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**THE ECOLOGICAL BEHAVIOR OF PLUTONIUM
AND AMERICIUM IN A FRESHWATER
ECOSYSTEM: PHASE II
IMPLICATIONS OF DIFFERENCES
IN TRANSURANIC ISOTOPIC RATIOS**

Pacific Northwest Laboratories
Richland, Washington 99352

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THE ECOLOGICAL BEHAVIOR OF PLUTONIUM
AND AMERICIUM **IN** A FRESHWATER ECOSYSTEM:
PHASE **II**
IMPLICATIONS OF DIFFERENCES IN TRANSURANIC ISOTOPIC RATIOS

by

Richard M. Emery and Thomas R. Garland
ECOSYSTEMS DEPARTMENT

December 1974

On January 19, 1975, research and development programs of the U.S. Atomic Energy Commission (AEC) became part of the newly formed Energy Research and Development Administration (ERDA). In this report, since it refers to work done in 1974, most references are to AEC programs.

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"Ecological Distribution and Fate of Plutonium and Americium
in a Processing Waste Pond on the Hanford Reservation."

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ABSTRACT

The ecological behavior of Pu and Am in a freshwater processing waste pond has been studied since July 1973 to characterize the pond's limnology and define the isotopic distributions in this ecosystem (Emery et al. 1974). Results from this study show that the history of transuranics discharged to the pond has created a complex combination of source terms and isotopic ratios. Since these source terms and chemical forms entering the pond have not been clearly defined, a material balance for Pu and Am in this ecosystem cannot be developed. Relatively large quantities of ^{238}U have been released to the pond, and these, along with unidentified levels of ^{232}Th and ^{228}Th create a problem of interpreting the ecological behavior of Pu and Am in this ecosystem. Ratios of ^{238}Pu to $^{239,240}\text{Pu}$ found in the pond are much higher than those in the processing wastewaters released to the pond. Ratios of ^{238}Pu to $^{239,240}\text{Pu}$ and ^{241}Am to $^{239,240}\text{Pu}$ are significantly higher in the pond biota than in the sediments, suggesting a common source of availability to the biota. This contention is supported by the rapid establishment of these ratios in goldfish (*Carassius*) which were experimentally introduced into the pond. Ratios of ^{241}Am to ^{238}Pu in the pond biota are also significantly different from those of the sediments but to a lesser degree than ratios of ^{238}Pu to $^{239,240}\text{Pu}$ and ^{241}Am to $^{239,240}\text{Pu}$. A wide range of particle sizes of ^{238}Pu and $^{239,240}\text{Pu}$ may exist in the pond sediments. The pond sediments, however, may not be the major source of "available" Pu and Am because results of this study suggest that sediments in a trench carrying the processing wastes to the pond may be the primary source.

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THE ECOLOGICAL BEHAVIOR OF PLUTONIUM AND AMERICIUM IN A FRESHWATER ECOSYSTEM

PHASE III - IMPLICATIONS OF DIFFERENCES IN TRANSURANIC ISOTOPIC RATIOS

INTRODUCTION

A plutonium (Pu) processing waste pond on the Hanford Reservation has been studied since mid-1973 to characterize the pond's limnology and determine the ecological distribution of Pu and americium (Am) in this freshwater ecosystem. Numerous findings which relate the concentrations of Pu and Am in biotic and abiotic components of the pond to limnological factors are described in an interim report (Emery et al. 1974). In the course of this study it has become apparent that the historical use of the pond for temporary storage of low-level wastes from several processing facilities has created a complex combination of source terms and isotopic ratios. The array of radionuclides in this pond cannot be described as typical for other aquatic systems having similar employment, and for this reason a discussion of the isotopic ratios of the transuranics in biotic and abiotic components of this ecosystem should be useful. The purpose of this report is to complement the descriptive interim report with a discussion of radiochemical factors which must necessarily be considered to develop a thorough understanding of the behavior of transuranics in this ecosystem.

A DESCRIPTION OF U-POND

A comprehensive description of U-Pond is already in print (Emery et al. 1974), but a brief summary of the pond's morphometry and historical use is provided here for the purpose of convenience to the reader.

U-Pond (specifically 216-U-10) was created in a shallow depression in the arid steppe-land of the Hanford region at the beginning of the Manhattan Project in 1944 (Figs. 1 and 2). The major purpose of the pond is to receive low-level rad-wastes from Pu processing and reclamation facilities, a laundry, a uranium recovery plant, and several laboratories. In addition to accidental Pu discharges, the aqueous effluents sometimes carry low-level

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Figure 2. U-Pond and the U-11 Basin (shaded).

fission products (^{137}Cs , ^{90}Sr , ^{106}Ru , ^{155}Eu), activation products (^{60}Co , ^{154}Eu , ^{54}Mn), and actinides (^{238}U , ^{232}Th , ^{241}Am). A few other radioisotopes have been released to the pond at marginally detectable levels. The pond presently exists with a surface area of $56,000 \text{ m}^2$ (14 acres), a volume of $22,700 \text{ m}^3$ (18 acre-ft), and a mean depth of about 0.4 m (1.3 ft). There was a period from 1952 to 1953 when the pond extended over an area of about $120,000 \text{ m}^2$ (30 acres) due to abnormally heavy water discharges from surrounding plant operations.

The water level in U-Pond is now maintained by three major sources. One is from Pu processing operations (234-5 plant) via Z-19 trench, another is from a laundry where protective clothing is cleaned (via U-14 trench), and

the third is cooling water from the evaporator-crystallizer plant (242-S plant) where liquid rad-wastes are reduced to salt cakes (via U-14 trench, Fig. 2). Another trench (Z-11 trench) carried Pu processing waste to U-Pond through the mid-1960's but became excessively contaminated and was subsequently backfilled. It ran parallel to the existing Z-19 trench (Fig. 2). U-Pond has received effluents from the 242-S plant since 1973. The total historic discharge of water into U-Pond is reported as $1.2 \times 10^9 \text{ m}^3$ (3.17×10^{11} gal or 9.7×10^5 acre-ft, Anderson 1973) with a current discharge rate of about $10 \text{ m}^3/\text{min}$ (5.9 cfs).

The reclamation and processing effluents from the 234-5 plant, which carry Pu to the pond, are discharged into Z-19 trench at a point about 885 m (970 yds) above the pond. Processing wastes continuously flow into this open trench, but Pu releases, which are usually at low levels, occur on an intermittent basis. Release records indicate that the total historic discharge of Pu into this trench is about 8.1 kg (Hanson et al. 1973 and Anderson 1973). (There are no release records kept for Am). These records show relatively low-level releases from 1944 to 1953, less than 2 g of Pu released over this period (Fig. 3). (The reliability of sampling and analyses of these early discharges is unknown). From 1953 through 1960 annual releases of Pu were considerably greater, but still amounted to less than 200 g (Fig. 3). A hiatus in the records appeared from 1961 through 1966. During this period (mid-1960's) the first purified ^{238}Pu (produced by the reactor irradiation of ^{237}Np for the SNAP program) was mixed with normal weapons grade ^{239}Pu in the waste discharges. These records also show that in 1967 7.9 kg of Pu (97% of total recorded release) was discharged into the waste trench. Further investigation revealed that the 1967 figure (7.9 kg) represents an accumulative release for a period running from 1959 through 1967. It was during this period that the Z-11 trench was being used to carry processing wastes to the pond. This trench became excessively contaminated with Pu by 1971 and was backfilled. In the remaining years less than 0.1 kg of Pu is reported to have entered the pond by way of Z-19 trench. This trench still remains in use.

Figure 3. Annual levels of Pu released into trenches leading to U-Pond since the start-up of Hanford operations (Hanson et al. 1973 and Anderson 1973). The vertical line at 1964-65 indicates the most likely time when ^{238}Pu was added to the wastes of processing ^{239}Pu . (Det. = detection limit, $<$ = less than).

Although the official figure for total historic Pu discharge into the Z-19 trench is 8.1 kg, some uncertainty exists concerning the accuracy of this value. It is also quite possible that the reported discharge of 8.1 kg of Pu was calculated excessively high because of an unknown amount of ^{238}Pu present in the wastes. Pu separations were probably made but the assay of wastes was done by total alpha count. Thus, from the mid-1960's to date the conversion of Pu activity to weight could cause Pu weight values to be excessively high. There have also been other indications that this estimate is too low, such as the possibility that periodic sampling has missed some higher level discharges, which adds further confusion to the matter. Such uncertainties will cause problems when attempts are made to balance to release of Pu into the pond with estimates of total pond Pu content obtained by sampling.

METHODS

All samples collected for Pu and Am analyses were prepared by drying in either a 105°C drying oven or by a Virtis Unitrap freeze dryer (Model 10-100). The dried samples were packaged and shipped to LFE Environmental Laboratories (Richmond, California) for transuranic analyses. At LFE the isotopes ^{238}Pu , ^{239}Pu + ^{240}Pu (expressed as $^{239,240}\text{Pu}$), and ^{241}Am were analyzed using isotope dilution methods, with high purity ^{236}Pu and ^{243}Am preparations used as tracers. Final measurements were made using alpha spectroscopy methods described by Major et al. (1971), Wessman et al. (1971), and Major et al. (1974).

Sediment samples were taken using a 1/4 ft² Ekman dredge and a coring tube. After a sample of the pond bottom was removed with the dredge, it was subsampled with the coring tube to yield a sediment plug 4.8 cm in diameter, 10 cm deep, with a volume of 0.18ℓ (10.8 in³). Four cores were removed from each dredge sample and placed immediately in aluminum drying pans. The four plugs were mixed and frozen to await processing.

Statistically significant differences of isotopic ratios between sediments and biota were determined using the Chi-square test for independence (Steel and Torrie 1960). All significant differences are expressed at the $\alpha = 0.001$ level unless stated otherwise.

Further details and additional information may be found in a descriptive limnological accounting of U-Pond and the transuranics present in it prepared by Emery et al. (1974).

RESULTS AND DISCUSSION

ACTINIDES ASSOCIATED WITH U-POND

Varying concentrations of weapons grade Pu have been discharged into trenches leading to U-Pond. The three isotopes associated with the production of weapons grade Pu, and assumed to have been present in Pu processing effluents, probably occur in the following proportions (weight percent): 93% ^{239}Pu , 6% ^{240}Pu , 0.6% ^{241}Pu . When considering radio-nuclides on a weight percent basis the ^{238}Pu isotope would have occurred at insignificant levels prior to the early 1960's. The source of ^{241}Am in U-Pond is the ^{241}Pu isotope. On an alpha percent basis these isotopes probably occur as $^{239}\text{Pu} + ^{240}\text{Pu}$ (i.e., $^{239,240}\text{Pu}$) = 98% and ^{238}Pu = 2%. Thus, on an activity basis one would expect a ratio of ^{238}Pu to $^{239,240}\text{Pu}$ in the pond to have been around 0.02. At present the ^{238}Pu to $^{239,240}\text{Pu}$ ratios in the pond are quite different, and a discussion of this difference will appear later. On a weight basis ^{241}Pu would occur at an undetectable level. In terms of weight $^{239,240}\text{Pu}$ comprises at least 98% of all Pu isotopes in the pond.

During the early 1960's fuel elements from power reactors were processed at Hanford. The Pu isolated from this fuel produced an entirely different isotopic ratio than those produced by the processing of weapons grade Pu. Generally, the isotopic composition approximates that of the fuel which will be used to charge fast-breeder reactors. On a weight basis the isotopic portions are about 55% ^{239}Pu , 25% ^{240}Pu , and 15% ^{241}Pu (the remaining 5% composed of ^{242}Pu , ^{243}Pu , and ^{244}Pu). The ratio of ^{238}Pu to $^{239,240}\text{Pu}$ on an activity basis is about 0.3. The quantity of this Pu isotopic mixture that was discharged into U-Pond is unknown.

Production of pure ^{238}Pu began in the mid-1960's at Hanford and has continued intermittently to date. This isotope is made specifically for use in power sources that convert the energy from alpha decay to electrical energy such as SNAP devices and pacemakers. To produce ^{238}Pu , ^{237}Np is separated and purified during normal fuels reprocessing and reirradiated in a reactor, producing ^{238}Pu . Since the specific activity of ^{238}Pu is about 270 times that of ^{239}Pu , a very small quantity of ^{238}Pu , in terms of weight, will contribute a proportionally large fraction of the total alpha activity in a mixture of ^{239}Pu and ^{238}Pu . Most of the routine monitoring of liquid effluents from processing plants in the 200 Areas is done on the basis of total alpha counts, so actual amounts of the isotopic components of Pu processing wastes are not determined. For this reason it is difficult, if not impossible, to compare isotopic ratios and quantities of Pu found in U-Pond to those released from refinement operations.

Substantial quantities of ^{241}Am are also found in U-Pond. The source of all ^{241}Am in refinement operations is from the beta decay of ^{241}Pu . (Routine sampling does not normally detect ^{241}Pu since its maximum beta energy is about 0.02 mev.). Because there is some ^{241}Am separated in the processing of Pu, there are actually two sources of ^{241}Am to the pond; one is the separated ^{241}Am which is generated from Pu processing, the other is ^{241}Am which "grows" continuously from the beta decay of ^{241}Pu . The maximum ratio of ^{241}Am to $^{239,240}\text{Pu}$ occurs about 68 years after the time of separation. Figure 4 shows the ratio of ^{241}Am to $^{239,240}\text{Pu}$ as a function of time for the two assumed isotopic sources of Pu discussed above. Particularly evident here is the effect of the content of ^{241}Pu (mass percent) present in reactor grade effluents on the maximum ratios of ^{241}Am to $^{239,240}\text{Pu}$. This relative difference in ^{241}Pu content between the two isotopic mixtures causes the ^{241}Am to $^{239,240}\text{Pu}$ ratios of reactor grade Pu to occur at least an order of magnitude higher than those of weapons grade Pu.

A source of other radionuclides in U-Pond was a uranium processing plant which operated from 1953 to 1957. This plant added very large quantities of ^{238}U , about 1400 kg (3000 lbs, Anderson 1973), in addition

Figure 4. Changes of $^{241}\text{Am} : ^{239}, ^{240}\text{Pu}$ ratios with time for two isotopic mixtures of Pu.

to unknown quantities of ^{232}Th and ^{228}Th during its operation. Processing and purification of several batches of Th fuel elements, used for the production of ^{233}U , could have released both ^{232}Th and ^{228}Th . An alternative source of ^{228}Th is from the decay of ^{232}U , which is found in the ^{233}U product as an impurity. Levels of these isotopes in the pond have not been determined.

If the 1400 kg of ^{238}U , the recorded discharged quantity through 1966, were evenly distributed across the pond's bottom to a depth of 10 cm the average concentration in the pond sediment would be about 170 μg of $^{238}\text{U}/\text{g}$ of sediment. Levels of ^{238}U measured in 51 samples of U-Pond sediment (down to 10 cm) show a mean concentration of 647 $\mu\text{g}/\text{g}$ (range of 70 to 2300 $\mu\text{g}/\text{g}$) or about 216 pCi of $^{238}\text{U}/\text{g}$ dry weight of sediment. This ^{238}U content in the sediments amounts to about four times more ^{238}U than the recorded discharge into the pond system would allow. At present there are no explanations for this difference. Whichever the case, this level of U in the pond becomes a matter of concern when attempting to interpret the ecological behavior of Pu or Am in this ecosystem. Since U is more mobile than Pu in aquatic systems and is also toxic to many organisms (Bowen 1966), determinations of the behavior of Pu or Am in this pond could be impaired by superimposed chemical and possibly radiological effects of ^{238}U on biota.

Concerns over the presence of Th in the pond, particularly ^{228}Th , is primarily due to the fact that ^{228}Th plus its daughters can bias the analytical determination of ^{238}Pu in a way to cause the levels to appear higher than they actually are. However, procedures used for Pu analysis have taken the levels of Th into account, and values of Pu have been corrected for the presence of Th.

Another matter of considerable importance is the noncontinuous nature in which Pu and Am are accidentally discharged into the pond. The complexity of interpretation problems is increased by not having sufficient historical or current discharge records to permit Pu and Am budgets for the pond. Highly variable levels of Pu and Am in aqueous Pu processing wastes prohibit reliable daily income calculation. For example, there are indications that from December 1973 to June 1974 the total alpha concentration in Pu processing

waste effluents (unknown ratios of ^{238}Pu to $^{239,240}\text{Pu}$ and ^{241}Am to $^{239,240}\text{Pu}$) varied by five orders of magnitude. The lower limit of "soluble" Pu and Am detection for these total alpha analyses is about 200 pCi/l which implies that potentially 2×10^8 pCi of soluble Pu and/or Am per day could be entering U-Pond without detection. This computation is based on a mean flow of the Z-19 trench of about $865 \text{ m}^3/\text{day}$ (Emery et al. 1974). The detection limit for particulate forms ($>0.45\mu$) is about 1 pCi/l using the total alpha technique, but the average quantity of particulate Pu and/or Am present in aqueous Pu processing wastes during the first 6 months of 1974 has been estimated at about 100 pCi/l or 1×10^8 pCi/day. Over a period of several weeks quantities of particulate Pu and Am in these wastes can vary by several orders of magnitude.

CHEMICAL FORMS OF ISOTOPES IN AQUEOUS WASTES

The only information concerning the chemical forms of Pu and Am in aqueous Pu processing wastes are extrapolations of forms generated in the processing plants. These include Pu and Am oxides, metals, nitrates, polymers, hydroxides, and organic complexes. The U present in the pond was probably discharged primarily of UO_3 , U_3O_8 , or $\text{UO}_2(\text{NO}_3)_2$.

LEVELS OF TRANSURANICS OCCURRING IN THE POND

Levels of Pu and Am which are present in the pond system have already been discussed in detail (Emery et al. 1974), and this report will not attempt to review these numerous findings. When the ecological behavior of Pu and Am in U-Pond is considered holistically the complexity of this ecosystem, from a chemical point of view, appears to be prohibitive to the understanding of the pond's radiochemical dynamics. Because the source terms and chemical forms of the actinides entering and present in the pond cannot be clearly defined, it is important to be realistic about the limitations to which the data generated by this study may be used. It is now clear that a material balance for Pu or Am between levels found in the pond and those entering and leaving the pond cannot be developed. This is true because the present inventory is based on a "total alpha, worst case" basis where no delineation of ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am isotopes is made. Of prime importance here is the fact that transuranic inputs were made at the

head end of an 885 m waste trench (Z-19 trench, Fig. 2). . No measurement of the loss of Pu and Am in this trench has been made, but a rough comparison of total alpha counts per liter of wastewater discharged during the first 6 months of 1974 with measured levels in the pond water during the early part of 1974 shows that most of the discharged Pu and Am does not reach the pond.

Adding further complexity to the problem of making ecological interpretations of the Pu and Am values in U-Pond is the existence of comparatively high levels of U in the pond sediments. The presence of these levels of U could influence the ecological behavior of Pu and Am in a unique way, possibly by way of chemically toxic effects on the biota.

All of these limitations in the application of the Pu and Am data for U-Pond are considered along with one additionally perplexing factor, the problem of determining the ecological availability of these transuranics. Until more is understood about the ecological dynamics of Pu and Am, any expression of availability will be less than accurate. The U-Pond system must be evaluated without accurate source terms for these transuranics. Internal turnover and cycling rates for Pu and Am are unknown in this pond which has a water retention time of about 40 hours. Thus, without accurate input-output information and knowledge of internal cycling, attempts to establish levels of availability or bases upon which to develop concentration factors or rates of exchange are essentially without meaning.

Although all of these concerns place obvious limitations on the degree to which the Pu and Am data may be synthetically developed, there are some considerations, additional to those discussed by Emery et al. (1974), which remain valid. These matters involve the relative differences between ratios of Pu and Am in biota to those in the sediments of the pond.

ISOTOPIC RATIOS OCCURRING IN U-POND

If ratios of ^{238}Pu to $^{239,240}\text{Pu}$ and ^{241}Am to $^{239,240}\text{Pu}$ which occur in U-Pond biota are compared to those occurring in the sediments, it is obvious that there are significant differences (Figs. 5 and 6). . In both cases the ratios of these isotopes are greater in the biota than in the

Figure 5. Ratios of $^{238}\text{Pu} : ^{239, 240}\text{Pu}$ in U-Pond sediments and biota. The ratio of $^{238}\text{Pu} : ^{239, 240}\text{Pu}$ is 1.91:1 in interstitial water and 3.5:1 in water (n = 3 in both cases).

Figure 6. Ratios of $^{241}\text{Am} : ^{239,240}\text{Pu}$ in U-Pond sediments and biota. The ratio $^{241}\text{Am} : ^{239,240}\text{Pu}$ is 0.67:1 in interstitial water and 540:1 in water ($n = 3$ in both cases).

sediments. The frequency histograms in Figs. 5 and 6 serve to show not only the differences in the distribution of these ratios in biota and sediments, but the consistency with which these ratios in all four divisions of the biota occur for both ^{238}Pu to $^{239,240}\text{Pu}$ and ^{241}Am to $^{239,240}\text{Pu}$. Such an array of these ratios could suggest that the ^{238}Pu and ^{241}Am isotopes are being solubilized from the sediments at a faster rate than the $^{239,240}\text{Pu}$ isotope, and some fraction of these soluble isotopes are being taken up by the biota before it is carried to the pond basin by the rapid downward movement of the pond water mass. These results might also suggest that the ^{238}Pu and ^{241}Am isotopes are being discharged from Pu processing operations in forms which are more available to the biota than the $^{239,240}\text{Pu}$ isotope. Another possible explanation is that the sampling and processing of the sediment caused a fractionation of the ^{238}Pu and $^{239,240}\text{Pu}$ isotopes. This could be possible if $^{239,240}\text{Pu}$ isotopes are present in larger particulate forms than ^{238}Pu . A final possibility is that the physiological processes occurring in all of the biota could provide a mechanism for selecting ^{241}Am over $^{239,240}\text{Pu}$, but this consideration would not explain the relatively higher ratios of ^{238}Pu to $^{239,240}\text{Pu}$ occurring in these biota. In view of the rapid exchange rate of pond water it seems unlikely that the pond sediments could contribute significant amounts of "soluble" Pu or Am to the biota. Since the biota appear to have ^{241}Am to $^{239,240}\text{Pu}$ and ^{238}Pu to $^{239,240}\text{Pu}$ ratios that do not vary greatly with time, it appears that there is some consistent source which remains available to the biota over extended time periods. On the basis of data already obtained, a likely source is the sediments of Z-19 trench where Pu and Am have been deposited for many years, and the general direction of movement of the solubilized material is horizontal and toward the pond.

With regard to the accumulation of these ratios in biota, one additional interesting point involves experimental goldfish (*Carassius*) which were imported from Arkansas and used for an in situ uptake experiment. This experiment was performed by isolating the Arkansas goldfish in cages that provided access to the bottom sediments. Within 2 weeks after these goldfish were placed in the pond they developed ratios of ^{238}Pu to $^{239,240}\text{Pu}$

and ^{241}Am to $^{239,240}\text{Pu}$ which were similar to those of the endemic pond biota and clearly higher than those of the sediments. This indicates a common source of "available" Pu and Am, but does not provide a basis to determine whether these ratios reflect a source from daily discharges with specific isotopic mixtures or a source from the sediments where these ratios are produced by weathering. Once again it is worth suggesting that physiological processes may have an influence on the isotopic ratios occurring in biota. These processes may occur within the organisms being analyzed for Pu and Am or may be carried out by microorganisms in the sediments which have created these "available" ratios of Pu and Am by their own metabolic activities (i.e., "biological weathering").

Ratios of ^{241}Am to ^{238}Pu occurring in U-Pond sediments were also significantly different from those in the biota (Fig. 7); however, these differences were not as striking as the differences occurring with ^{238}Pu to $^{239,240}\text{Pu}$ and ^{241}Am to $^{239,240}\text{Pu}$ ratios. It is interesting to note that while the medians and means of ^{241}Am to ^{238}Pu ratios ranged from about 0.6 to 1.0 for sediments, invertebrates, and goldfish there were no occurrences of such ratios in plant material. Ratios of ^{241}Am to ^{238}Pu that were found in plant material (macrophytes and algae inclusive) fell on either side of the medians and means for the other four divisions of the pond's ecosystem (i.e., sediments, insect larvae, noninsect invertebrates, and goldfish; Fig. 7).

When the pond sediments are sampled repeatedly in the same location over a short time interval, a substantial variation in the concentrations of ^{238}Pu and $^{239,240}\text{Pu}$ is observed. This may indicate the particulate nature of Pu which occurs in these sediments. Since the Pu and Am which actually reach the pond must first travel 885 m down a discharge trench with relatively little current, very large particles of these elements would be expected to settle out before reaching the pond, assuming their density is around 10. It is possible to estimate a maximum particle size occurring in the discharge by assuming that PuO_2 is the chemical form present in the waste effluents. Calculated levels of activity relative to the particle sizes of PuO_2 for the ^{238}Pu and $^{239,240}\text{Pu}$ isotopes are shown in

Figure 7. Ratios of $^{241}\text{Am} : ^{238}\text{Pu}$ in U-Pond sediments and biota. The ratio $^{241}\text{Am} : ^{238}\text{Pu}$ is 0.40:1 in interstitial water and 154:1 in water (n = 3 in both cases).

Table 1. When the maximum concentration of ^{238}Pu found in the sediments is considered, and it is assumed that all alpha activity comes from one particle of $^{238}\text{PuO}_2$, it can be shown that the maximum particle size of any $^{238}\text{PuO}_2$ sampled is less than 4μ . It is unlikely that only one particle of PuO_2 exists in each sample but it is worth noting that a small change in particle dimension (i.e., by a factor of 2) makes a large change in the activity (i.e., by a factor of about 8) of an individual particle. Therefore, there may be a substantial range in the size of ^{238}Pu and $^{239,240}\text{Pu}$ particles existing in the pond sediments which could explain the wide range of Pu concentrations found by repetitive sampling of the sediments.

Table 1. A comparison of activity per particle to particle sizes of $^{238}\text{PuO}_2$ and $^{239,240}\text{PuO}_2$ (assuming a cube-shaped particle with density of 10.0).

pCi/ Particle	Size of $^{238}\text{PuO}_2$ (Diameter- μ)	Size of $^{239,240}\text{PuO}_2$ (Diameter- μ)
10^6	18.0	112
10^5	8.3	52
10^4	3.9	24
10^3	1.8	11.2
10^2	0.83	5.2
10^1	0.39	2.4
1	0.18	1.12
0.1	0.083	0.52
0.01	0.039	0.24
0.001	0.018	0.112
0.0001	0.0083	0.052
0.00001	0.0039	0.024

$$^{238}\text{PuO}_2 \mu \text{ diameter} = 10^4 \times \left(\frac{\text{pCi} \times 2.22}{3.862 \times 10^{13} \times 10} \right)^{1/3}$$

$$^{239,240}\text{PuO}_2 \mu \text{ diameter} = 10^4 \times \left(\frac{\text{pCi} \times 2.22}{1.58 \times 10^{11} \times 10} \right)^{1/3}$$

Since the input of Pu and Am to U-Pond has been intermittent over a long period, it is not possible to calculate precisely what the ^{241}Am to $^{239,240}\text{Pu}$ ratio should be. However, most of the U-Pond sediments sampled have ratios that are greater than the expected maximum for weapons grade Pu (i.e., about 0.26), thus providing evidence that there are other sources of ^{241}Am . There is the possibility that $^{239,240}\text{Pu}$ is selectively leached downward in the U-Pond basin leaving the surface sediments with relatively higher levels of ^{241}Am , but the environmental translocation of ^{241}Am is likely more rapid in soils and sediments than $^{239,240}\text{Pu}$, which tends to negate the preceding possibility.

CONCLUSIONS

With all foregoing considerations taken into account, the following conclusions, although tentative in nature, may be drawn about the actinide isotopes and ratios which are present in U-Pond.

1. Because the source terms and chemical forms of actinides entering and in U-Pond cannot be clearly defined, a material balance for Pu and Am between levels found in the pond and those entering and leaving the pond cannot be developed.
2. About 1400 kg of ^{238}U have been discharged into waste trenches leading to U-Pond. These high levels of U, along with potential quantities of other unknown isotopes, become a matter of concern when attempting to interpret the ecological behavior of Pu and Am in this ecosystem because of the potential toxicity of these elements.
3. Although weapons grade Pu processing operations should have discharged wastes containing ratios of ^{238}Pu to $^{239,240}\text{Pu}$ of about 0.02, these ratios in the pond sediments are much higher, about 1.0, indicating the contribution of ^{238}Pu production processing after the early 1960's.
4. Ratios of ^{238}Pu to $^{239,240}\text{Pu}$, and ^{241}Am to $^{239,240}\text{Pu}$ are significantly higher in the pond biota than in the pond sediments. These

results primarily indicate that transuranics are being made "available" and/or utilized by pond organisms in ratios which are not reflected by pond sediment concentrations.

5. A common source of "available" Pu and Am for pond biota is suggested by the rapid establishment of ^{238}Pu to $^{239,240}\text{Pu}$, and ^{241}Am to $^{239,240}\text{Pu}$ ratios in imported goldfish. Within 2 weeks after these fish had been introduced into the pond they had accumulated transuranic ratios which were similar to those of all other pond biota and dissimilar to those of the pond sediment.
6. Ratios of ^{241}Am to ^{238}Pu in U-Pond biota are significantly different from those of the sediments but to a lesser degree than ratios of ^{238}Pu to $^{239,240}\text{Pu}$ and ^{241}Am to $^{239,240}\text{Pu}$. In particular, ratios of ^{241}Am to ^{238}Pu in plant material were different from those of sediments, invertebrates, and goldfish in that they fell either below or above the means and medians for the other four categories of the pond's ecosystem.
7. Sampling of U-Pond sediments done frequently in the same location shows a substantial range in ^{238}Pu and $^{239,240}\text{Pu}$ concentrations. This may be due to a wide range in Pu particle sizes existing in U-Pond sediments.
8. Considering the rapid exchange rate of water in U-Pond (40 hours) and other foregoing conclusions, it is possible that the source of Pu and Am which is "available" to the pond biota is not the U-Pond sediments, but the sediments of the Z-19 trench.

REFERENCES

- Anderson, J. D. 1973. Radioactive Liquid Wastes Discharged to Ground in the 200 Areas During 1972. Doc. No. ARH-2757, Atlantic Richfield Hanford Co., 130 pp.
- Bowen, H. J. M. 1966. Trace Elements in Biochemistry. Academic Press, Inc. (London) Ltd.
- Emery, R. M., D. C. Klopfer and W. C. Weimer. 1974. The Ecological Behavior of Plutonium and Americium in a Freshwater Ecosystem: Phase I, Limnological Characterization and Isotopic Distribution. BNWL-1867, Battelle, Pacific Northwest Laboratories, Richland, Washington, 76 pp.
- Hanson, G. L., J. D. Anderson, G. R. Kiel, B. J. McMurray, and N. P. Nisick. 1973. Input and Decayed Values of Radioactive Liquid Wastes Discharged to the Ground in the 200 Areas through 1971. Atlantic Richfield Hanford Co., Doc. No. ARH-2761, p. 41.
- Major, W. J., K. D. Lee, R. A. Wessman and L. Leventhal. 1971. Rapid Dissolution of Large Soil Samples for ^{239}Pu and ^{241}Am Analysis. TLW-6102, 17th Annual Bio-Assay and Analytical Chemistry Meeting, Boulder, Colorado, October 13-14, 1971.
- Major, W. J., K. D. Lee and R. A. Wessman. 1974. Analysis of ^{238}Pu and ^{241}Am in Larger Size Bovine Samples. TLW-6124, presented at the 12th Annual Conference on Bioassay, Environmental and Analytical Chemistry, Cincinnati, Ohio, Sept. 24-25, 1974.
- Steel, R. G. D. and J. H. Torrie. 1960. Principles and Procedures of Statistics. McGraw-Hill Book Company, Inc., New York, pp. 370-373.
- Wessman, R. A., W. J. Major, K. D. Lee, and L. Leventhal. 1971. Commonality in Water, Soil, Air, Vegetation, and Biological Sample Analysis for Plutonium. TLW-6098, Environmental Plutonium Symposium, University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, August 4-5, 1971.

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