

Pu(V) AS THE STABLE FORM OF OXIDIZED PLUTONIUM IN NATURAL WATERS*

K.A. ORLANDINI, W.R. PENROSE and D.M. NELSON

Argonne National Laboratory, Environmental Research Division, 9700 South Cass Avenue, Argonne, IL 60439 (U.S.A.)

(Received November 5, 1984; revision accepted October 3, 1985)

ABSTRACT

Orlandini, K.A., Penrose, W.R. and Nelson, D.M., 1986. Pu(V) as the stable form of oxidized plutonium in natural waters. *Mar. Chem.*, 18: 49–57.

This work presents analytical evidence supporting the proposition that Pu(V) is the sole or predominant form of oxidized plutonium in natural waters. Two independent methods, the selective adsorption of Pu(VI) by silica gel, and the somewhat less selective coprecipitation of Pu(V) with calcium carbonate, were developed to separate Pu(V) from Pu(VI). Measurements of ambient plutonium in several natural waters by these methods found only Pu(V). In laboratory tracer studies, Pu(VI) was shown to be highly unstable in dilute bicarbonate solution and in Lake Michigan water, reducing in first-order fashion to Pu(V).

INTRODUCTION

Studies of plutonium speciation have shown that the oxidized form of the element constitutes a major fraction of the dissolved plutonium in some natural waters (Nelson and Lovett, 1978; Wahlgren and Orlandini, 1982). For methodological reasons, oxidized plutonium has been regarded as the sum of the oxidation states (V) and (VI), and reduced plutonium as the sum of (III) and (IV). For many purposes, this distinction has been adequate, since it has been assumed that the behaviors of Pu(III) and Pu(IV) in natural water were similar to each other, but quite different from those of Pu(V) and Pu(VI). This assumption is based on analogies between the behaviors of the lanthanide rare earths (e.g., La(III)), thorium(IV), neptunium(V), uranium(VI), and plutonium of the corresponding oxidation state. Reduced plutonium consists of the cations Pu^{3+} and Pu^{4+} (and their complexes), and binds readily to particles and surfaces in natural waters, as do La(III) and Th(IV). Oxidized plutonium consists of the cations PuO_2^+ and PuO_2^{2+} (and their complexes), whose affinities for particles are substantially less, and similar to those of Np(V) and U(VI). The distinction between oxidized and reduced Pu has been shown to be a very important factor in determining the fate of this element in natural waters (Wahlgren and Orlandini, 1982).

The actual distribution of oxidized plutonium between the (V) and (VI)

* Work performed under the auspices of the U.S. Department of Energy.

states in natural waters has been a subject of speculation for several years. In the absence of suitable analytical techniques for distinguishing them at environmental concentrations, much of the debate has been based on theoretical arguments. Aston (1980) suggested that the most likely form of plutonium would be the (VI) state, based on calculations considering hydrolysis and complexation of plutonium with carbonate, sulfate, fluoride, nitrate, and chloride. The values for the association constants of these complexes were drawn from Gel'man et al. (1962) and Cleveland (1970), which had been compiled from the work of many authors on many types of water, over a long period of time, and with undetermined quality control. Furthermore, constants for some potentially important complexes are not available at all. Silver (1983) contested the presence of Pu(VI), pointing out that the distribution of oxidation states would be very sensitive to small uncertainties in the various association constants. He ended by suggesting that pentavalent plutonium was the most likely species.

Experimental measurements which differentiate Pu(V) from Pu(VI) are sparse. Bondiotti and Trabalka (1980) employed the differential adsorption of Pu(V) and Pu(VI) to titanium oxide to assign the (V) state to Pu in a small alkaline pond of pH 9–11. They simultaneously demonstrated a strong pH dependence of the differential adsorption. Separations were based on an approximately twofold difference in adsorption between Pu(V) and Pu(VI).

We have made use of the much greater selectivity of silica gel and calcium carbonate. Silica gel was used by Inoue and Tochiyama (1977) to distinguish the (V) and (VI) oxidation states of neptunium. The adsorption properties of both Np(V) and Np(VI) are strongly dependent on pH, but a useful pH range (5–7.5) is available where most Np(VI) is adsorbed, and little Np(V). We have now modified this method for the separation of Pu(V) and Pu(VI) in natural water samples. In addition, we have found that Pu(V) is coprecipitated with calcium carbonate, leaving Pu(VI) in solution; this process is somewhat less selective than the silica gel method, but serves to complement and confirm the results obtained with silica gel.

METHODS

Preparation of tracers

Samples of Pu in oxidation states (IV) and (VI) were generated according to the methods of Lovett and Nelson (1981). Pu(IV) was produced by evaporating a sample to dryness several times in concentrated nitric acid, Pu(VI) was produced by electrolysis in 0.8 M HNO₃. Pu(V) was also generated by electrolysis, but in 1 M HCl. The HCl concentration decreased from 1.0 to 0.1 M during the course of the electrolysis due to the evolution of Cl₂. Pu(IV) was stored in 8 M HNO₃, Pu(V) in 0.1 M HCl, and Pu(VI) in 0.8 M HNO₃. No change in oxidation state was noted in any of these solutions over the course of several months. Np(V) was prepared by heating in 1 M HNO₃.

^{237}Pu and ^{235}Np were prepared in the cyclotron facility of Argonne National Laboratory and radiochemically separated and purified by J.J. Hines of the Chemistry Division.

Silica gel adsorption

Commercially available silica gel (Mallinkrodt AR, 100 mesh) was used throughout this study. It was normally added as a slurry to the water being tested; the pH was adjusted to match that of the water.

Laboratory experiments, done to develop the method, used ^{237}Pu of known initial oxidation state. Batch equilibrations using 100–200-ml samples were shaken for 2–5 min by hand in polyethylene bottles. The silica gel was separated immediately by filtration through 0.45- μm filters (Millipore HA). Both filter and filtrate were counted on a NaI(Tl) gamma-ray spectrometer, with appropriate corrections for counting geometry.

Samples of natural waters in which the ambient plutonium was to be measured were processed in the field after filtration through 0.45- μm membranes. To facilitate handling of large (~ 50 l) samples, the adsorption step was normally done on several portions of the sample sequentially. Typically, 100 g of silica gel was added to each 10-l subsample, which was then shaken for 5 min and filtered to remove the silica gel. Because the Pu in these natural samples did not consist of a single oxidation state, as was the case in the laboratory studies, the concentrations of dissolved Pu in both the oxidized and reduced forms were measured before and after silica gel treatment. The method used was the rare earth fluoride procedure described by Lovett and Nelson (1981). Samples were spiked with internal standards of $^{236}\text{Pu}(\text{VI})$ and $^{242}\text{Pu}(\text{IV})$ to monitor recovery of the oxidized and reduced Pu fractions, and made 0.8 M in HNO_3 . Lanthanum (or neodymium) fluoride was generated to coprecipitate Pu(III, IV). Ferrous iron was then added to the filtrate to reduce Pu(V, VI) to Pu(III, IV) and a second LaF_3 (or NdF_3) precipitation was performed to recover this fraction. Plutonium in these precipitates was purified, electrodeposited, and counted by high-resolution alpha-spectrometry. Controls consisted of identical samples of water concurrently carried through the same series of steps to determine the initial concentrations of Pu(III, IV) and Pu(V, VI) but with the silica gel adsorption step omitted.

Calcium carbonate coprecipitation

Laboratory tracer experiments were conducted in filtered Lake Michigan water using ^{237}Pu or ^{235}Np of known initial oxidation state. Calcium nitrate was added to these solutions to raise the total calcium concentration to 0.01 M and calcium carbonate was precipitated by the addition of a slight excess of sodium carbonate. The calcium carbonate was removed by filtration and both filter and filtrate were counted on a NaI(Tl) gamma-ray spectrometer.

We observed that preformed CaCO_3 scavenged Pu much less efficiently, and that homogeneous precipitation gave the best yields.

Samples in which ambient Pu was to be measured were prefiltered through $0.45\text{-}\mu\text{m}$ filters (Millipore HA). Calcium nitrate and sodium bicarbonate were added to raise the total calcium content to 0.06 M, and the bicarbonate content to 0.04 M. After mixing, the pH of the sample was raised to 9 ± 0.5 with sodium hydroxide to initiate precipitation of calcium carbonate. The precipitate was removed by filtration and dissolved in 8 M nitric acid. This solution was then passed through a Dowex 1 anion exchange column to remove any Pu(IV). The effluent from the column was heated in the presence of hydrogen peroxide (0.1 M) to reduce any Pu(V) or Pu(VI) to Pu(IV) and then passed through a second anion exchange column. The Pu was eluted from these columns with 0.1 M HCl/0.01 M HF, electrodeposited and counted on high-resolution alpha-spectrometers. Internal standards added to the original sample demonstrated that this procedure yielded the same distribution of plutonium, between reduced and oxidized forms, as did the LaF_3 precipitation procedure.

RESULTS AND DISCUSSION

Binding of tracer Pu(V) and Pu(VI) to silica gel

The distribution coefficients, $K_D = \text{concentration on solids (fCi kg}^{-1}\text{) divided by the concentration in solution (fCi l}^{-1}\text{)}$, of Pu(V) and (VI) onto silica gel were measured across the pH range encountered in most natural waters using ^{237}Pu tracers added to 0.002 M NaHCO_3 . The pH was adjusted with HCl or NaOH. Pu was maintained in the (VI) state by the presence of 10^{-5} M KMnO_4 in the relevant experiments. The results for the pH range 2.6–7.9 are shown in Fig. 1. Although the K_D values are similar and very low at low pH, the K_D of Pu(VI) rises substantially as the pH approaches neutrality. The K_D values of Pu(VI) and Pu(V) differ by a factor of approximately 200 between pH 6 and 8. This is sufficient to ensure good analytical separation of the two oxidation states. For example, using 2 g of silica gel per liter, about 95% of the Pu(VI) and only 5% of the Pu(V) would be extracted. Separate experiments demonstrated that the reduced form of Pu is extracted almost quantitatively throughout this range.

Instability of tracer Pu(VI) in neutral solutions

Based on silica gel adsorption, Pu(VI) was found to be very rapidly converted to Pu(V) in both sodium bicarbonate solution and natural waters (Fig. 2). In 0.01 M NaHCO_3 , the conversion of Pu(VI) to Pu(V) proceeded very rapidly ($K = 0.184 \text{ min}^{-1}$), and was essentially complete in one half hour. In Lake Michigan water, the rate was substantially slower ($K = 0.020 \text{ min}^{-1}$), for reasons that were not apparent, but reduction to Pu(V) was still

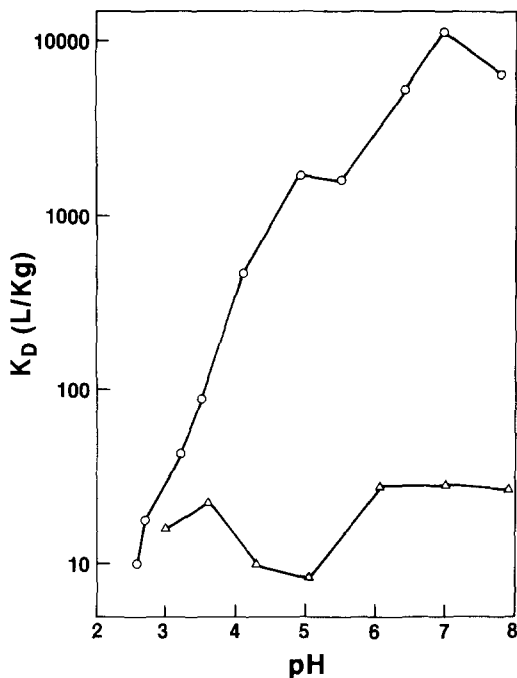


Fig. 1. Effect of pH on the sorption of Pu(V) (Δ) and Pu(VI) (\circ) to silica gel. Propagated counting errors (1σ) are $\leq 10\%$.

complete within a few hours. If a trace of permanganate ($\sim 10^{-5}$ M) was present in the lake water, no reduction whatever was observed. Rare earth fluoride precipitations carried out at the end of these experiments demonstrated that a negligible fraction of the Pu had been reduced to the (III) or (IV) state.

We therefore concluded that (a) Pu(VI) was inherently unstable in Lake Michigan water, and (b) Pu(V) could be prepared and maintained for experimental purposes by diluting electrolytically produced Pu(VI) into NaHCO_3 solution. Pu(VI) was stable indefinitely in 0.8 M HNO_3 or 10^{-5} M KMnO_4 .

Coprecipitation of tracer Pu(V) and Pu(VI) with calcium carbonate

The selectivity of CaCO_3 coprecipitation was investigated using ^{237}Pu in the (IV), (V) and (VI) oxidation states, as well as ^{235}Np in the (V) and (VI) states. Both Pu(VI) and Np(VI) were held in the (VI) state by the presence of 10^{-5} M KMnO_4 in the relevant experiments. Lake Michigan water, filtered through $0.45\text{-}\mu\text{m}$ filters, was used in these experiments. Precipitation of 0.01 moles of CaCO_3 per liter carried 75% of the tracer Pu(V) but only 18% of the Pu(VI). The corresponding figures for neptunium(V) and -(VI) were 92 and 15%.

An attempt was made to optimize the separation by varying the amount

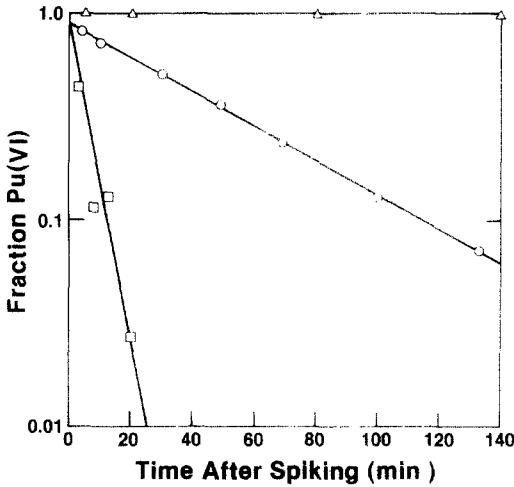


Fig. 2. Reduction of Pu(VI) to Pu(V). Solutions were spiked with $^{237}\text{Pu(VI)}$ and at timed intervals aliquots were withdrawn and equilibrated with silica gel (10 g l^{-1}). Solutions tested were 0.01 M NaHCO_3 (\square); Lake Michigan water (\circ); and Lake Michigan water plus 10^{-5} M KMnO_4 (\triangle). Propagated counting errors (1σ) are $\leq 10\%$.

of CaCO_3 precipitate. However, when the yield of pentavalent actinide was increased or decreased, the yield of the hexavalent form varied accordingly. The CaCO_3 method was therefore somewhat less selective than silica gel adsorption, but could be employed nonetheless to confirm the results of the silica gel procedure.

Measurements using ambient plutonium in natural waters

Duplicate samples of water were recovered from Lake Michigan, the Irish Sea near the Windscale reprocessing plant, and two stations in the mid-Pacific Ocean. One of each duplicate was treated with silica gel, and both were analyzed for reduced and oxidized plutonium. The results are shown in Table I. Little difference is observed in the concentrations of oxidized plutonium between the samples before and after silica gel treatment. Since Pu(VI) was shown to be effectively removed by silica gel in the laboratory studies, this implies that the ambient oxidized plutonium in these waters is predominantly Pu(V). Concentrations of Pu(III, IV) are much lower in the seawater samples after silica gel treatment, in agreement with the laboratory observations of nearly complete adsorption. We have no explanation for why Pu(III, IV) was not removed efficiently from the Lake Michigan sample. The overall effectiveness of the extraction procedure toward hexavalent actinides was confirmed by measurements of ambient uranium in the Lake Michigan sample. The concentration of ^{238}U decreased from 93 to 5.3 fCi l^{-1} following silica gel treatment, as would be expected from the behavior of Pu(VI) in the laboratory studies.

TABLE I

Comparison of the concentrations (fCi l^{-1}) of reduced and oxidized plutonium found in natural waters before and after equilibration with silica gel

Sample	Reduced Pu		Oxidized Pu	
	No silica gel	After silica gel	No silica gel	After silica gel
Irish Sea ^a	35 ± 2^e	5 ± 1	99 ± 4	123 ± 4
Pacific Ocean #1 ^b	1.08 ± 0.06	0.10 ± 0.02	1.75 ± 0.05	1.48 ± 0.08
Pacific Ocean #2 ^c	0.93 ± 0.06	0.11 ± 0.01	1.41 ± 0.07	1.07 ± 0.05
Lake Michigan ^d	0.06 ± 0.02	0.08 ± 0.02	0.41 ± 0.03	0.47 ± 0.03

^a April 1979, "Cirolana" 4/79, Station 98, surface, $54^{\circ}20'N$, $3^{\circ}37'W$.

^b May 1980, "Thomas Washington" RAMA02, Station 161, 550 m depth, $29^{\circ}57'N$, $158^{\circ}46'W$.

^c May 1980, "Thomas Washington" RAMA02, Station 166, 550 m depth, $30^{\circ}03'N$, $158^{\circ}49'W$.

^d July 1979, mid-Southern Basis, 100 m depth, $42^{\circ}40'N$, $87^{\circ}00'W$.

^e Single determinations; errors shown are 1σ statistical errors of counting.

The observation that the ambient oxidized Pu in Lake Michigan behaved like Pu(V) and not like Pu(VI), i.e., it was not adsorbed by silica gel, was confirmed by its coprecipitation with calcium carbonate. Table II compares the oxidation state distributions measured by direct lanthanum fluoride coprecipitation with those found in CaCO_3 precipitated from Lake Michigan water. The agreement in the data for the two treatments shows that the ambient plutonium, in both the oxidized and reduced forms, was carried almost quantitatively by CaCO_3 . Pu(VI) was shown to be very poorly carried ($< 20\%$) in laboratory experiments conducted under similar conditions, suggesting that Pu(VI) was not an abundant form and that the oxidized fraction must have been dominated by Pu(V). Separate experiments in which ambient ^{238}U was measured demonstrated that hexavalent actinides were poorly carried ($\sim 7\%$) under the same conditions.

These observations agree with the findings of Bondietti and Trabalka (1980) and suggest that Pu(V) is the predominant form of oxidized plutonium in most natural waters. Although only a few waters have been tested, they cover a wide range of conditions from a small eutrophic pond to a major oligotrophic lake to coastal seawater to open ocean water, and all point to Pu(V). Furthermore, the source of the plutonium was apparently not important as two of the areas (Lake Michigan and the central Pacific Ocean) contained only Pu from global fallout while the other two were contaminated by local industrial sources. Experiments using three different extractants (SiO_2 , CaCO_3 , and TiO_2) all agree and show the results are not method dependent.

Since Pu(V), and not Pu(VI), was the major oxidized form in solution, it appears that uranium is not the proper analogue element to use in predicting

TABLE II

Comparison of the concentrations (fCi l^{-1}) of reduced and oxidized plutonium found in Lake Michigan Water using two coprecipitation methods

Date of sampling	Reduced Pu		Oxidized Pu	
	LaF ₃ method	CaCO ₃ method	LaF ₃ method	CaCO ₃ method
April 1977 ^a	0.07 ± 0.03	0.04 ± 0.01	0.20 ± 0.04	0.17 ± 0.02
June 1977 ^b	0.06 ± 0.03	0.07 ± 0.01	0.26 ± 0.04	0.28 ± 0.04
October 1977 ^b	0.04 ± 0.01	0.06 ± 0.01	0.26 ± 0.04	0.31 ± 0.04

^a Chicago water filtration plant inlet.

^b 15 km SW of Grand Haven, MI, 60 m depth.

the behavior of oxidized plutonium. Neptunium, because of the increased stability of the pentavalent oxidation state, is the more logical choice. Keeney-Kennicutt and Morse (1984) have recently examined the sorption behavior of Np(V) toward a variety of common mineral surfaces and find calcium carbonate minerals (aragonite and calcite) to be the best adsorbers. This agrees with our observation that freshly precipitated CaCO₃ is a good carrier for Pu(V). Fowler and Aston (1982) have demonstrated a positive correlation between the K_D value of neptunium toward a variety of natural sediments and the total carbonate content of those sediments. These observations suggest that, in natural water systems, the presence of carbonate minerals could play an important role in determining the partitioning of oxidized plutonium between dissolved and particulate forms.

ACKNOWLEDGMENTS

Measurements in the Irish Sea were done in cooperation with scientists from the Fisheries Radiobiological Laboratory, Lowestoft, United Kingdom, aboard the R/V "Cirolana" operated by the Ministry of Agriculture, Fisheries, and Food. Measurements in the Pacific were done in cooperation with scientists from the Woods Hole Oceanographic Institution aboard the R/V "Thomas Washington" operated by the Scripps Institution of Oceanography.

REFERENCES

- Aston, S.R., 1980. Evaluation of the chemical forms of plutonium in seawater. *Mar. Chem.*, 8: 319–325.
- Bondietti, E.A. and Trabalka, J.R., 1980. Evidence for plutonium(V) in an alkaline, freshwater pond. *Radiochem. Radioanal. Lett.*, 42: 169–176.
- Cleveland, J.M., 1970. *The Chemistry of Plutonium*. Gordon and Breach, New York, 653 pp.
- Fowler, S.W. and Aston, S.R., 1982. Application of ²³⁵Np in experimental aquatic radioecology: preliminary observations on neptunium behavior in sea water, sediments, and zooplankton. *Health Phys.*, 42: 515–520.

- Gel'man, A.D., Moskvina, A.I., Zaitsev, L.M. and Mefod'eva, M.P., 1962. The Complex Compounds of the Transuranium Elements. Consultants Bureau, New York, 208 pp.
- Inoue, Y. and Tochiyama, O., 1977. Determination of the oxidation states of neptunium at tracer concentrations by adsorption on silica gel and barium sulfate. *J. Inorg. Nucl. Chem.*, 39: 1443-1447.
- Keeney-Kennicutt, W.L. and Morse, J.W., 1984. The interaction of Np(V)O_2^+ with common mineral surfaces in dilute aqueous solutions and sea water. *Mar. Chem.*, 15: 133-150.
- Lovett, M.B. and Nelson, D.M., 1981. Determination of some oxidation states of plutonium in sea water and associated particulate matter. In: *Techniques for Identifying Transuranic Speciation in Aquatic Environments*. International Atomic Energy Agency, Vienna, pp. 27-35.
- Nelson, D.M. and Lovett, M.B., 1978. Oxidation state of plutonium in the Irish Sea. *Nature (London)*, 276: 599-601.
- Silver, G.L., 1983. Comment on the evaluation of the chemical forms of plutonium in seawater and other aqueous solutions. *Mar. Chem.*, 12: 91-96.
- Wahlgren, M.A. and Orlandini, K.A., 1982. Comparison of the geochemical behavior of plutonium, thorium, and uranium in selected North American Lakes. In: *Environmental Migration of Long-Lived Radionuclides*. IAEA-SM-257/89, International Atomic Energy Agency, Vienna, pp. 757-774.