0.075		
3.5 - 4.0	0.042	0.067	0.083	0.038	0.029	0.093	0.041	0.020	0.010	0.330		
4.0 - 5.0	--	--	0.038	0.067	0.010	0.13	0.010	0.220	0.003	0.130		
5.0 - 6.0	--	--	0.008	0.079	0.003	0.65	0.003	--	--	--		
6.0 - 8.0	--	--	--	--	--	--	--	--	--	--		
Station	74-1(c1) 42°17'N 86°38'W		74-2(c1) 42°23'N 86°30'W		74-3(c4) 42°33'N 86°38'W		74-5(c1) 42°43'N 87°00'W		ANL 74-5(c1) 43°00'N 86°23'W			
0.0 - 0.5	0.116	0.059	0.144	0.13	0.286	0.056	0.143		0.143	0.037		
0.5 - 1.0	0.158	0.061	0.110	0.031	0.213	0.070						
1.0 - 1.5	0.126	0.054	0.148	0.050	0.293	0.065	0.114		0.114	0.051		
1.5 - 2.0	0.106	0.080	0.150	0.050	0.258	0.038						
2.0 - 2.5	0.167	0.055	0.095	0.083	0.260	0.033	--		--	--		
2.5 - 3.0	0.110	0.066	0.028	0.043	0.155	0.050						
3.0 - 3.5	0.139	0.065	0.007	0.077	0.101	0.056	0.056		0.056	0.045		
3.5 - 4.0	0.153	0.071	0.004	--	0.070	0.059						
4.0 - 4.5	--	--					0.004		0.004	0.72		
4.5 - 5.0	0.19	0.034										
5.0 - 5.5	0.21	0.032					0.002		0.002	0.71		
5.5 - 6.0	0.26	0.031										
6.0 - 6.5	0.23	0.031										
6.5 - 7.0	0.17	--					0.004					
7.0 - 7.5	0.12	--										
7.5 - 8.0	0.04	--										

TABLE 2. Concentrations of ^{241}Am and ^{239,240}Pu in Lake Michigan sediments (1973—1974).

Sample Station	Depth (cm)	^{241}Am (pCi/g dry)	^{239,240}Pu (pCi/g dry)	^{239,240}Pu/^{241}Am
73-5	0—2	0.054	0.25	4.5 ± 5%
Core #1	2—4	0.035	0.13	3.8 ± 6%
73-6	0—2	0.051	0.23	4.6 ± 6%
Core #1	2—4	0.041	0.17	4.1 ± 5%
73-8	0—4	0.022	0.13	6.1 ± 8%
Core #3				
74-2	0—2	0.023	0.14	6 ± 6%
Core #1	2—4	0.009	0.035	3.9 ± 10%
74-4	0—4	0.008	0.048	6 ± 12%
Core #1				

TABLE 3. Distribution of ^{239,240}Pu in Lake Michigan sediments

Sample	Total		$MgCl_2$		Citrate-Dithionite		NaOH		Fusion		% Total Recovery
	N[(a)]	pCi/g	N	%[(b)]	N	%	N	%	N	%	
(F) Grand River near bridge	5.2	0.006	0	0	2.49	47.9	0	0	0	0	47.9
(G) Grand River upstream of the power plant	3.6	0.005	0.22	6.1	2.30	63.9	0	0	0	0	70.0
(B) Grand River downstream of the power plant	13.1	0.017	0.50	3.8	12.56	95.9	0	0	0	0	99.7
(A) 2 miles offshore Lake Michigan	12.1	0.016	0.07	0.6	9.68	80.0	0.02	0.17	0	0	80.0
(D) 4 miles offshore Lake Michigan	0.6	0.001	0.24	40.0	0.37	61.7	0.02	3.30	0	0	105.0
(C) 6 miles offshore Lake Michigan	10.3	0.013	0	0	8.25	80.0	0	0	0	0	80.1
(E) 10 miles offshore Lake Michigan	1.7	0.002	0.05	2.9	2.55	150.0	0	0	0	0	152.9
(I) Station 5A (85 m depth)	13.4	0.017	0	0	6.12	45.7	0	0	0	0	45.7
(H) Station 5B (84 m depth)	34.9	0.045	0	0	31.30	89.7	0	0	0.51	1.46	91.2
(H) Station 5B NaOH before Citrate-Dithionite			1.94	5.6	33.60	96.3	1.75	5.00	ND		106.9
(H) Station 5B Citrate without Dithionite			0	0	12.20	35.0					
(H) Station 5B Citrate with Dithionite			0	0	31.90	91.4					
(H) Station 5B $MgCl_2$ with Dithionite			3.40	9.7							
(J) Station 6 (88 m depth)	18.7	0.024	0	0	24.20	129.4	0.12	0.60	0	0	130.0

[(a)] N = number of counts/1000 minutes/g dry weight sediment.

[(b)] % = ± a maximum of 20%.

TABLE 4. Fulvic acid versus humic acid distribution of $^{239,240}Pu$ in Lake Michigan and Grand River sediments.

Sample	$^{239,240}Pu$ Fulvic Acid Fraction		$^{239,240}Pu$ Humic Acid Fraction		$^{239,240}Pu$ Total Sediment
	fCi/g(a)	% total	fCi/g(a)	% total	fCi/g(a)
Grand River upstream of power plant	0.04	0.80	0.3	6.0	5.0
Grand River downstream of power plant	0.14	0.58	0.8	3.3	24.0
Lake Michigan, 4 miles off Grand Haven	0.008		0.01		1.0
Lake Michigan station 5	0.16	0.80	0.1	0.5	20.0
Lake Michigan station 6	0.10	0.36	0.2	0.7	28.0

(a) dry weight

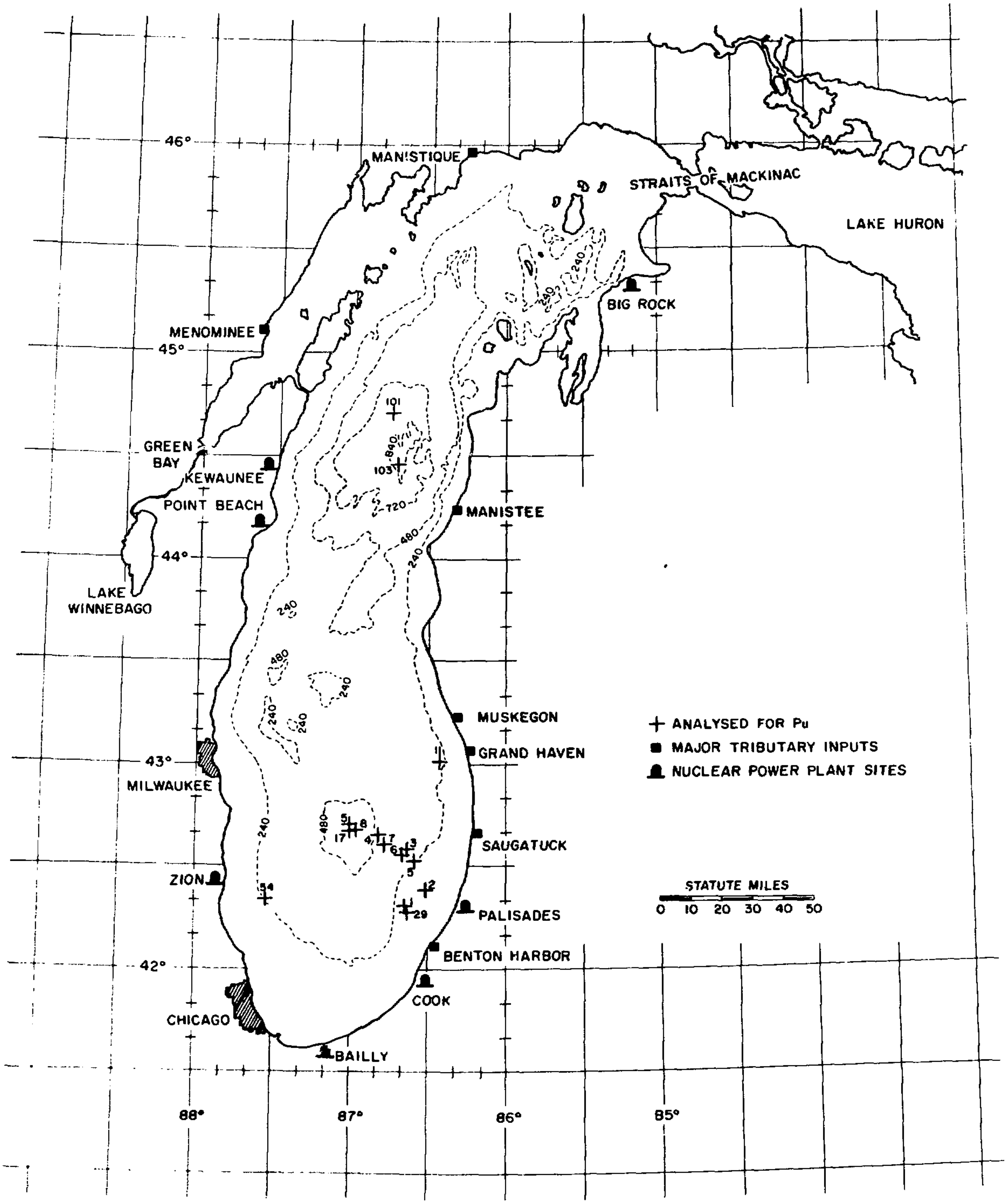


FIGURE 1. Stations occupied in Lake Michigan for the sampling of sediments for plutonium in 1972, 1973, and 1974.

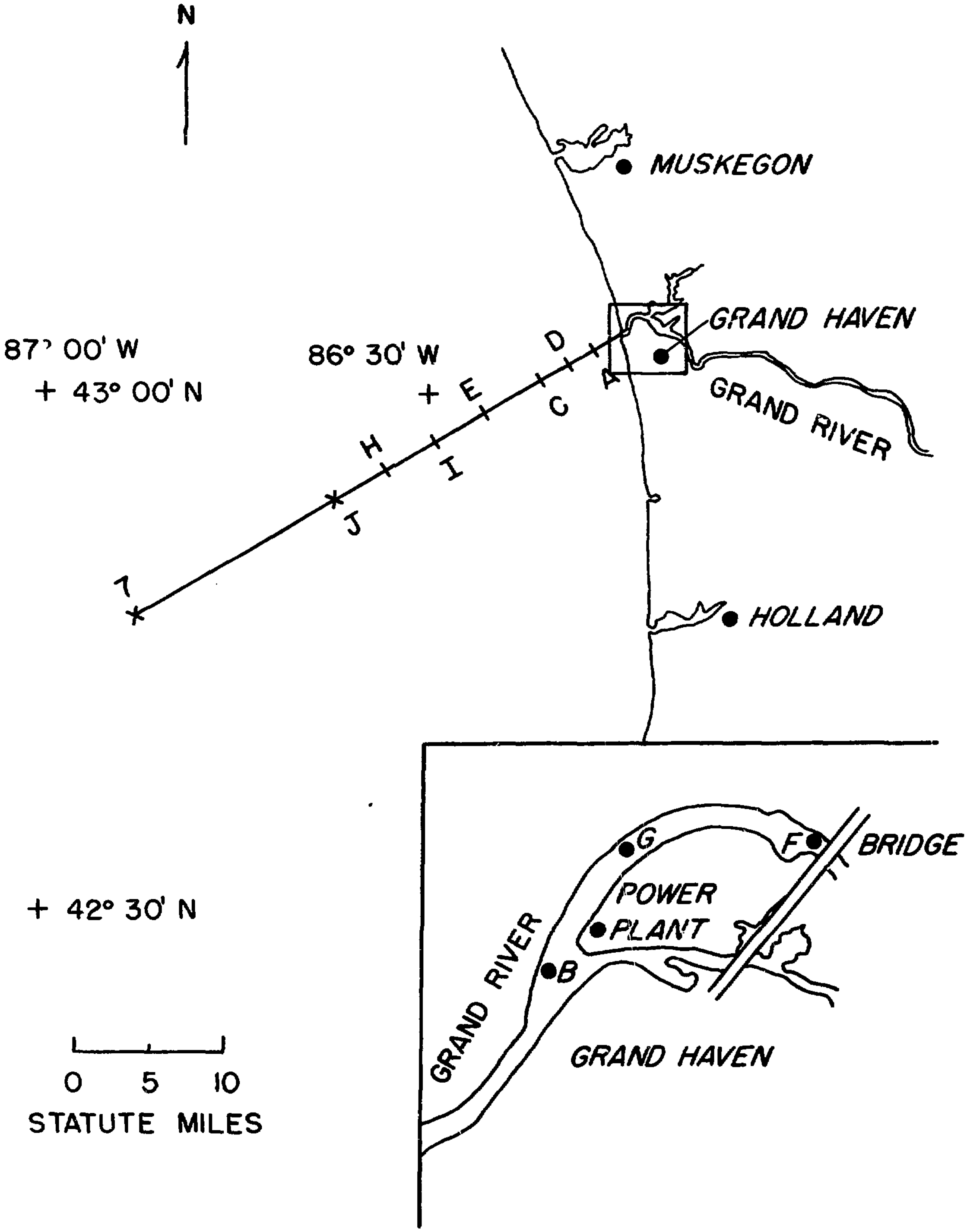
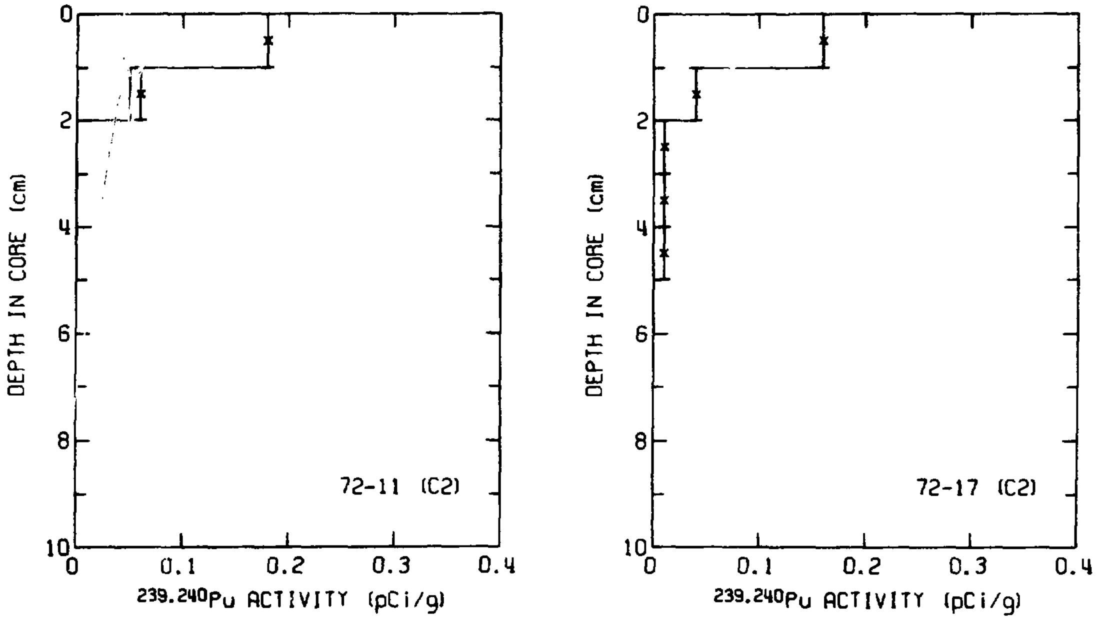
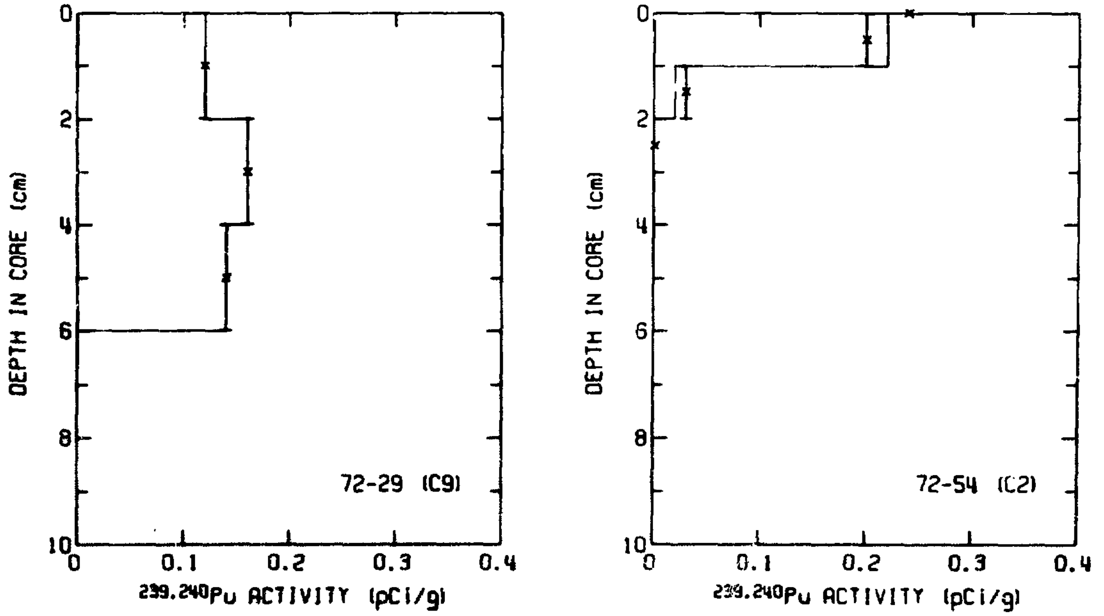


FIGURE 2. Station locations of grab samples used in sequential extraction for $^{239,240}Pu$.



(a) R = 0.08, ω = 21.8, S = 0.5(7), f = 0.46

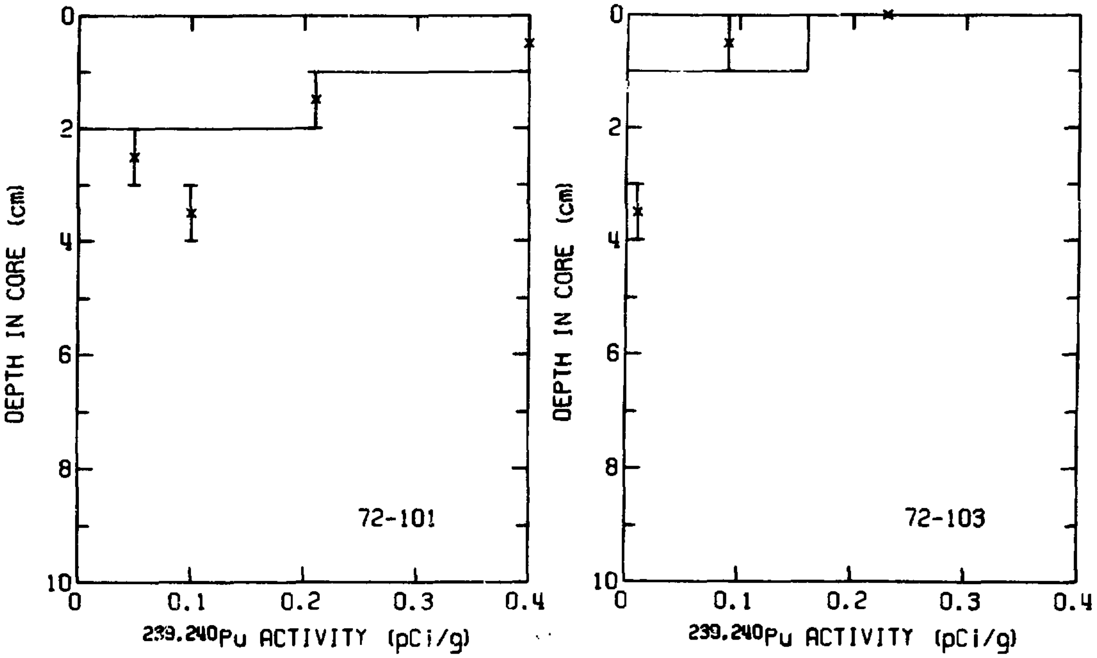
(b) R = 0.07, ω = 15.1, S = 0.5(7), f = 0.30



(c) R = 0.32, ω = 114 S = 2.5(8), f = 2.18

(d) R = 0.02, ω = 5.9, S = 1.0(68), f = 0.58

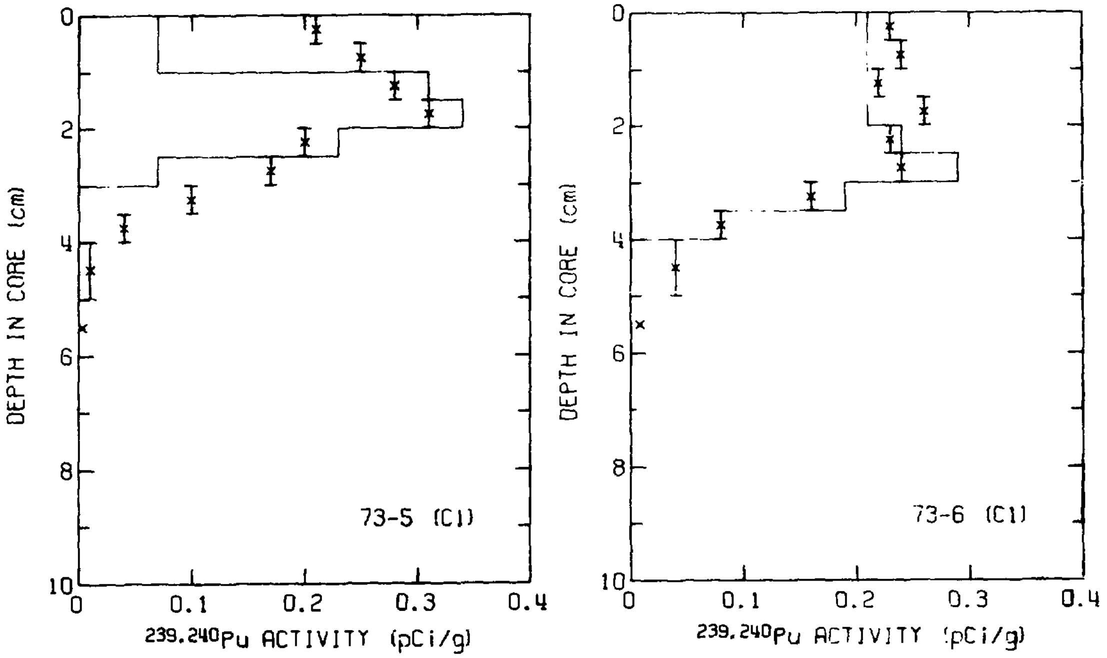
FIGURE 3. Measured and calculated plutonium profiles in the sediments. R and ω are the sedimentation rates in cm/yr and g/cm^2/yr, respectively. S is the mixing depth in cm, and (years), and f is the flux multiplier.



(e) R = 0.05, ω = 11.0, S = 1.0(24), f = 0.91

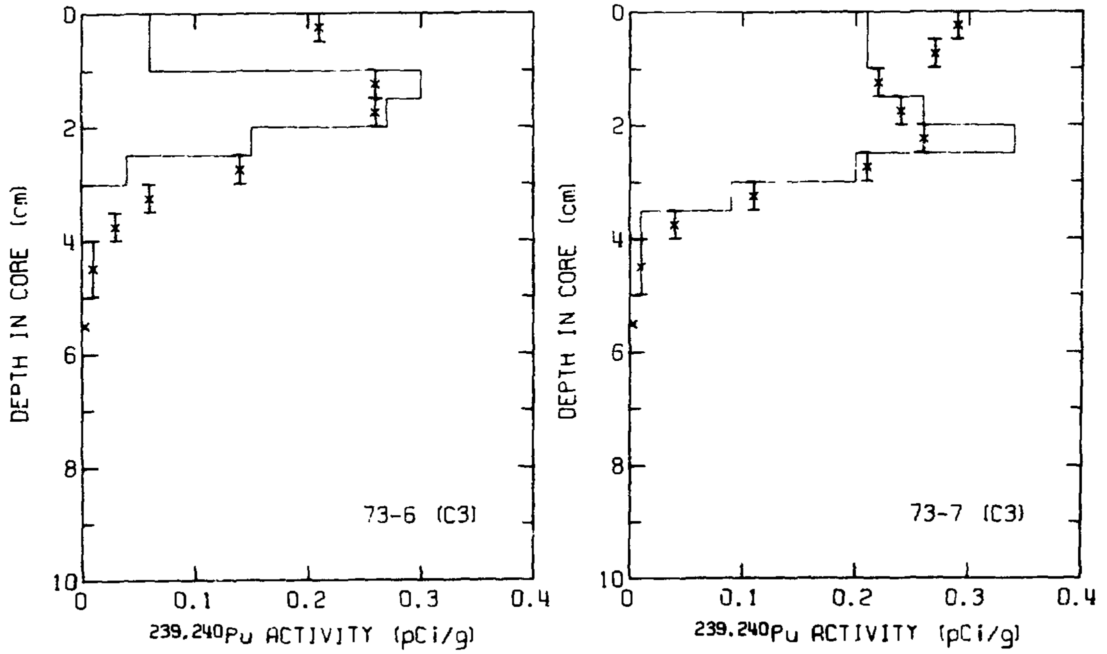
(f) R = 0.05, ω = 10.5, S = 1.0(20), f = 0.31

FIGURE 3 (Contd.)



(g) R = 0.17, ω = 34.3, S = 0,
f = 0.80

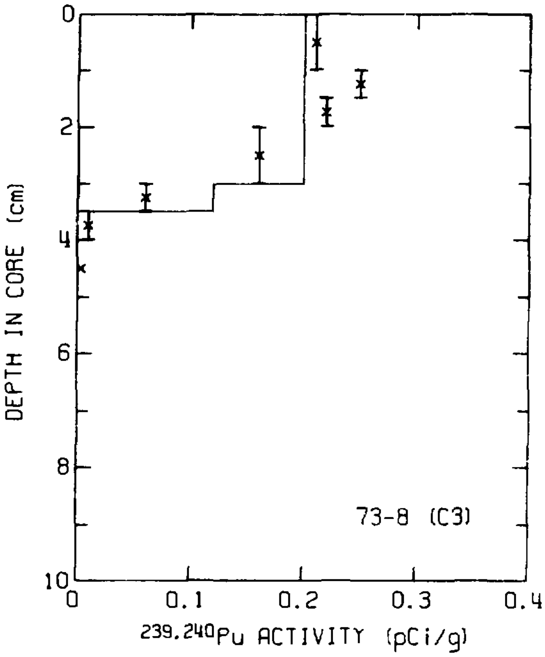
(h) R = 0.18, ω = 31.8, S = 2.0 (14),
f = 1.1



(i) R = 0.17, ω = 32.0, S = 0,
f = 0.65

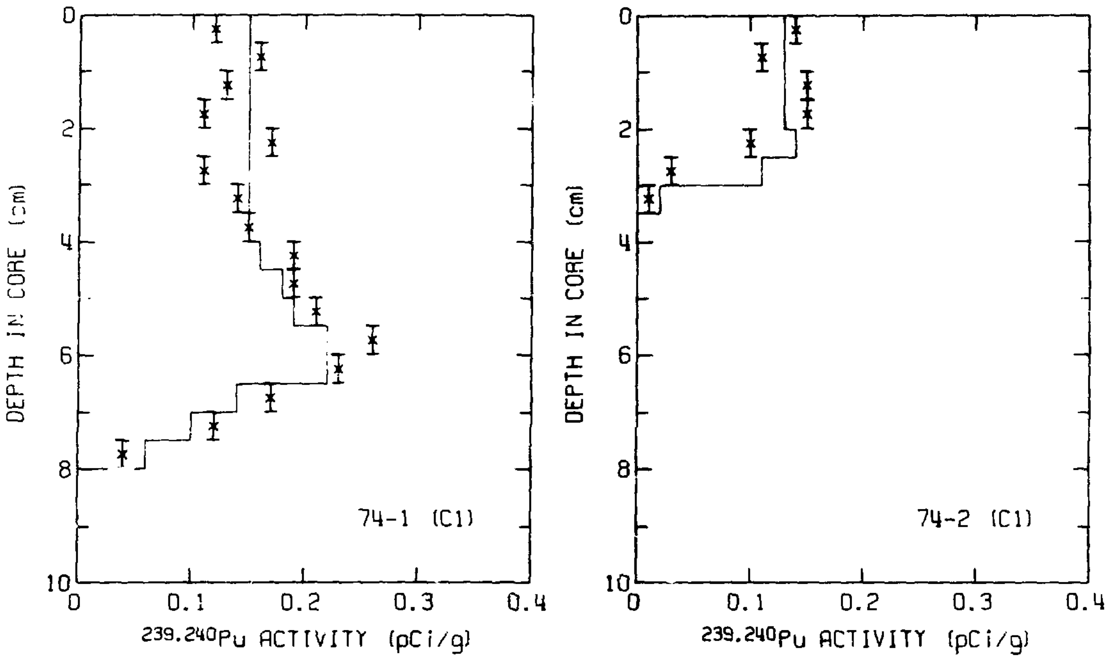
(j) R = 0.15, ω = 28.5, S = 1.5(10),
f = 0.95

FIGURE 3 (Contd.)



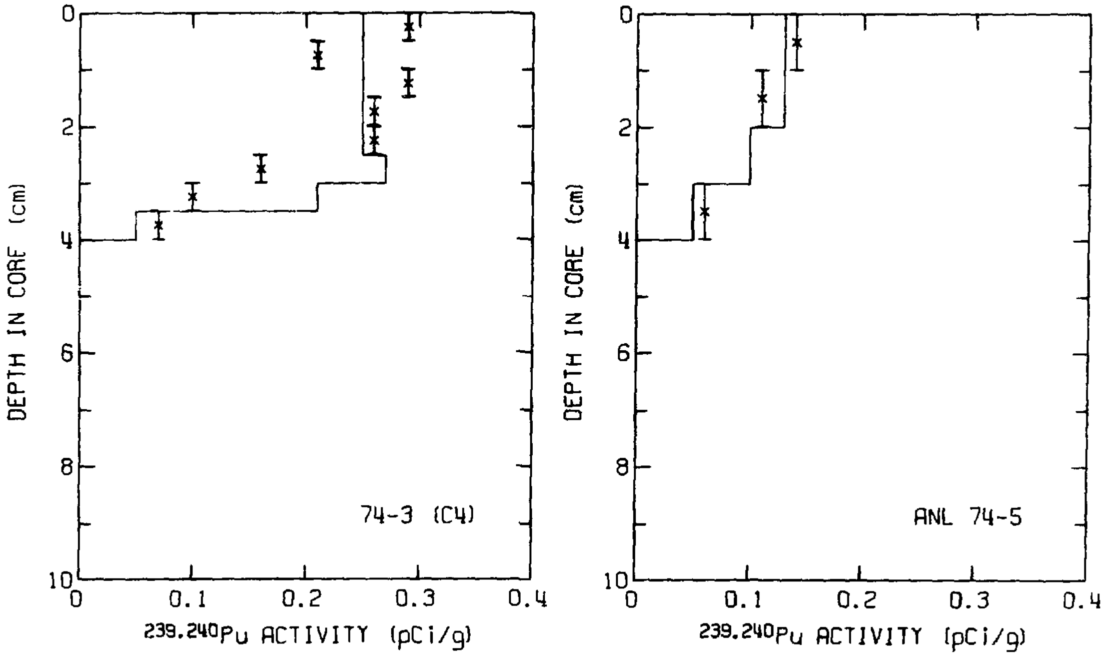
(k) R = 0.06, ω = 8.7, S = 2.0(35),
f = 0.48

FIGURE 3 (Contd.)



(l) R = 0.5, ω = 96.3, S = 4.0(12), f = 2.5

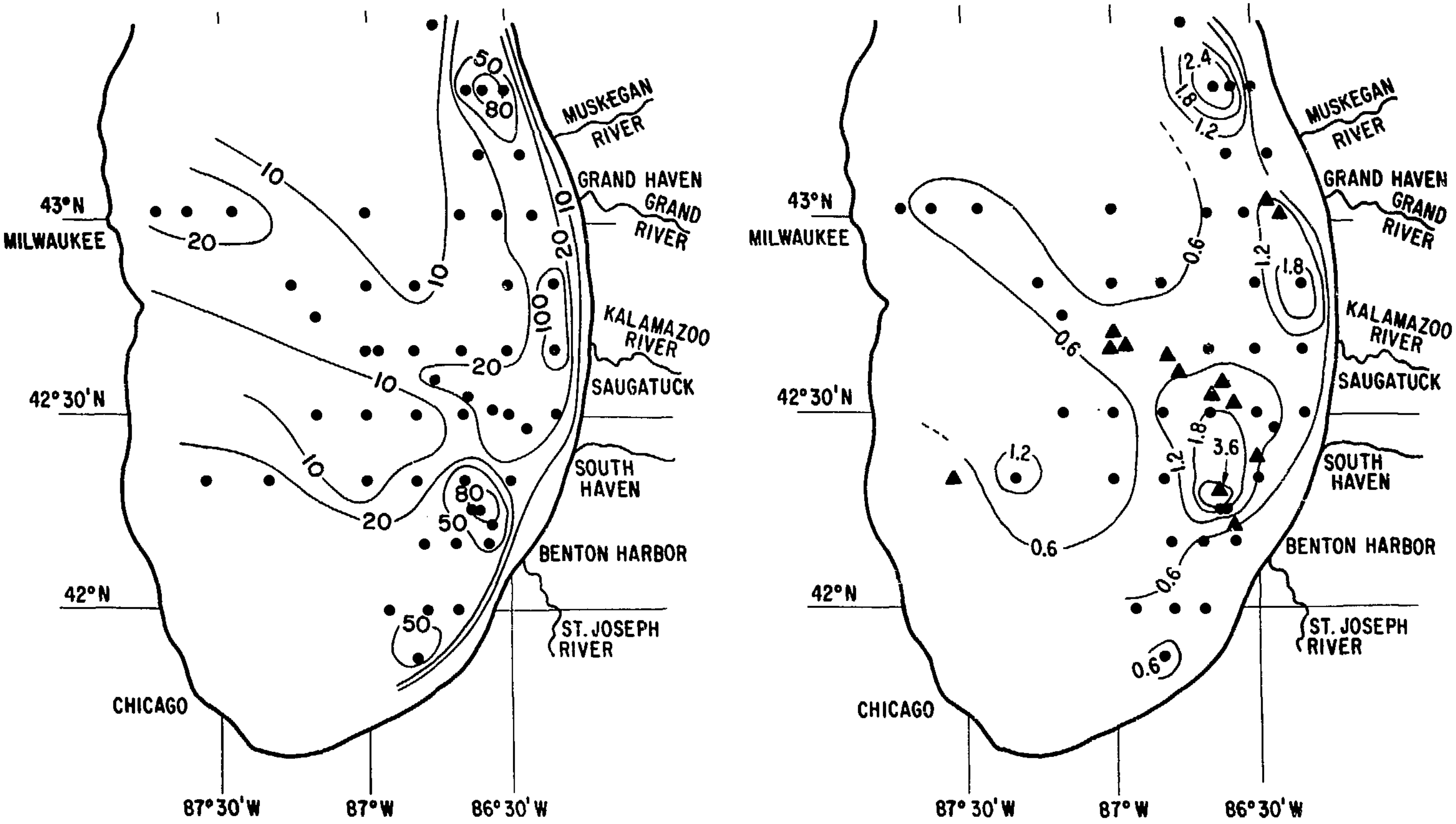
(m) R = 0.10, ω = 23.8, S = 2.0(18), f = 0.61



(n) R = 0.12, ω = 18.8, S = 2.0(25), f = 0.93

(o) R = 0.14, ω = 31.0, S = 2.0(18), f = 0.77

FIGURE 3 (Contd.)



(a) (b)

FIGURE 4. Comparison of the mass sedimentation rate and deposition of plutonium in southern Lake Michigan. (a) Mass sedimentation rate; (b) total distribution of plutonium in terms of the flux multiplier (▲ represents stations where plutonium and ^{137}Cs were measured, and ● where ^{137}Cs was measured alone).