# ACTINIDE BEHAVIOR IN A FRESHWATER POND*

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Abstract - Long-term investigations of solution chemistry in an alkaline freshwater pond have revealed that actinide oxidation state behavior, particularly that of plutonium, is complex. The Pu(V,VI) fraction was predominant in solution, but it varied over the entire range reported from other natural aquatic environments, in this case, as a result of intrinsic biological and chemical cycles (redox and pH-dependent phenomena). A strong positive correlation between plutonium (Pu), but not uranium (U), and hydroxyl ion over the observation period, especially when both were known to be in higher oxidation states, was particularly notable. Coupled with other examples of divergent U and Pu behavior, this result suggests that Pu(V), or perhaps a mixture of Pu(V,VI), was the prevalent oxidation state in solution. Observations of trivalent actinide sorption behavior during an algal bloom, coupled with the association with a high-molecular weight (nominally 6000-10,000 mol. wt) organic fraction in solution, indicates that solution-detritus cycling of organic carbon, in turn, may be the primary mechanism in amercium-curium (Am-Cm) cycling. A significant difference in observed behavior between Am and Cm (25:1 in sediment-water exchange) is believed to be attributable to anthropogenic influences. Sorption by sedimentary materials appears to predominate over other factors controlling effective actinide solubility and may explain, at least partially, the absence of an expected strong positive correlation between carbonate and dissolved U. Long-term studies of several labelled natural ecosystems, coupled with laboratory research to resolve questions of system redox effects on actinide oxidation states and sorption specificity of characteristic sorbents, will be

required before accurate predictions on the principal mechanisms controlling the biogeochemical behavior of the thorium-curium series, so important in nuclear fuel cycles, can be made.

# INTRODUCTION

The physicochemical behavior of both naturally occurring and nuclear-fuel-cycle-produced actinide elements in aqueous systems is of considerable interest from both a purely scientific and a practical public health standpoint (Bondietti et al. 1979, Larsen and Oldham 1978, Murray and Avogadro 1979, Langmuir 1978, Stenstrand et al. 1979, and Wahlgren et al. 1977b). While the chemistry of the actinides, particularly the thorium-curium (Th-Cm) subgroup, is well understood at the laboratory scale, relatively little is known about solution chemical behavior at potential environmental levels ($<10^{-11}$ $\underline{M}$ for plutonium, for example) which are many orders of magnitude less than those used in laboratory studies. Investigators have generally been forced to make predictions about transuranic behavior, based either on naturally occurring lanthanide or actinide analogues or on limited data from studies on nuclear weapons fallout into the oceans and the U.S. Great Lakes. They have been hampered by the extremely low fallout concentrations present ($\sim 10^{-18}$ $\underline{M}$ for plutonium) and have further recognized that the patterns observed may not apply to those from other anthropogenic sources (Alberts et al. 1977).

Research on behavior of actinides associated with nuclear fuel cycle sources is also limited by a number of factors, although higher concentrations and a more varied assemblage of isotopes are generally present. Researchers are usually presented with nonequilibrium conditions caused by discharges which may vary considerably with time or with complex sources containing considerable quantities of pollutants

and other chemical constituents associated with processing, waste treatment, etc., which make interpretation of results difficult (Emery et al. 1974, 1978; Kuzo et al. 1978; Murray and Avogadro 1979; Nelson and Lovett 1978; and Pentreath and Lovett 1978). Consequently, the form in which actinides entered the aquatic environment is often important to these nonequilibrium systems. It would be ideal to study an equilibrium system in which interfering pollutants or chronic inputs are absent, but one which contains relatively high concentrations of a wide variety of actinides originally derived from a nuclear fuel cycle source.

For several years, we have studied the distribution and behavior of a varied assemblage of actinides in the water, sediment, and biota in a system which appears to fulfill most of the criteria described above. The system is Pond 3513, the former final low-level radioactive waste settling basin of Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee at 35°55'N, USA (Cowser et al. 1958). The ultimate objective of this research is the development of additional predictive capability on the biogeochemical behavior of actinides which are important radiological constituents of wastes from nuclear fuel cycles (isotopes of U, Pu, Am, and Cm). This paper will discuss results of research on solution chemistry and sediment characteristics of the system.

The surface sediments in ORNL Pond 3513 are a relatively thick [(>20 cm, except in areas of scour, Tamura et al. 1977)], homogeneous mixture of materials which were used or produced in the lime-soda-clay waste treatment process (Cowser and Tamura 1963, Cowser et al. 1966):

primarily grundite™ (produced by the Illinois Clay Products
Company, Joliet, Illinois, containing 65 to 75% illite, 10 to 20%
kaolinite, and 5 to 15% quartz), calcium carbonate, magnesium hydroxide
(originally), and magnesium basic carbonate. Autochthonous organic
matter (primarily derived from aquatic vegetation) contributed a
moderate organic content (7 ± 2% loss on ignition) to surficial
sediments. For purposes of discussion, the system is now a freshwater
pond, square in outline ($4 \times 10^3$ $m^2$ surface; 1-m mean depth),
steeply trapezoidal in cross section, with a low degree of bottom
relief, and with a relatively slow turnover ($\geq 2$ y) now due solely to
rainwater flow-through.

For several years following the retirement of ORNL Pond 3513 as a
waste effluent settling basin, and preceding our studies, the system
was subjected to a more rapid turnover by rainwater runoff (now
prevented by a weir at the pond outlet). As a consequence, and because
low-level process waste prior to treatment had essentially the same
chemical composition as Laboratory tap water (Cowser et al. 1966),
residual biological effects from nonradiological constituents of former
waste effluents were expected to be minimal. The diverse assemblage of
aquatic invertebrates (over 30 taxa of insects, including two caddisfly
and one mayfly species) supported this assumption. ORNL Pond 3513 may
be characterized as eutrophic with a mixed phytoplankton (Hutchinson
1967). benthic filamentous algae and submerged macrophytes are
seasonably abundant; the pond is fringed by an approximately 1-m-wide
strip of dense emergent vegetation (Typha, Juncus, and Eleocharis).

## METHODS

### Water sampling

Paired water samples were collected near the surface and at a depth of 1 m at a fixed location near the center of ORNL Pond 3513. Sampling frequency over the period of observation (9 March 1977 to 27 May 1982) is indicated on later tables and figures of data. Water was collected with a 2.2-liter Beta Plus● Water Sampler (Wildco 1920H, Wildlife Supply Company, Saginaw, Michigan, USA), transported in polyethylene bottles and then immediately filtered through 0.22-μm pore-size membrane filters in a Millipore● apparatus.

### Radioanalytical procedures for water samples

One-liter aliquots for radiochemical analysis were spiked with appropriate standards ($^{232}U$, $^{237}U$, $^{236}Pu$, $^{242}Pu$, and $^{243}Am$), evaporated, and organic matter destroyed with 8 $\underline{M}$ $HNO_3$ and $H_2O_2$ (plutonium valence adjusted to IV). In cases where the plutonium oxidation state distribution was desired, water samples received valence-adjusted Pu spikes (IV) or (V,VI) and then were subjected to $BiPO_4$ precipitation for Pu oxidation-state separation prior to $HNO_3$ $H_2O_2$ treatment (see companion paper by Bondietti et al.). Conventional ion exchange separation (Dowex 1) of Am, Cm, Pu, and $^{233,234}U$ was carried out after resin loading for the 8 $\underline{M}$ $HNO_3$ solution. Americium and curium were co-precipitated with $CaF_2$ in the column eluate, extracted into a quaternary amine (Moore 1966), and then re-extracted in TTA-xylene for mounting on counting discs. Individual isotopes were

then determined by alpha spectrometry (Reynolds and Scott 1975, Scott and Reynolds 1975). Total uranium was analyzed by a fluorimetric method (Centanni et al. 1956).

## Physicochemical determinations on water samples

Temperature, pH, and dissolved oxygen were measured in the field at the time of collection. Hydrogen-ion was determined with an Orion Model 401 pH meter (Orion Research Inc., Cambridge, Massachusetts, USA). Dissolved oxygen was initially determined by a modified Winkler procedure described in Standard Methods (1975), but during most of the observation period, oxygen concentrations and temperature were obtained with a polarographic sensor-thermistor probe (YSI Model 57, Yellow Springs Instrument Co., Yellow Springs, Ohio, USA).

Cation concentrations were determined by atomic absorption spectrophotometry: flame aspiration for Na, K, Mg, Ca, and flameless technique for Fe, Mn, and Zn (2100 HGA Graphite Furnace) with a Perkin-Elmer Model 503 instrument (Perkin-Elmer Corporation, Norwalk, Connecticut, USA). Dissolved organic carbon concentration was obtained by the combustion-infrared method, alkalinity by the titrimetric procedure, and F ion by the electrode method (Standard Methods 1975). Remaining anions and silica were obtained by colorimetric procedures using a Technicon Auto-Analyzer II [a] (Technicon Instruments Corporation, Tarrytown, N.Y., USA).

## Ultrafiltration and gel-filtration chromatographic experiments

Ultrafiltration of selected samples was accomplished with 10,000-mol. wt (PM-10) and 500-mol. wt (UM-05) membranes in a 2-liter

high output cell (2000 B) (Amicon Corporation, Lexington, Massachusetts, USA). Gel-filtration chromatographic separation of organic fractions in water was conducted initially with Sephadex® G-15 (5- x 100-cm column) using 254 nm UV absorption-recording spectrophotometry equipment (Pharmacia Corporation, Piscataway, New Jersey, USA) to monitor organic content. Later, Bio-Gel® P-6 polyacrylamide gel (Bio-Rad Laboratories, Richmond, California, USA) was substituted to overcome apparent losses of material by gel adsorption. Elution buffer for all gel-filtration experiments was $2 \times 10^{-3}$ $\underline{M}$ NaHCO$_3$ (pH 9) in distilled water. Void volume of the Sephadex® column was determined with Blue Dextran® (Pharmacia) and of the Bio-Gel® column with equine ferritin in 0.5% NaCl.

## Sediment sampling and radioanalysis

Sediment was collected on 9 March 1978 (month 14) at 24 stations set out on a 10-m grid. Samples were taken with a 15- x 10- x 23-cm Ekman box sediment sampler (Wildco 196T). A 0.3-kg subsample (0-5 cm depth) was removed from the center of each box sediment sample, homogenized, and divided for radiological analysis, determination of organic content, and frozen storage. Sediment was then leached sequentially with boiling 8 $\underline{M}$ and 1 $\underline{M}$ HNO$_3$. Leachates were combined and analytical procedures from this point were identical to those described previously for water samples. Loss on ignition of a subsample ($\geq$500 C for 16 h) was used to represent organic content. Selected sediment (and biota) samples were isotopically analyzed for uranium and plutonium by resin bead ion exchange using a tandem high abundance sensitivity mass spectrometer (Walker et al. 1974).

## Sediment anaerobiosis experiment

Two water-tight, 500-liter Plexiglas™ columns were inserted side-by-side into the sediments at the approximate center of Pond 3513. The walls of the columns (enclosures) reached above the water line, and the enclosures were open to the atmosphere. One enclosure was dosed with sucrose to produce anaerobic conditions (treatment date 9 May 1980; month 44); the other served as a control. Surficial sediments to a depth of 10 cm were thoroughly stirred and mixed with the water column before the treatment was applied. Water samples were collected at appropriate time intervals over 91 days following sucrose treatment. Sample collection and treatment methods were described earlier. Plutonium oxidation state determinations were performed on the 0.22-µm filtrate in samples collected on days 63, 72, 76, and 91 post-treatment.

## Statistical procedures

The Pearson product-moment correlation coefficients (r) and associated statistical significance levels ($\alpha$) for comparisons of actinides and physicochemical variables were obtained by computer using the CORR-SAS procedure (SAS User's Group, 1979). Isotopic activity ratio estimates for actinide pairs obtained from sediment and water sample data were analyzed statistically by techniques described by Cochran (1963).

## RESULTS

### Actinide distribution in sediment

Analyses of sediment are summarized in Table 1. Two types of
sediment strata were identified, based on physical and radiological
characteristics. Scoured areas (located in shallow water exposed to
prevailing winds) contained thin sediment deposits with higher ($^{244}$Cm
excepted) and more variable actinide concentrations than unscoured
areas (the primary sediment stratum). Correlation coefficients for
$^{241}$Am with $^{238}$Pu, $^{239,240}$Pu, and $^{244}$Cm in sediments were +0.91,
+0.95, and -0.38, respectively. Older deposits, exposed to varying
degrees by wave action, account for the higher and more variable
concentrations in scoured areas; radioactive releases from ORNL
declined monotonically in the period when the pond received treated
wastes (Blaylock and Frank, in press). The negative correlation
between $^{244}$Cm and Am-Pu isotopes is related to sharp differences in
waste effluent concentrations with time and potential differences in
waste chemical associations. Plutonium (and $^{241}$Am, decay product of
$^{241}$Pu) entered the system over a 30-y period with reprocessed fission
wastes, but the bulk of the $^{244}$Cm inventory originated from
radioisotope production wastes toward the end of the pond's use as a
settling basin. Significant quantities of $^{233}$U (Table 1) reached the
pond as a result of $^{232}$Th breeder reactor research programs at ORNL.

The dominant actinide in sediments on the basis of chemical mass
was $^{238}$U ($10^4$ greater than $^{233,234}$U and $^{239,240}$Pu, Table 1).
However, partial analyses indicate that $^{232}$Th concentrations (not
reported) in these same samples will average 2 to 3 times higher than

Table 1. Actinide concentrations in surface sediment strata (0-5 cm) from ORNL Pond 3513. Values expressed as arithmetic mean (dry wt) ±95% C.L.

| | Strata | | Pooled estimate | |
| | Unscoured | Scoured | | |
| Actinides | N = 18 (Bq/g) | N = 6 (Bq/g) | (Bq/g) | (ng/g)[a] |
|---|---|---|---|---|
| $^{233,234}$U | 4.0 ± 0.55 | 7.8 ± 3.0 | 5.0 ± 0.87 | $1.6 \times 10^1$ |
| $^{238}$U | 3.1 ± 0.15 | 2.3 ± 1.0 | 1.2 ± 0.27 | $1.0 \times 10^5$ |
| $^{238}$Pu | 1.7 ± 0.32 | 6.2 ± 3.3 | 2.8 ± 0.87 | $4.4 \times 10^{-3}$ |
| $^{239,240}$Pu | 16 ± 1.7 | 98 ± 57 | 33 ± 12 | $1.3 \times 10^1$ |
| $^{241}$Am | 5.2 ± 0.90 | 30 ± 17 | 11 ± 4.2 | $9.4 \times 10^{-2}$ |
| $^{244}$Cm | 13 ± 1.7 | 8.3 ± 3.8 | 12 ± 1.6 | $3.8 \times 10^{-3}$ |

[a]Based on mass spectrometry results on selected samples: $^{238}$U/$^{235}$U/$^{234}$U = 99.3/0.69/0.006% and $^{239}$Pu/$^{240}$Pu/$^{241}$Pu = 94/5.7/0.3%, respectively.

[b]N = 5, one high value (360 Bq/g) removed by Chauvenet's criterion.

$^{238}U$ concentrations. Mass concentrations of $^{241}Am$ are $10^4$ lower than $^{239,240}Pu$; $^{238}Pu$ and $^{244}Cm$ are 20 times lower than $^{241}Am$. Correlations between organic content and U, Pu, Am, or Cm were nonsignificant ($\alpha > 0.05$).

## Primary features of actinide variations in pond water

Concentrations of $^{238}U$ and $^{239,240}Pu$ (Fig. 1), along with $^{241}Am$ and $^{244}Cm$ (Fig. 2), in 0.22- m membrane filtered pond water varied significantly with time over the observation period (9 March 1977 to 27 May 1982; months 2 to 64) in response to both intrinsic and extrinsic conditions. A common, prominent feature was a concentration minimum which occurred between 10 May and 12 July 1977 (months 4 to 6) associated with a massive benthic algal bloom. Another prominence was caused by an extrinsic spike input of transuranics and $^{233}U$ (not shown) resulting from malfunction of a water diversion valve between 12 November and 15 December 1978 (months 22 and 23).

## Physicochemical characterization of the pond ecosystem

Because only a small fraction of the concentration declines during the algal bloom could be attributed to uptake by biota (e.g., $^{244}Cm$ concentration in biota <30 Bq/m$^2$ opposed to 3000 Bq/m$^2$ equivalent loss from water column), other explanations were sought (solution-sediment chemical variations, etc.). Under conditions more typical of the system, during the year following the bloom (7 November 1977 to 14 November 1978; months 10 to 22) and preceding the accidental spike, physicochemical conditions in pond water (Table 2) appeared comparable to other well-aerated, natural systems (Hutchinson 1957, Welch 1952);

Figure 1. Concentrations of $^{238}U$ amd $^{239,240}Pu$ in 0.22-$\mu$m-membrane filtered water during the period 9 March 1977 (month 2) to 27 May 1982 (month 64). Dates, given as month post-reference date, are referenced to 1 January 1977 (time-zero).

LEGEND
△ = PU-239,240(SURFACE)
+ = PU-239,240(1 METER)
□ = U-238(SURFACE)
✕ = U-238(1 METER)

PU-239,240 & U-238(BQ/CUBIC METER)

DATE

Figure 2.   Concentrations of $^{241}$Am amd $^{244}$Cm in 0.22-µm-membrane
            filtered water during the period 9 March 1977 (month 2) to
            27 May 1982 (month 64).  Dates, given as month post-reference
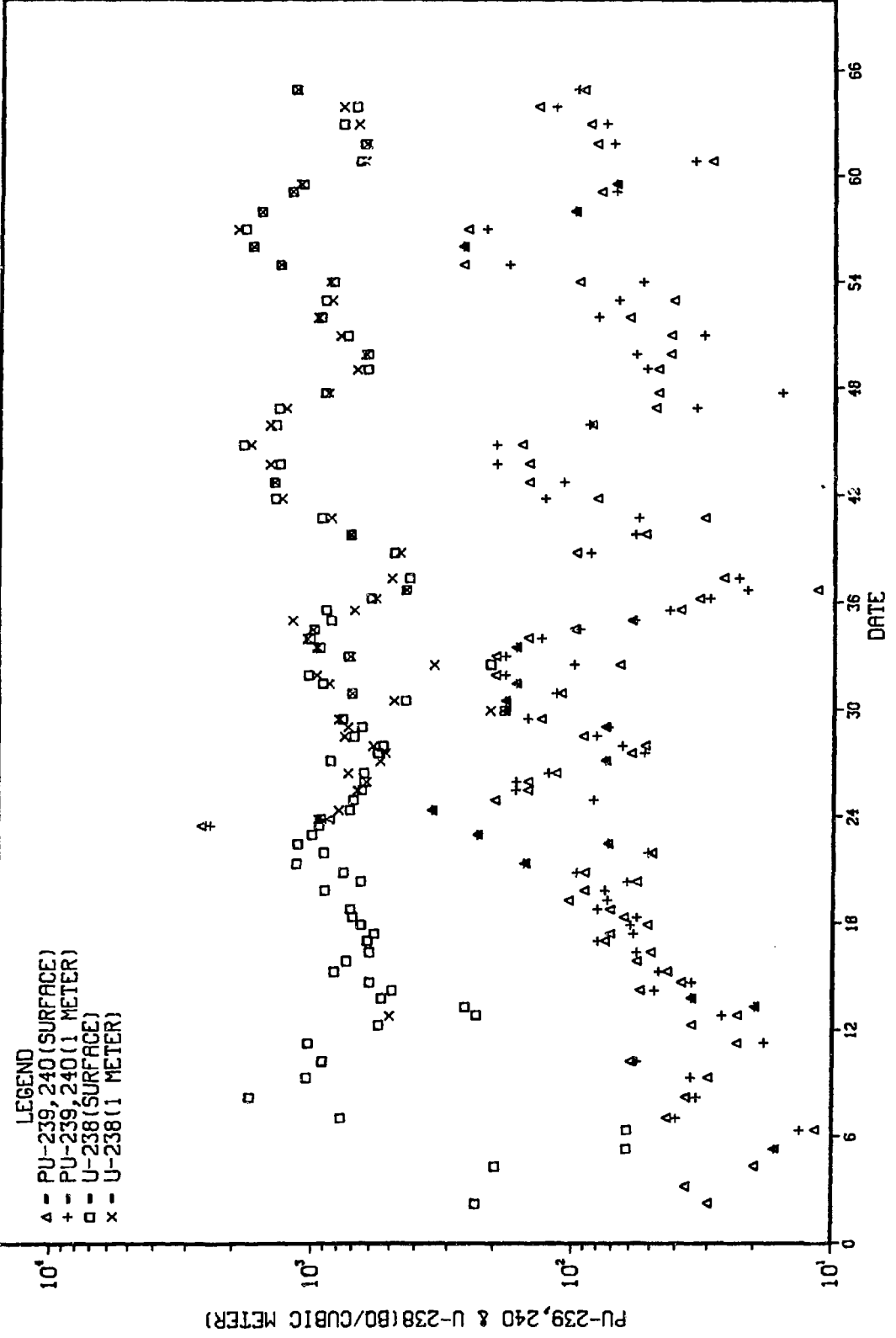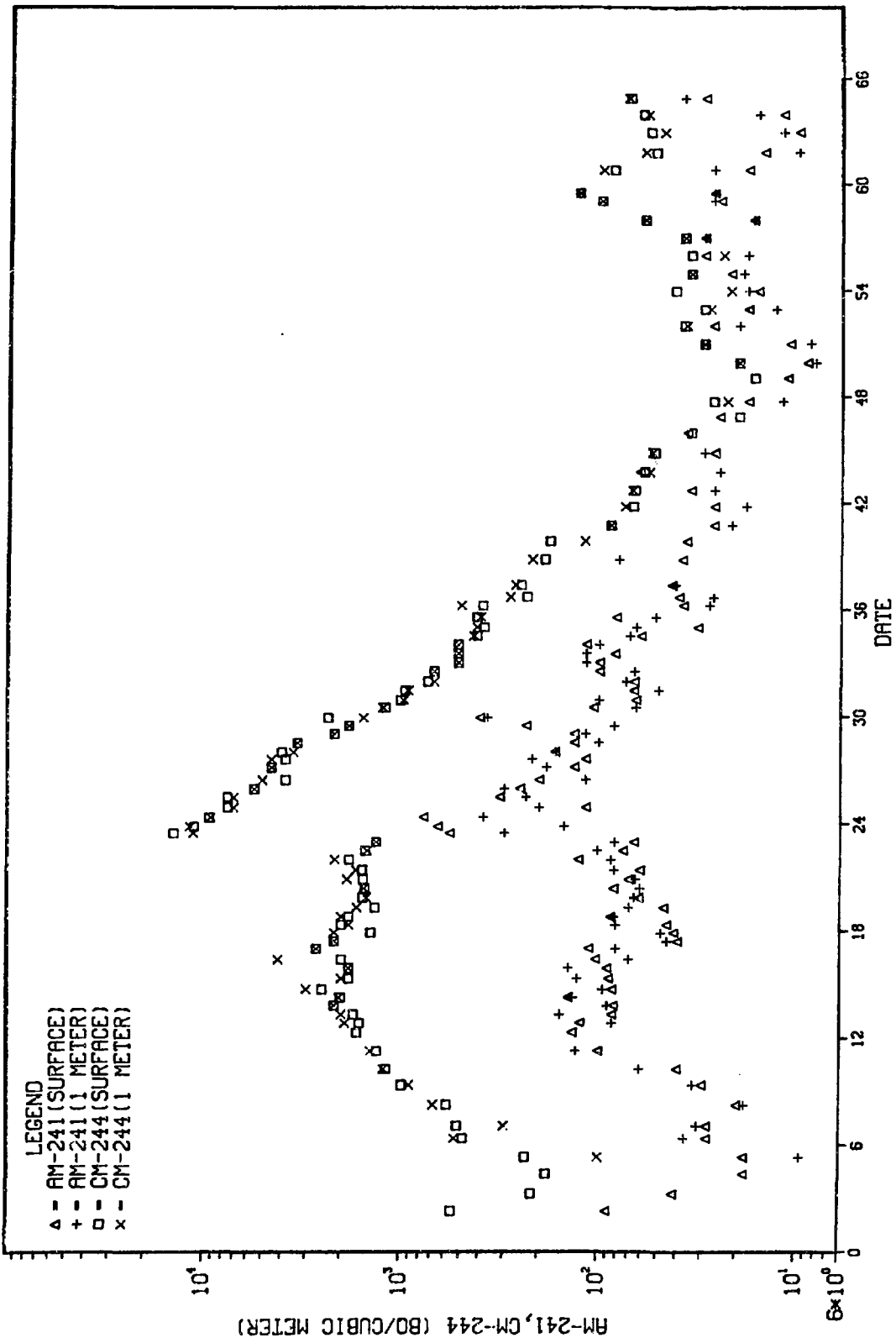            date, are referenced to 1 January 1977 (time-zero).

Table 2. Physicochemical characteristics of ORNL Pond 3513 water in the year (7 November 1977 - 14 November 1978; months 10 to 22) preceding accidental spike input. Values shown are arithmetic means and ranges (N = 23)

| Field measurements (surface) | | |
|---|---|---|
| Temperature ( C) | 17.6[a] | (2.9-30.4) |
| Dissolved oxygen (% saturation) | 110 | (48[b]-160) |
| pH | 9.1 | (7.9-9.6) |

$0.22-\mu m$-membrane filtrate concentration ($mmole/m^3$)

| Major constituents | | Trace constituents | |
|---|---|---|---|
| Na | 290 (210-380) | $SiO_2$ | 7.0 (0.03-63) |
| K | 66 (39-100) | $NO_3$-N | 3.1 (0.29-87) |
| Ca | 500 (300-670) | $NH_3$-N | 2.6 (1.4-9.6) |
| Mg | 750 (560-970) | Total P | 0.94 (0.29-1.9) |
| | | $PO_4$-P | 0.32 (0.03-1.1) |
| $HCO_3$ | 1700 (1400-2100) | Mn | 0.046 (0.005-0.20) |
| $CO_3$ | 140 (9-330) | Fe | 0.047 (0.007-0.12) |
| DOC | 860[c] (530-1500) | Zn | 0.12 (0.004-0.91) |
| $SO_4$ | 130 (87-200) | | |
| Cl | 190 (130-260) | | |
| F | 23[d] (11-32) | | |
| OH | 12 (0.79-40) | | |

[a]Mean (range) at 1-m depth - 17.6 (3.2-30.1).

[b]Values as low as 3% saturation recorded at 1-m depth in late summer.

[c]Dissolved organic carbon, as carbon.

[d]From 27 September 1978 to 29 June 1979; months 8 to 29 (N = 19).

Welch 1952); somewhat elevated pH (mean 9.1) and carbonate alkalinity seemed to be the only significant residuals of the lime-soda waste treatment process. Thermal stratification was not possible, but some oxygen depletion in the water column was observed over a 4-week period in late summer, a consequence of high productivity coupled with shallow depth (maximum 2 m).

Significant effects on the redox potential of the system, in particular, at the sediment-water interface, were observed over a 12-week period (7 April to 12 July 1977; months 3 to 6) during the previous year's algal bloom. This was indicated by pulses of Mn, Fe, $NH_3$-N, and $PO_4$-P into the water column (Table 3). Pulses of Fe and $NH_3$-N were not observed in the following summer (1978; months 17 to 20) in the absence of an algal bloom; Mn concentrations were also an order of magnitude lower (Table 2).

### Actinide decline association with reducing conditions at the sediment-water interface

Concentration minima for $^{241}$Am and $^{244}$Cm (Table 3) were associated with the corresponding maxima for Mn, Fe, $NH_3$-N, and $PO_4$-P in 10 May (month 4) and 9 June 1977 (month 5) water samples. Minima for $^{238}$U and $^{239,240}$Pu (Table 3), on the other hand, were reached a month later and maintained in the 12 July 1977 (month 6) sample, when $^{241}$Am and $^{244}$Cm had already rebounded. The minimum pH in the water column (8.3) was recorded on 12 July (month 6; mean 9.1 ± 0.4 for other samples during the year of the algal bloom).

Table 3. Association of actinide concentration minima with chemical indicators of redox conditions during 1977 algal bloom

| | 0.22-μm-membrane filtrate concentration | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | 1977 sampling dates/month | | | | | | |
| | 9 Mar / 2 | 7 Apr / 3 | 10 May / 4 | 9 Jun / 5 | 12 Jul / 6 | 3 Aug / 7 | 3 Sep / 8 |
| Actinides $(Bq/m^3)$ | | | | | | | |
| $^{238}U$ | 230 | – | 180 | 60 | 60 | 750 | 1700 |
| $^{239,240}Pu$ | 30 | 37 | 20 | 17 | 13 | 42 | 35 |
| $^{241}Am$ | 90 | 42 | 180 | 14 | 34 | 30 | 20 |
| $^{244}Cm$ | 550 | 220 | 180 | 170 | 520 | 420 | 630 |
| Redox indicators $(mg/m^3)$[a] | | | | | | | |
| DO[b] | 110 | 120 | 100 | 30 | 48 | 150 | 160 |
| Mn | 0.8 | 8.6 | 100 | 130 | 36 | 1.9 | 0.9 |
| Fe | 2.0 | 8.8 | 17 | 9.5 | 6.9 | 4.7 | 3.2 |
| $NH_3$-N | 40 | 60 | 120 | 78 | 62 | 4.0 | 50 |
| $PO_4$-P | 3.0 | 2.0 | 34 | 13 | 14 | 5.0 | 4.0 |

[a]Mean pH was 9.1 ± 0.4 without low value (pH 8.3) recorded on 12 July 1977 (month 6).

[b]Dissolved oxygen (DO) measured in field; value expressed as % saturation at ambient temperature.

## Post-algal bloom solution behavior

Concentrations of $^{238}U$ and $^{239,240}Pu$ (Fig. 1) appeared to re-establish levels more typical of the unperturbed system during late summer and fall of 1977 (months 8 to 10), but then fell to secondary minima in water under winter ice cover from late December 1977 (month 11) through mid-February 1978 (month 13). Both rate of change and extremes for $^{238}U$ concentrations were greater than those for $^{239,240}Pu$ during this same period. A decline in $\Sigma$ alkalinity (from 130 to 107 $g/m^3$), cations, silica, and dissolved organic carbon was also noted; sulfate concentration increased over the same time interval. Dissolved oxygen concentrations remained at or above saturation, but a pulse of Mn (11 $mg/m^3$ - 0.2 $mmole/m^3$) was measured on 27 January 1978 (month 12). The pH remained relatively constant (9.1 ± 0.2) over the time interval.

Concentrations of $^{241}Am$ and $^{244}Cm$ (Fig. 2) rose to re-establish a quasi-stable baseline by 8 December 1977 (month 11) and 10 February 1978 (month 13), respectively. Note that $^{244}Cm$ required three months more than $^{241}Am$ to re-establish an apparent concentration plateau, and did so at mean levels (1800 to 3200 $Bq/m^3$) approximately four times that (550 $Bq/m^3$) recorded on 9 March 1977 (month 2) before the bloom. Mean concentrations of $^{241}Am$ over the period 8 December 1977 (month 11) to 14 November 1978 (month 22; 89 ± 27 $Bq/m^3$) are comparable to the pre-bloom value (90 ± 22 $Bq/m^3$). Concentrations of $^{241}Am$ and $^{244}Cm$ declined slightly from spring values, but the depression in concentration was much less than that observed during the 1977 algal bloom. In contrast, both $^{238}U$ and $^{239,240}Pu$ concentrations

in water (Fig. 1) actually increased through the summer and fall of 1978 (months 17 to 22), a period characterized by significantly below-average rainfall and above-average temperatures.

## Soluble plutonium valence behavior
## before accidental spike

Plutonium oxidation states were determined in samples collected on 1 July 1977 (month 6), and then on 12 October and 30 October (month 21), and 14 November 1978 (month 22), just prior to the accidental spike. The $^{239,240}Pu(III,IV)$ fractions (% of total concentration in fraction) contained 86, 14, 32, and 27%, respectively on the four dates, but variations in absolute concentrations of $^{239,240}Pu(III,IV)$ were not as great (16 to 22 $Bq/m^3$, see companion paper by Bondietti et al.). Thus, during the Pu concentration minimum associated with the 1977 algal bloom, reduced Pu was predominant; a similar observation was reported previously by Bondietti and Sweeton (1977) for $^{239,240}Pu$ in White Oak Lake [another highly eutrophic environment, but one more subject to algal blooms and reducing conditions, Trabalka and Allen (1977)]. Following the minimum associated with the 1977 algal bloom in ORNL Pond 3513, $^{239,240}Pu$ concentrations increased up to an order of magnitude (160 ± 16 $Bq/m^3$) in 1978 before the accidental spike. The data indicate that the increased $^{239,240}Pu$ concentration was attributable to inputs of Pu(V,VI) from sediments to the water column. Note also that the two instances when the largest percentage changes in $^{239,240}Pu$ concentrations occurred between adjacent sampling dates (between 12 July (month 6), 13 ± 3.3 $Bq/m^3$, and 3 August 1977 (month 7), 42 ± 6.7 $Bq/m^3$ and between 12 October (month 12), 160 ± 16 $Bq/m^3$, and 30 October 1978

(month 21), 52 ± 8.4 $Bq/m^3$) were also marked by the largest shifts in hydrogen-ion concentration (pH rose from 8.3 to 9.4 and fell from 9.4 to 7.9, respectively).

## Correlations of solution variables in period before accidental spike

Significant correlations (r) and associated statistical significance levels ($\alpha \leq 0.01$) between pond solution chemistry variables in the observation period (9 March 1977 to 14 November 1978; months 2 to 22) preceding the accidental spike are shown in Table 4. Strongest correlations for $^{239,240}Pu$ and $^{244}Cm$ were with time (+0.711 and +0.716, respectively). Curium-244 and $^{241}Am$ were also correlated as expected (r = +0.622); a much stronger association was observed, r($\alpha$) = +0.839 (0.0003), over the 9 March 1977 to 10 February 1978 (months 2 to 13) period. Uranium was most strongly correlated with Mg (+0.720). Another significant positive correlation for U was observed with K (+0.628); weaker associations were noted with $SiO_2$ (+0.491) and Na (+0.468). Plutonium was also positively correlated with hydroxyl ion (+0.457).

In the time period (10 February to 14 November 1978; months 13 to 22) when $^{238}U$ and $^{239,240}Pu$ increased steadily prior to the accidental spike (Fig. 1) both actinides were strongly correlated with time, r($\alpha$) = +0.791 (0.0001) and +0.663 (0.002), respectively. The strongest correlation for $^{238}U$ in this same time interval was with time, and the best correlation for $^{239,240}Pu$ was with $^{238}U$, r($\alpha$) = +0.699 (0.001). Both time and $^{238}U$ were strongly positively correlated ($\alpha \leq 0.01$) with Na and Cl ions, indices of evaporative concentration processes (Hutchinson 1957).

Table 4

Table 4. Correlation coefficients (r, above the diagonal) and significance levels (α, below the diagonal) for paired physicochemical variables in 0.22- m-filtered ORNL Pond 3513 water in the period (9 March 1977 to 14 November 1978; months 2 to 22) before the accidental spike input

| | 238U | 239Pu | 241Am | 244Cm | Time | T( C) | Mg | Ca | Na | K | Mn | Fe | OH | SO4 | SiO2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 238U | . | | | | | | +0.720 | -0.582 | +0.468 | +0.628 | -0.508 | | | -0.632 | +0.491 |
| 239Pu[a] | | . | | +0.711 | | | | -0.546 | | | | -0.548 | +0.457 | -0.516 | |
| 241Am | | | . | +0.622 | | -0.679 | | | -0.466 | | -0.483 | -0.565 | | | |
| 244Cm | | 0.0002 | . | | +0.716 | | | | -0.459 | | -0.524 | -0.549 | | | |
| Time | | 0.0001 | | 0.0001 | . | | | -0.477 | | | -0.469 | | | -0.650 | |
| T( ) | | | 0.0001 | | | . | | | | | | | | -0.478 | |
| Mg | 0.0001 | | | | | | . | -0.532 | +0.585 | +0.697 | | | | -0.657 | +0.464 |
| Ca | 0.0009 | 0.002 | | | 0.007 | | 0.002 | . | | | | | -0.534 | +0.649 | |
| Na | 0.01 | | 0.008 | 0.009 | | | 0.0006 | | . | +0.577 | | | | | +0.639 |
| K | 0.0003 | | | | | | 0.0001 | | 0.0007 | . | | | | | +0.572 |
| Mn | 0.005 | | 0.006 | 0.003 | 0.008 | | | | | | . | +0.722 | | | |
| Fe | | | 0.001 | 0.0009 | 0.001 | | | | | | 0.0001 | . | | | |
| OH | | | | | | | | 0.002 | | | | | . | | |
| SO4 | 0.0002 | 0.003 | | 0.0001 | 0.007 | 0.0001 | 0.0001 | | | | | | | . | |
| SiO2 | 0.007 | | | | | | 0.009 | | 0.0001 | 0.0008 | | | | | . |

[a]Representing 239,240Pu.

Both $^{238}U$ and $^{239,240}Pu$ were negatively correlated with Ca and $SO_4$ ions over the 9 March 1977 to 14 November 1978 (months 2 to 22) period (Table 4). Calcium and $SO_4$ were positively correlated (+0.649); both were negatively correlated with Mg ($r$ = -0.532 and -0.657, respectively). Uranium was negatively associated with Mn ($r$ = -0.508), but not Fe; Pu association was the reverse. Americium and Cm were both negatively correlated with Fe and Mn (stronger association) and Na. Americium exhibited its strongest association with time (-0.679); both $^{241}Am$ and $^{244}Cm$ were highly negatively correlated with temperature in the time interval 9 March 1977 to 10 February 1978 (months 2 to 13; $r$ = -0.891 and -0.790, respectively).

Actinide solution behavior after the accidental spike

The accidental spike input of transuranics and $^{233}U$ which occurred between 29 November and 15 December 1978 (months 22 and 23; Figs. 1 and 2, $^{233}U$ data not shown) permitted us to test a hypothesis that a dynamic sediment-water exchange equilibrium existed in ORNL Pond 3513. The actinide activity ratios which were observed for sediment, seston, and filtered water prior to the spike are presented in Table 5. Transuranic activity ratios in sediment and seston were not significantly different; neither were ratios for U and Pu in water and sediment (U was not determined in seston samples). However, $^{241}Am$ and $^{244}Cm$ were obviously not exchanging uniformly between sediment and the water column. There was a great disparity between $^{244}Cm:^{241}Am$ isotopic activity ratios in water and sediments (25 to 1.0, respectively). This difference is also expressed in the comparison between estimated distribution coefficients (in situ $K_d$) for the two

Table 5. Isotopic activity ratio estimates in surface sediments, seston, and filtered water of ORNL Pond 3513. Values expressed as arithmetic mean ±95% C.L.

| Actinide comparisons | Isotope activity ratios | | |
| --- | --- | --- | --- |
| | Pooled sediment[a] | 0.22-μm-membrane filtered | |
| | | Seston[b] | Water[c] |
| $^{239,240}Pu:^{238}Pu$ | 12 ± 2.3 | 15 ± 4.1 | 13 ± 1.9 |
| $^{241}Am:^{239,240}Pu$ | 0.34 ± 0.064 | 0.32 ± 0.057 | 1.7 ± 0.62 |
| $^{244}Cm:^{239,240}Pu$ | 0.35 ± 0.16 | 0.34 ± 0.16 | 37 ± 10 |
| $^{244}Cm:^{241}Am$ | 1.0 ± 0.48 | 1.1 ± 0.59 | 25 ± 4.5 |
| $^{233,234}U:^{238}U$ | 4.1 ± 0.46 | - | 4.0 ± 0.49[d] |

[a]N = 24, samples collected on 9 March 1978 (month 14); see Table 1.

[b]N = 4, samples consisting of four subsamples each, collected between 10 February and 10 April 1978 (months 13 to 15).

[c]N = 19, paired samples collected between 10 February and 14 November 1978 (months 13 to 22).

[d]N = 4, paired samples collected on 29 November 1978 (month 22) and between 1 June and 29 June 1979 (month 29).

elements in the Pond 3513 system (Table 6). Note also that the average concentrations for Am and Cm are quite similar when expressed on a mass basis (Table 6).

## Results of ultrafiltration of pond water during spike maximum

The accidental spike effectively re-labelled the water column, but not the sediments, with new activity ratios of the actinide isotopes ($^{233,234}$U:$^{238}$U rose to 9.7; $^{239,240}$Pu:$^{238}$Pu fell to 1.8; and $^{244}$Cm:$^{241}$Am rose to 40) (Table 7). Ultrafiltration of water during the spike maximum (Table 7) indicated that all actinides were in true solution because concentrations in 0.22-µm and 10,000-mol. wt filtrates were not significantly different. However, differences in solution behavior-chemical associations of the elements were revealed by passage through the 500 mol. wt ultrafilter. The bulk of the $^{244}$Cm ($\sim$80%), but not $^{233,234}$U or Pu isotopes, was retained by the system (Table 7).

## Differences between biogeochemical removal rates of actinides from water

Rate of Pu decay (biogeochemical) from the water column after the spike was rapid (half-time 7 ± 1 d) and concentrations had apparently reached pre-spike values by 15 March 1979 (month 26) (Fig. 1). Curium-244 concentration was reduced at a much slower rate (half-time 70 ± 9 d). The decline in $^{241}$Am was similar until 30 April 1979 (month 27) when the $^{244}$Cm:$^{241}$Am ratio appears to converge rapidly toward the pre-spike value (Fig. 2). However, we should point out that $^{241}$Am concentrations during this time have a significantly higher associated variance (Fig. 2) because of tailing from relatively high

Table 6. Mean concentration of actinides in ORNL Pond 3513 water and estimated $K_d$ during apparent equilibrium period (10 February to 14 November 1978; months 13 to 22)

| Actinides | Concentration 0.22- m-filtered water | | $K_d$ estimate[a] |
|---|---|---|---|
| | (dpm/liter) | (moles/liter) | (ml/g) |
| $^{238}U$ | 720 | $2.4 \times 10^{-7}$ | $1.7 \times 10^3$ |
| $^{238}Pu$ | 5.5 | - | $5.2 \times 10^5$ |
| $^{239,240}Pu$ | 65 | $1.0 \times 10^{-13}$ | $5.1 \times 10^5$ |
| $^{241}Am$ | 85 | $2.9 \times 10^{-15}$ | $1.3 \times 10^5$ |
| $^{244}Cm$ | 2000 | $2.7 \times 10^{-15}$ | $5.9 \times 10^3$ |

[a]Pooled concentration in surface sediment (Bq/g)/concentration in filtered pond water (Bq/$m^3$) x $10^{-6}$ $m^3$/ml.

Table 7. Results of ultrafiltration of 22 December 1978 (month 23) water sample from ORNL Pond 3513 following accidental spike. Values expressed as arithmetic mean ±95% C.L.

| Actinides | Concentration 0.22-μm filtrate (Bq/m$^3$) | Percent of 0.22- m filtrate concentration in fraction | | |
|-----------|-------------------------------------------|------------------|------------------------------|----------------------|
| | | 10,000-mol. wt filtrate | Retained by 500 mol. wt UF | 500-mol. wt filtrate |
| $^{233,234}$U | 7300 ± 820 | 97 ± 17 | 17 ± 2.4 | 88 ± 10 |
| $^{238}$U | 780 ± 110 | 106 ± 20 | 17 ± 3.2 | - |
| $^{238}$Pu | 620 ± 92 | 89 ± 14 | 32 ± 5.2 | 76 ± 17 |
| $^{239,240}$Pu | 1200 ± 120 | 99 ± 11 | 29 ± 3.7 | 74 ± 16 |
| $^{241}$Am | 280 ± 38 | 99 ± 12 | - | - |
| $^{244}$Cm | 11000 ± 670 | 104 ± 12 | 78 ± 17 | 22 ± 4.2 |

$^{244}$Cm activity into the $^{241}$Am peak in some samples in $\alpha$-spectrometry. Thus, comparisons between the two actinides were more difficult when $^{244}$Cm:$^{241}$Am activity ratios were large, i.e., during the entire period after the 1977 algal bloom, but between 15 December 1978 and 29 June 1979 (month 23 to month 35), in particular.

In addition to the slower rate of decline in $^{244}$Cm ($^{241}$Am) than in $^{239,240}$Pu, the rate of removal of the Pu (III,IV) fraction was significantly less than that for Pu(V,VI). The rates of re-establishment of isotopic equilibrium for U(VI), Pu(V,VI), or Pu(III,IV) (slowest) were all significantly slower than the decay rate of total Pu or Pu(V,VI) concentrations from the water column after the spike (Bondietti et al., companion paper). However, both the $^{239,240}$Pu:$^{238}$Pu and $^{244}$Cm:$^{241}$Am activity ratios converged on the pre-spike values rapidly after the 30 April 1979 sample (month 27) (Bondietti et al., companion paper and Fig. 2). After this date, significant increases in $^{239,240}$Pu and $^{241}$Am concentrations were observed (Figs. 1 and 2). After 15 March 1979 (month 26), Pu(V,VI) accounted for 72 ± 8% of dissolved Pu in pond water (see companion paper by Bondietti et al.).

All actinide activity ratios and concentrations had returned to pre-spike levels by June 1979 (month 35) (Figs. 1, 2, Table 8, also see companion paper by Bondietti et al.). However, the behavior of Pu and U in solution was quite different from that of Am and Cm in the period thereafter (months 35 to 64) (Figs. 1 and 2). Annual cycles of Pu and U are evident with peak concentrations in late summer/fall (e.g., months 33, 45, and 57) and minima in winter (months 38, 47, and 61).

Table 8

Table 8.  Results of ultrafiltration on ORNL Pond 3513 water samples.  Values expressed as arithmetic mean ±95% C.L.

| Sample date | Concentration | | | | | |
| | $^{239,240}Pu(V,VI)$ | | $^{239,240}Pu(III,IV)$ | | $^{244}Cm(III)$ | |
| | 0.22-μm filtrate (dpm/liter) | % in 500-mol. wt ultrafiltrate | 0.22-μm filtrate (dpm/liter) | % in 500-mol. wt ultrafiltrate | 0.22-μm filtrate (dpm/liter) | % in 500-mol. wt ultrafiltrate |
|---|---|---|---|---|---|---|
| 22 Dec. 1978 | 750 ± 170 | 98 ± 30 | 400 ± 110 | 27 ± 8.7 | 11000 ± 670 | 22 ± 4.2 |
| 14 Feb. 1978 | 55 ± 18 | - | 100 ± 9.5 | - | 7200 ± 350 | 27 ± 3.1 |
| 16 Apr. 1979 | 42 ± 5.3 | - | 20 ± 2.0 | - | 4200 ± 107 | - |
| 31 May 1979 | 52 ± 5.3 | 90 ± 11 | 12 ± 2.3 | 61 ± 18 | 2200 ± 170 | - |
| 14 Jun. 1979 | 89 ± 13 | 81 ± 13 | 28 ± 3.4 | 52 ± 9.3 | 1800 ± 170 | - |
| 10 Sep. 1979 | 99 ± 15 | 90 ± 16 | 48 ± 2.8 | 39 ± 6.2 | 750 ± 80 | 56 ± 12 |

The peaks occur at times when pH and biological production are high, and the minima are associated with lower pH and biological productivity. Concentrations of Pu and U are higher toward the end of the observation period than at the beginning. The concentrations of Am and Cm continue to decline until winter 1980 (months 49 and 50), no annual cycles are evident, and the average solution concentrations are lower at the end of the observation period than at the start.

## Results of ultrafiltration of pond water during post-spike recovery period

Similarities in the solution behavior of Pu(III,IV) and Cm(III) were revealed by ultrafiltration of water samples following the spike (Table 8). Approximately 90% of the $^{239,240}$Pu(V,VI) fraction was found in the 500-mol. wt ultrafiltrate independent of sampling date. However, both $^{239,240}$Pu(III,IV) and $^{244}$Cm(III) were primarily retained ($\sim$75%) by the system in the period immediately after the spike. After re-establishment of sediment-water equilibrium (31 May 1979; month 28, and ff.), $^{239,240}$Pu(III,IV) and $^{244}$Cm(III) were partitioned in approximately equal amounts between the 500-mol. wt filter and filtrate fractions (Table 8).

## Ion exchange behavior

Essentially all of the soluble U, Pu, Am and Cm behaved as anions (negatively charged complexes) when passed through Dowex$^{\bullet}$ 1 x 4 columns. Very little cationic behavior was evident upon passage through Dowex$^{\bullet}$ 50 x 4.

## Gel-filtration chromatography results

Differences in the types of solution chemical associations maintained by Pu(III,IV) and Cm(III) were revealed by gel-filtration chromatography (Table 9). Significantly higher sorption of $^{239,240}$Pu(III,IV) occurred with Sephadex® G-15, but the reverse was observed for BioGel® P-6. The exact nature of the associations is not yet known, but the gel void volume (into which molecules $\geq 6000$ daltons should elute) was the only fraction which contained measurable Pu or Cm activity. This fraction also contained the bulk of the dissolved organic matter in pond water (indicated by the 254-nm UV absorption spectrum, Fig. 3). Sorption of the 254-nm absorbing organic matter by BioGel® P-6 was determined to be $\leq 10\%$. Qualitative and quantitative changes in the UV absorption spectrum of gel-filtered pond water were also noted with time (Fig. 3). The quantitative differences appeared to be related to differences in DOC (maxima in late summer toward close of growing season; minima in early spring).

## Physicochemical character of pond changes after spike

A residual effect noted after the accidental spike was a relatively steady decline in carbonate alkalinity and cation (Ca, Mg, Na, K) concentrations, culminating in high pH values (9.9-10.3) in June 1979 (month 35). A sharp fall in alkalinity, Mg, K, and $^{238}$U between 1 June and 29 June 1979 was accompanied by an increase in pH from 8.8 to 10.3 and in $^{239,240}$Pu concentration from $75 \pm 13$ to $184 \pm 33$ Bq/m$^3$ (highest nonspike shift in concentration ever recorded in pond water). The highest nonspike $^{239,240}$Pu concentration was reached on 1 August 1981 (month 56), $270 \pm 20$ Bq/m$^3$.

Table 9

Table 9. Results of gel filtration chromatography on ORNL Pond 3513 water

| Sample date | Gel type | Nominal molecular weight excluded | Percent of 0.22- m filtrate concentration eluted with 2 x $10^{-3}$ M NaHCO$_3$ buffer (pH 9) in gel void volume | | |
|---|---|---|---|---|---|
| | | | $^{238}$Pu | $^{239,240}$Pu | $^{244}$Cm |
| 22 Dec. 1978 | Sephadex® G-15 | 1500 | - | 32 ± 16 | 85 ± 13 |
| 14 Feb. 1979 | Sephadex® G-15 | 1500 | - | 2.9 ± 0.70 | 88 ± 4.6 |
| 16 Apr. 1979 | Bio-Gel® P-6 | 6000 | 106 ± 36 | 117 ± 19 | 86 ± 4.5 |

[a]Expressed as mean ±95% C.L. of total $^{244}$Cm and Pu(III,IV), respectively. Detectable activity was observed only in void volume fraction. Remaining activity was adsorbed by gel and/or apparatus.

Figure 3. Elution profiles of 254-nm UV absorbing materials in polyacrylamide (Bio-Gel® P-6) gel-filtered pond water (buffer 2 x $10^{-3}$ $\underline{M}$ NaCHO$_3$, pH 9).

Fig. 3

Fig. 3
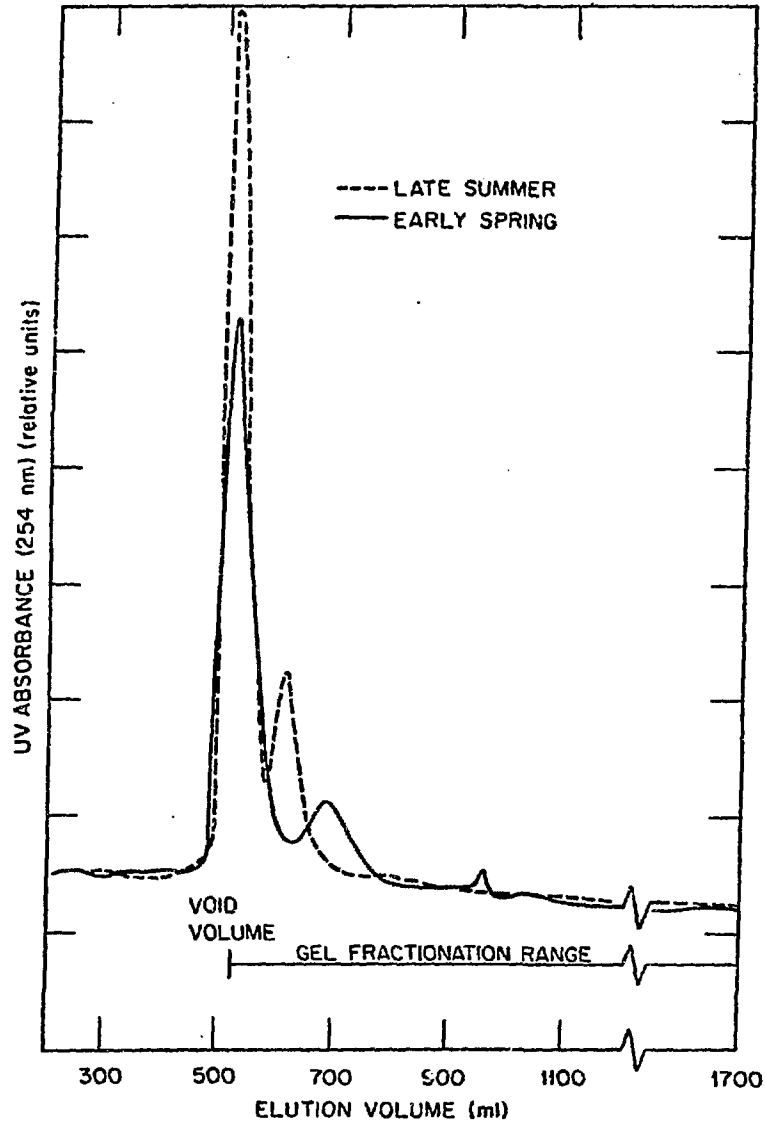
Correlations of solution variables
in the post-spike period

Correlations between $^{241}$Am or $^{244}$Cm and solution variables were not attempted for the time (14 November 1978 to 29 June 1979; month 22 to month 35) following the accidental spike because equilibrium had not been re-established at the end of the period. Data for the period between 29 November 1978 (month 22) and 28 February 1979 (month 25) were deleted in $^{239,240}$Pu and $^{238}$U correlations to allow for re-establishment of prespike Pu levels and to allow for amelioration of chemical effects on the system resulting from the spike (40% initial reduction in carbonate alkalinity and 100% increase in $SO_4$). The dominant association for $^{239,240}$Pu in the post-spike period (not unexpectedly) was with hydroxyl ion (+0.891) (Table 10). Uranium was (again) strongly positively correlated with Mg (+0.798); other positive associations with $HCO_3$, K, and Na ions appeared to be a result of stronger partial correlations with Mg (+0.882, +0.961, and +0.912, respectively). Uranium was negatively correlated with time and $SO_4$ ion (-0.744 and -0.722, respectively), while $^{239,240}$Pu was correlated with $HCO_3$ (-0.827). A significant proportion of the Pu-$HCO_3$ association also appeared to be referrable to strong partial correlations with OH and $CO_3$.

If the data sets for pre- and post-spike periods are pooled, the dominant associations for $^{239,240}$Pu were with time, $r(\alpha)$ = +0.729 (0.0001), and those variables identified during the post-spike period. If we ignore the fact that some chemical differences were introduced by the accidental spike and, thus, pool all the $^{238}$U data for correlation analysis, the dominant associations would be with K, +0.594 (0.0001);

Table 10

Table 10. Correlation coefficients (r, above the diagonal) and significance levels (α, below the diagonal) for paired physicochemical variables in 0.22-μm-filtered ORNL Pond 3513 water in the period (14 November 1978 to 29 June 1979; months 22 to 35) after the accidental spike input

| | $^{238}$U | $^{239}$Pu | Time | Mg | K | OH | HCO$_3$ | CO$_3$ | SO$_4$ |
|---|---|---|---|---|---|---|---|---|---|
| $^{238}$U | • | | −0.744 | +0.798 | +0.754 | | +0.758 | | −0.722 |
| $^{239}$Pu[a] | | • | | | | +0.891 | −0.827 | +0.824 | |
| Time | 0.02 | | • | −0.865 | −0.916 | | −0.848 | | |
| Mg | 0.01 | | 0.003 | • | +0.961 | | +0.882 | | |
| K | 0.02 | | 0.0005 | 0.0001 | • | | +0.941 | | |
| OH | | 0.001 | | | | • | −0.790 | +0.884 | |
| HCO$_3$ | 0.02 | 0.006 | 0.004 | 0.002 | 0.0002 | 0.01 | • | | |
| CO$_3$ | | 0.006 | | | | 0.002 | | • | |
| SO$_4$ | 0.03 | | | | | | | | • |

[a]Representing $^{239,240}$Pu.

Mg, +0.461 (0.002); Na, +0.330 (0.03); Mn, -0.469 (0.001); $SO_4$, -0.412 (0.006); and Ca, -0.326 (0.03), respectively. Deletion of the time period immediately following the spike did not change the types of correlations, only the rank order ($\alpha \leq 0.02$); $SO_4$ became the dominant variable, but relative positions of other ions were unchanged.

## Sediment anaerobiosis experiment

A significant lowering of the $^{244}Cm$:$^{241}Am$ activity ratio was observed in water above surficial sediments (Figs. 4 and 5), which had been mixed and isolated inside both the treated and untreated plexiglas™ enclosures. However, the shift in isotopic ratios required a period of several months to complete in the untreated enclosure. In the treated enclosure, in which anaerobic conditions were produced by addition of sucrose, the change occurred within a few days, and strikingly divergent behavior between $^{244}Cm$ and $^{241}Am$ was observed (Fig. 5). During the period of anaerobiosis, the solution concentrations of $^{241}Am$, $^{239}Pu$, and $^{238}Pu$ all increased by over an order of magnitude ($^{241}Am$ and $^{239}Pu$ strongly correlated; $r = 0.99$, $\alpha \leq 0.0001$, $n = 13$) while the concentration of $^{244}Cm$ changed by less than a factor of 2. The former three isotopes were all strongly correlated with dissolved iron ($r = 0.83$ to $0.91$, $\alpha \leq 0.001$), and with orthophosphate and pH, but not with calcium ($r \leq 0.21$, $\alpha \geq 0.50$) nor with manganese ($r \leq 0.50$, $\alpha \geq 0.10$). Although dissolution of a significant amount of sedimentary carbonate resulted, as indicated by an order of magnitude increase in soluble calcium, this did not produce an increase in transuranic concentrations. In fact, when calcium and

Figure 4

Fig. 4

UNTREATED ENCLOSURE



LEGEND
∇ = MN(MICROGRAM/LITER)
+ = FE(MICROGRAM/LITER)
□ = CA(MILLIGRAM/LITER)×10
△ = PU-239,240(BQ/CUBIC METER)
◇ = AM-241(BQ/CUBIC METER)×10
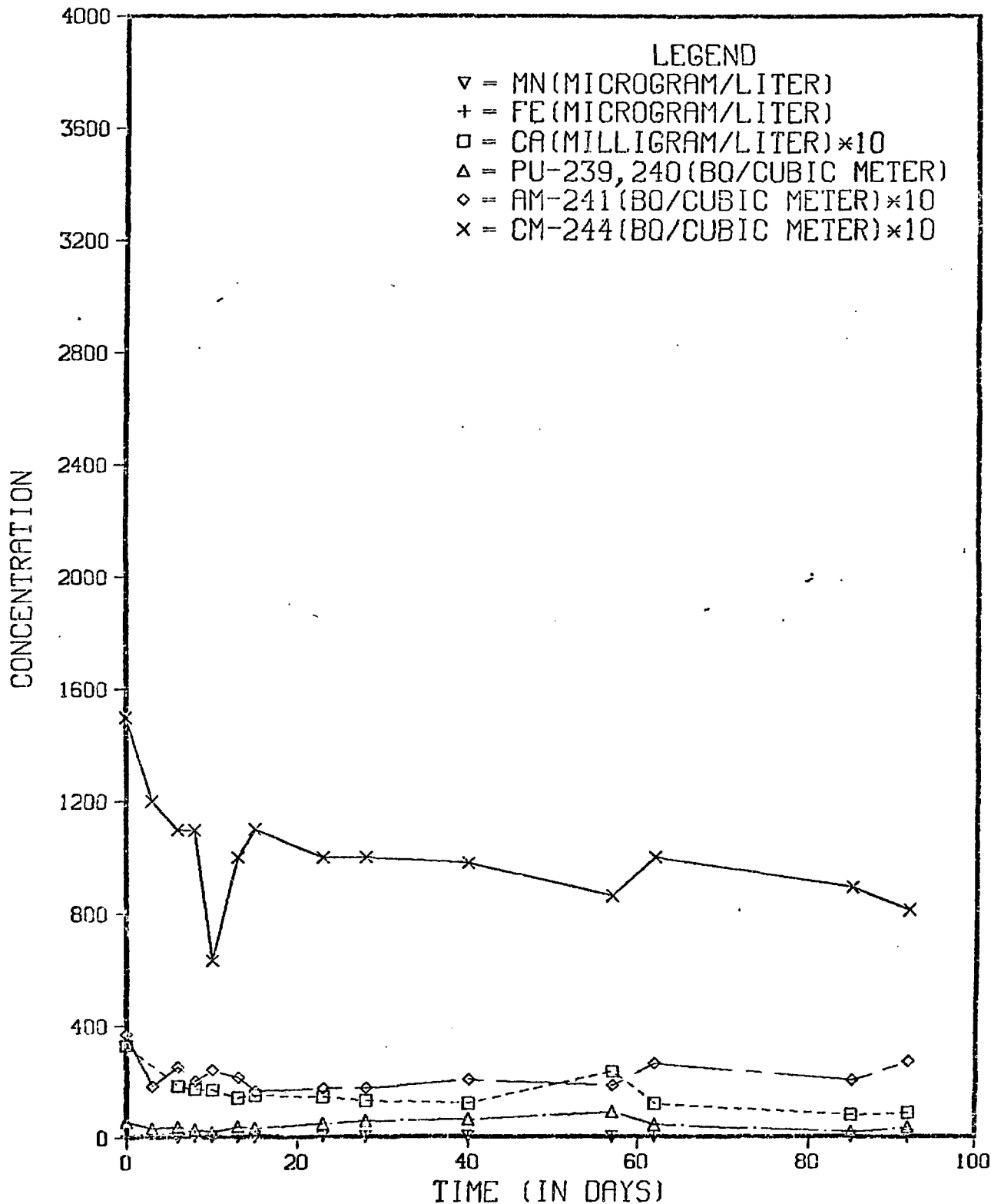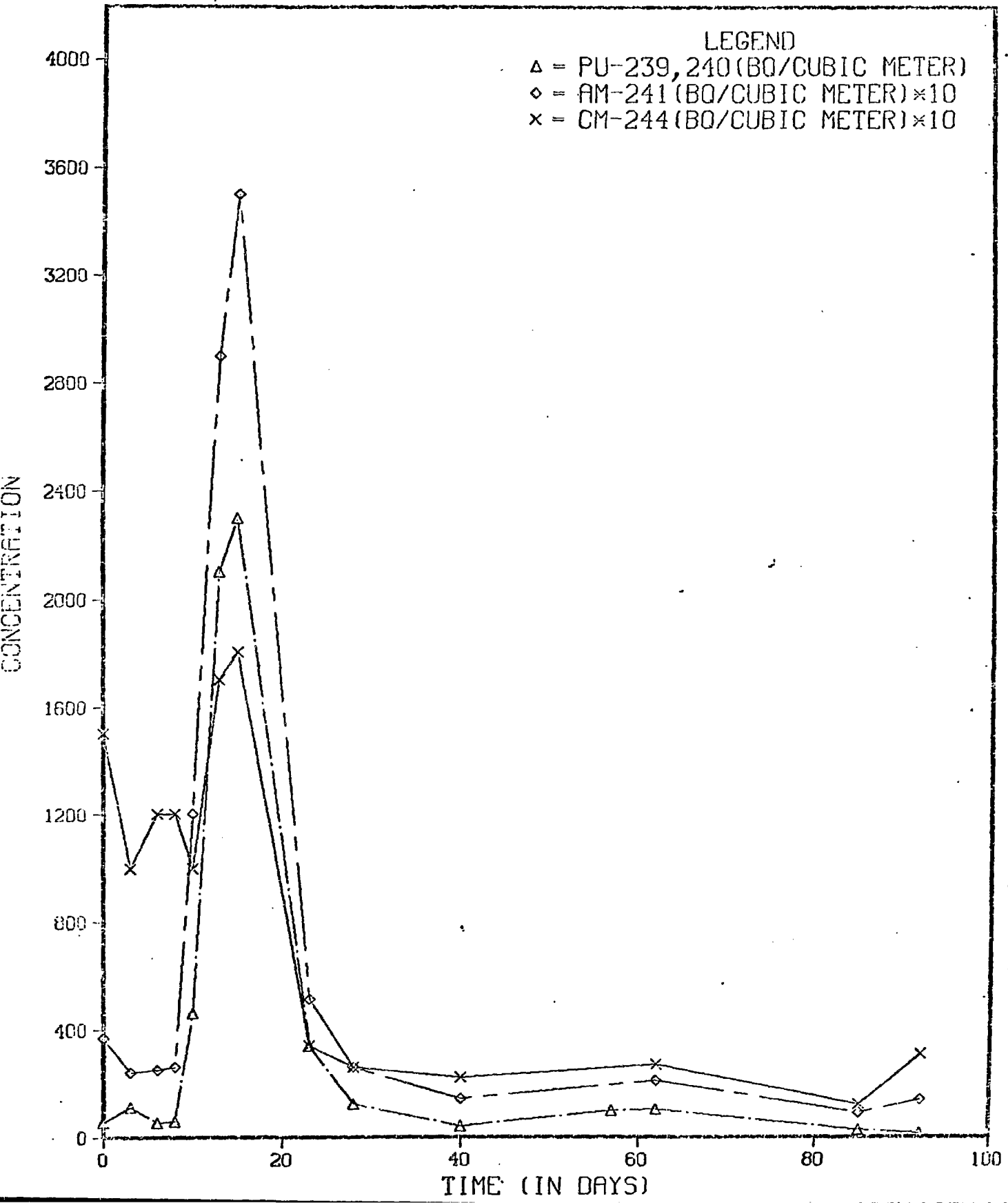× = CM-244(BQ/CUBIC METER)×10

CONCENTRATION

TIME (IN DAYS)

Figure 5

Fig. 5.

TREATED ENCLOSURES

manganese had reached maximum values during the observation period (Fig. 6), transuranic concentrations had returned to ambient or minimal levels.

The large spike of transuranics into the water column during the anaerobic period in the treated enclosure represented only a small fraction (<1%) of the surficial sediment inventory (Table 11). Higher sorption of uranium occurred in the treated enclosure during the anaerobic period. This resulted in a decline in the uranium concentrations in the water column, and a net uptake by the sedimentary pool (Table 11).

Measurements of plutonium oxidation state distributions were made well after aerobic conditions had been restored in the treated enclosure (63 days after treatment with sucrose, Fig. 6 and Table 12). As expected, the oxidation state distribution of dissolved plutonium in the untreated enclosure was similar to that in ambient pond water, and was dominated by the oxidized form (V +VI). However, the dominant oxidation state in the treated enclosure was reduced plutonium (III + IV). Significant reoxidation did not occur during the remainder of the observation period in the sediment anaerobiosis experiment.

## DISCUSSION

### Lability of plutonium oxidation states

Within the time span of our investigations on ORNL Pond 3513, the Pu(V,VI) fraction in the 0.22-$\mu$m membrane filtrate varied over the entire range ($\leq$10 to >80%) reported from other natural environments (Bondietti and Sweeton 1977, Nelson and Lovett 1978, and Wahlgren
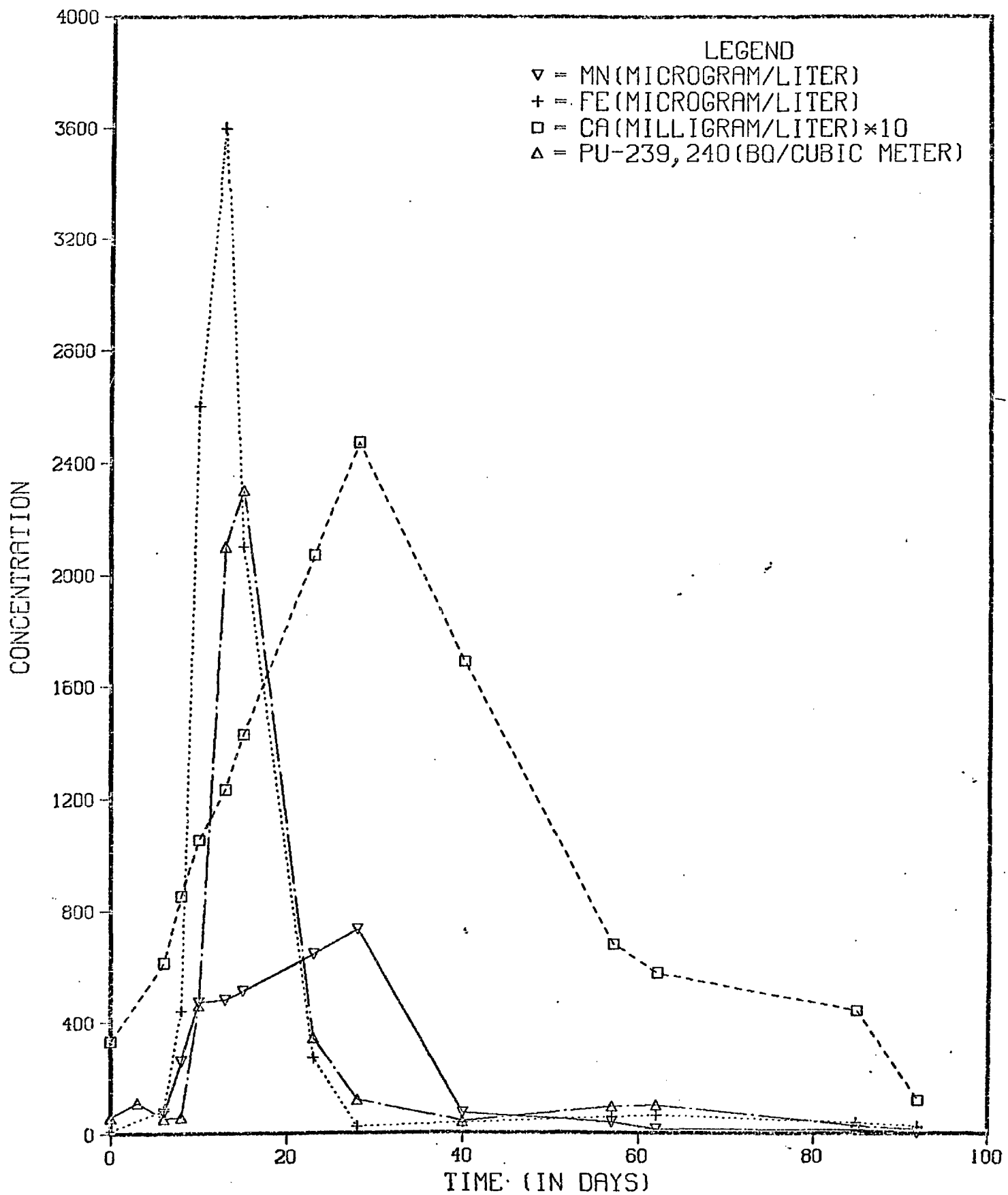
Figure 6

Fig. 6

TREATED ENCLOSURES

LEGEND
▽ = MN(MICROGRAM/LITER)
+ = FE(MICROGRAM/LITER)
□ = CA(MILLIGRAM/LITER)×10
△ = PU-239,240(BQ/CUBIC METER)

Table 11. Transuranic activity lost from sediments during anaerobic period in sucrose-treated enclosure

| | Nuclide | | | | | |
|---|---|---|---|---|---|---|
| | $^{239}Pu$ | $^{238}Pu$ | $^{241}Am$ | $^{244}Cm$ | $^{238}U$ | $^{233}U$ |
| Percent change in sediment concentration (0-1 cm) | -0.93 | -0.93 | -0.96 | -0.20 | +5.1 | +5.1 |
| Activity lost from surface sediment (Bq/sq. m.) | 1800 | 53 | 260 | 65 | -- | -- |
| Peak concentration in 1-m deep water column (Bq/cu. m) | 1850 | 56 | 280 | 150 | -- | -- |

Table 12.  Plutonium oxidation state distributions
in 0.22-μm-filtered water from the
sucrose-treated enclosure

| Sample location | Days Post-Treatment | $^{239}$Pu Concentration (Bq/cu. m.) | |
|---|---|---|---|
| | | III + IV | V + VI |
| Untreated enclosure | 63 | 33 ± 1 | 66 ± 0.8 |
| Treated enclosure | 63 | 140 ± 8 | 23 ± 2 |
| | 72 | 120 ± 6 | 19 ± 0.8 |
| | 76 | 12 ± 1 | 7.7 ± 0.5 |
| | 91 | 11 ± 0.5 | 8.2 ± 0.5 |

et al. 1977b), in our case, as a result of intrinsic biological and chemical cycles. Because the data on Pu oxidation states from some other aquatic systems are based on relatively few samples (Irish Sea, Lake Michigan, and White Oak Lake excepted), investigators may find significant internal temporal variability in valence behavior when other environments are scrutinized more closely. In three extremely dissimilar aquatic ecosystems, the Irish Sea (Nelson and Lovett 1978), Lake Michigan (Wahlgren et al. 1977a), and Pond 3513, estimates of $K_d$'s are quite comparable ($1\text{-}5 \times 10^5$) and oxidized Pu predominates the solution association; dissolved concentrations range from $10^{-13}$ to $10^{-18}$ $\underline{M}$.

## Uranium oxidation state behavior

The data from Pond 3513 indicate that with the exception of the 1977 algal bloom period, Pu was the only actinide which exhibited significant oxidation state variation in solution. The redox potential of the sediment-water interface during the algal bloom [(Eh = -0.1 to 0.0 V, estimated from soluble Fe concentration, Hutchinson (1957)] may have played a role in the $^{238}U$ concentration minimum by reduction of U(VI) to U(IV) (see companion paper by Bondietti et al.). However, even during this period, sorption characteristics of the system could have predominated. Formation and sedimentation of hydrous Fe and Mn oxides in the water column following $Fe^{++}$ and $Mn^{++}$ release from sediments could have scavenged dissolved actinides, especially U(VI) or Pu(V,VI) (Langmuir 1978, Murray 1975, and Stumm and Morgan 1970). Note that the concentration minima for U and Pu in pond water during the 1977 algal bloom were delayed for a month after the pulse of Fe and Mn

was detected. A strong inference from the sediment anaerobiosis experiment is that hydrous iron oxides, perhaps associated with organo-clay matrices, are the dominant sediment sorption site for transuranics in Pond 3513. Uranium, which exhibited the largest decrease in solution concentration, correlated with Mn, but not Fe (Table 4). Manganese may be released from sediments under redox conditions which could not promote reduction of U(VI) to U(IV) or Fe(III) to Fe(II) (Hutchinson 1957, Stumm and Morgan 1970, and companion paper by Bondietti et al.). The fall in pH (to 8.3) observed on 12 July 1977 (month 6) could have enhanced the sorption of U(VI) and prevented desorption until high pH values (with associated increase in OH and $CO_3$ concentration) were restored (see Fig. 22 in Langmuir 1978). Enhanced sorption was also observed during the period of low pH in the treated enclosure in the sediment anaerobiosis experiment. The rebound in U (and Pu) values was relatively rapid, apparently complete within one month. Thus, at least two mechanisms exist to explain U-Pu solution behavior during the algal bloom, but both are directly controlled by redox conditions at the sediment-water interface.

## Association of trivalent (tetravalent) actinides with organic matter

The observations of earlier sorption of [241]Am and [244]Cm during the bloom, coupled with the association with a high-molecular weight (nominally 6000-10,000 mol. wt) organic fraction in solution, and their subsequent re-release over a much longer time period, indicate that sorption and/or incorporation into algal detrital material plays a major role in the cycling of these elements. Conversion of insoluble

detrital organic mattter to smaller molecular weight fragments (humic materials) by microbial degradation could explain the observed solubility pattern. Humic relationships are known to be important for U(IV) (Szalay 1964 and Langmuir 1978), and are inferred for Pu(III,IV), as well. Sorption of $^{238}$Pu, $^{239,240}$Pu, and $^{241}$Am to algal detritus in Hanford's U-Pond, a shallow, organically enriched, hypereutrophic aquatic system, produced concentrations 50 to 60 times those in bed sediment, a $10^6$ to $10^8$ enrichment relative to water (Emery et al. 1974, 1978). The importance of dissolved organic matter in increasing mobility of transition metals in natural waters is well recognized, but the exact nature of the association and the significance to biological systems is not yet well understood (Stumm and Morgan 1970); the same must be said for actinide associations at present.

## Long-term changes expected in trivalent actinide behavior in ORNL Pond 3513

Although Pond 3513 currently maintains a sediment-water exchange equilibrium for the actinides, it is clearly only quasi-stable for Pu (significant long-term correlations with time) and for Cm and Am, as well (nonuniformity in sediment-water exchange). The nonuniformity in Am-Cm exchange behavior will eventually resolve itself when differences in chemical associations and depth distribution in sediments are eliminated with time. The results of the sediment anaerobiosis experiment indicated that $^{241}$Am was obth chemically and physically occluded relative to $^{244}$Cm in sediments. In this case, differing chemical and temporal factors, $^{241}$Am being formed in situ under the chemical conditions of a $^{241}$Pu parent nuclide buried in sediments and

$^{244}$Cm entering the system in a soluble waste stream at a much later date, thus, localizing in the upper sediment layer, produced these differences in behavior. This phenomenon, often hypothesized, but seldom, if ever, demonstrated, may be more widespread than formerly believed. If such phenomena are not correctly interpreted, significant deviations in predictions of transuranic biological availability will result. On a geologic time scale, equilibrium differences in geochemical behavior of Am(III) and Cm(III) must be relatively insignificant because of similar chemistries (Gel'man 1962, Moskvin 1971a, Taylor 1973, Thompson et al. 1949). It is nonetheless significant that such a difference in observed behavior (25:1 in sediment-water exchange) can occur because of anthropogenic influences over a very short time scale ($\leq$10 y). Similar phenomena were observed for anthropogenic sources of nonradioactive heavy metals and transition elements in sediments, most recently by Skei and Paus (1979).

Under laboratory conditions of pH, ionic strength, and carbonate comparable to Pond 3513 values, Allard and Beall (1979) reported $K_d$'s for $^{241}$Am primarily in the range 1 to 10 x 10$^3$ for over 30 natural minerals (including quartz, gibbsite, biotite, dolomite, calcite, albite, olivine, montmorillonite, kaolinite, muscovite, olivine, chlorite, augite, etc.). The estimated $K_d$ for $^{244}$Cm from Pond 3513 was 5.9 x 10$^3$, very comparable to the median value of the data above. This observation suggests that the $^{241}$Am $K_d$ obtained from Pond 3513 data, 1.3 x 10$^5$, is high because $^{241}$Am is occluded relative to $^{244}$Cm in the surficial sediment layer.

## Apparent dominance of U sorption processes over carbonate complexation

The results of correlation analyses for $^{238}$U in pond water support the notion that sorption processes are dominant in the long term: strongest positive associations are with Mg and monovalent cations rather than with carbonate. Negative correlations with Ca and $SO_4$ may be caused by carbonate precipitation by biological activity and by seasonal sulfide-sulfate equilibria which are, in turn, superimposed on local rainfall-evapotranspiration cycles. Lowered Ca (carbonate precipitation) and $SO_4$ (reduction to sulfide in sediments) observed in late summer and fall were coupled with increased Mg, K, and Na because of evaporative concentration (low rainfall, high temperatures). Increased Ca and $SO_4$ (by reverse mechanisms) observed in winter and early spring were associated with lower Mg, K, and Na concentrations because of water volume increases (high rainfall, low temperatures). Theoretical considerations would seem to dictate a strong $CO_3^{--}$ correlation for $^{238}$U in an alkaline system like Pond 3513 (Langmuir 1978). A relatively weak association was observed in the 9 March 1977 to 14 November 1978 period, $r(\alpha) = 0.426$ (0.02) (compare with values in Table 4), but no significant association was evident thereafter.

## Potential difference in valence between oxidized Pu and U

Although oxidized Pu is predominant in Pond 3513, significant differences in behavior between Pu and U are evident (Fig. 1, Tables 4, 10). The strong correlation between Pu, but not U, and hydroxyl ion over the observation period is particularly notable. Under laboratory conditions of pH (8.8) and carbonate comparable with the pond, Moskvin

(1971b) determined that the Np(V) hydroxyl complex would predominate, but that carbonate would prevail in Np(VI) associations. Because Np(V) and Pu(V) behavior should be comparable, the Pond 3513 field data provide support for the hypothesis that Pu(V) is the prevalent oxidation state in solution (see companion paper by Bondietti et al.).

## CONCLUSIONS

Observed variations in actinide solubility in Pond 3513 are superimposed on an apparent baseline much higher than that which all but a few other natural aquatic ecosystems possess, yet well below chemical saturation levels (see companion paper by Bondietti et al.). Observed uranium concentrations (closest of the actinides to saturation) are several orders of magnitude lower than carbonate equilibrium would indicate. This may be a partial explanation for the lack of strong carbonate correlations.

Dissolved actinide concentrations in natural aquatic ecosystems are controlled by (adapted from Langmuir 1978):

(1) concentrations in minerals, sediments, and relative leachability;

(2) proximity to actinide-mineral deposits or anthropogenic sources;

(3) relative hydrologic isolation from rainfall dilution and actinide fluxes in tributaries;

(4) evapotranspiration;

(5) pH and redox conditions;

(6) concentrations of complexing or precipitating ligands; and

(7) concentrations of highly sorptive materials, organic matter, hydrous oxides, and clays.

Reasons for the high baseline solubility of actinides in ORNL Pond 3513 are obvious to some extent: large historical inputs of relatively soluble compounds and, consequently, relatively high leachability from sediments [factors (1) and (2)]. Given the high source-terms associated with some anthropogenic sources, sorption [factor (7)] by sedimentary materials should be most important in both anthropogenically disturbed and pristine environments (Bondietti et al. 1979; Emery et al. 1974, 1978; Eyman and Trabalka 1978; Eyman and Trabalka, in press; Hetherington et al. 1975, 1976; Koval'skii and Voronitskaya 1965; Murray and Avogadro 1979; Murray and Fukai 1975; Nelson and Lovett 1978; Pillai and Mathew 1976; and Wahlgren et al. 1976, 1977a, 1977b). Factors (3), (4), (5) and (6) all play a role in controlling temporal fluctuations around the baseline; in the short term, factor (5) was observed to be most significant in Pond 3513. Concentrations of hydroxyl and carbonate ions are obviously correlated with pH; thus, factors (5) and (6) are intimately associated, at least in relation to U and Pu behavior.

Analyses of field sampling data from ORNL Pond 3513 indicate that actinide solubility is dominated by:

(1) pH-dependent effects on sorption of U(VI), Pu(V,VI), and a fraction of Am, Cm(III);

(2) system redox effects on sorbents (e.g., hydrous oxides) and U(VI), Pu(V,VI); and

(3)  internal solution-detritus cycling of organic carbon on

Pu(III,IV) and Am, Cm(III).

However, relatively little is known of the detailed mechanisms of actinide oxidation state-specific sorption from natural waters onto characteristic sorbents, of in situ redox effects in natural sedimentary materials, or of specific actinide-organic association mechanisms and cycles in natural systems. Long-term studies of labelled natural systems coupled with laboratory research to resolve questions of specificity outlined above will be required before accurate predictions on the principal mechanisms controlling the biogeochemical behavior of the Th-Cm actinide series, so important in nuclear fuel cycles, can be made.

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