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Plutonium and Americium Behavior in coral Atoll  
Environments

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## Chapter 14

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### Plutonium and Americium Behavior in Coral Atoll Environments

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#### ABSTRACT

Inventories of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  greatly in excess of global fallout levels persist in the benthic environments of Bikini and Enewetak atolls. Quantities of  $^{239+240}\text{Pu}$  and lesser amounts of  $^{241}\text{Am}$  are continuously mobilizing into solution from these sedimentary reservoirs. The amount of  $^{239+240}\text{Pu}$  mobilized at any time represents 0.08–0.09% of the sediment inventories to a depth of 16 cm. The mobilized  $^{239+240}\text{Pu}$  has solute-like characteristics, and different valence states coexist in solution; the largest fraction of the soluble Pu is in an oxidized form (V and/or VI). The adsorption of Pu onto sediments is not completely reversible because of changes that occur in the relative amounts of the mixed oxidation states in solution with time. Furthermore, any characteristics of  $^{239+240}\text{Pu}$  described at one location may not necessarily be relevant in describing its behavior elsewhere following mobilization and migration. The relative amounts of  $^{241}\text{Am}$  to  $^{239+240}\text{Pu}$  in the sedimentary deposits at Enewetak and Bikini may be altered in the future because of mobilization and radioactive decay. Mobilization of  $^{239+240}\text{Pu}$  is not a process unique to these atolls, and quantities in solution derived from sedimentary deposits can be found at other global sites. These studies in the equatorial Pacific have significance in assessing the long-term behavior of the transuranic elements in any marine environment.

## 14.1. INTRODUCTION

Many of the questions regarding deep-sea disposal of transuranic elements and other long-lived radionuclides can be partially answered from studies at contaminated, more accessible locations where some of the processes, reactions, and rates that influence the fate of these radionuclides in the marine environment can be identified and evaluated. Reliable information on the behavior of these radionuclides in the ocean is required to improve one's understanding of the pathways that may lead back to humans from future practices involving disposal either onto or into marine sediments,

One important question related to the long-term behavior of transuranic elements in the marine environment is whether the radionuclides, after deposition in the bottom sediments, can return to the water column and eventually reenter food chains remote from the point of origin. At some sites contaminated by global fallout or surface discharges in which high concentrations of Pu are maintained in the overlying water column, mobilization of Pu from sedimentary sources to solution is difficult to demonstrate (Carpenter and Beasley, 1981; Nelson and Lovett, 1981). At sites where Pu was introduced in sufficient quantities directly onto sedimentary materials or where present inputs to sediments are small, however, mobilization of Pu can be easily identified (Noshkin et al., 1978; Noshkin, 1980; Noshkin and Wong, 1980; Schell et al., 1980; Noshkin et al., 1981; Nelson and Metta, 1983). For example, the bottom sediments in the lagoons at Bikini and Enewetak atolls, the sites previously known as the Pacific Proving Grounds, were contaminated with fission and activation products from nuclear devices tested there between 1946 and 1958 by the United States. Following the last nuclear test at Enewetak in 1958, the residual radionuclides in the lagoon water either settled rapidly to the bottom sediments or remained as dissolved or particulate species in the water and were eventually discharged into the open ocean. If the thesis of no mobilization is accepted, a concentration of dissolved Pu in the water mass of the lagoon during any time subsequent to 1958 should be observed at a concentration equivalent to that from global fallout in the northern equatorial Pacific surface water, the replacement water for the lagoon. Since 1972, a considerable number of filtered water samples from the lagoons at Enewetak and Bikini have been analyzed. Invariably these samples contained concentrations of  $^{239+240}\text{Pu}$  and  $^{238}\text{Pu}$  in solution and in association with suspended particulate matter greatly exceeding that of the background levels

from fallout in the northern equatorial Pacific surface water. The mean concentration estimated for Enewetak and Bikini lagoons has been relatively constant for at least the last 10 y. It appears that a steady-state condition has been established for  $^{239+240}\text{Pu}$  partitioning from the sedimentary reservoirs at the atolls to solution (Noshkin and Wong, 1980).

Results discussed in this chapter address the question of both  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  mobilization at Bikini and Enewetak atolls and the geochemical properties of Pu in regions of the equatorial Pacific marine environment.

## 14.2. METHODS

### 14.2.1. History of Radionuclides in Enewetak and Bikini Atolls

Bikini and Enewetak atolls, shown with other atolls in the Marshall Islands Fig. 14.1, were the sites for 22 and 43 nuclear tests, respectively, conducted by the United States between 1946 and 1958. The testing produced fallout debris that was contaminated with transuranic elements and other radionuclides. A large amount of this labeled material entered the aquatic environment of the test sites. Other atolls to the east of the test sites were contaminated to lesser degrees by fallout.

In the United States, a moratorium on testing began on 31 October 1958, marking the end of all nuclear testing at Enewetak and Bikini atolls. The fallout debris and other post-testing activities produced a very heterogeneous distribution of radionuclides in the lagoon sediments. Today, quantities of long-lived fission products such as  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ , and  $^{155}\text{Eu}$ ; activation products such as  $^{55}\text{Fe}$ ,  $^{60}\text{Co}$ , and  $^{207}\text{Bi}$ ; and transuranic elements such as  $^{238}$ ,  $^{239}$ ,  $^{240}$ ,  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  persist in the atolls' environment. The largest inventory of Pu at Enewetak and Bikini is associated with lagoon sediments.

Analysis of grab and core samples from the lagoons defined the areal distribution of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  in the sediment. It is estimated that approximately 9.3 and 2.8 TBq, respectively, are associated with the surface 2.5-cm layer at Enewetak, and at Bikini the inventories of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  in the surface layer are 11.5 and 6.7 TBq, respectively. The inventories to a depth of 16 cm in the sediment column at Enewetak are estimated to be 44.4 and 17.8 TBq of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$ , respectively, and at Bikini the respective values are 54.4 and 42.2 TBq (Noshkin, 1980).

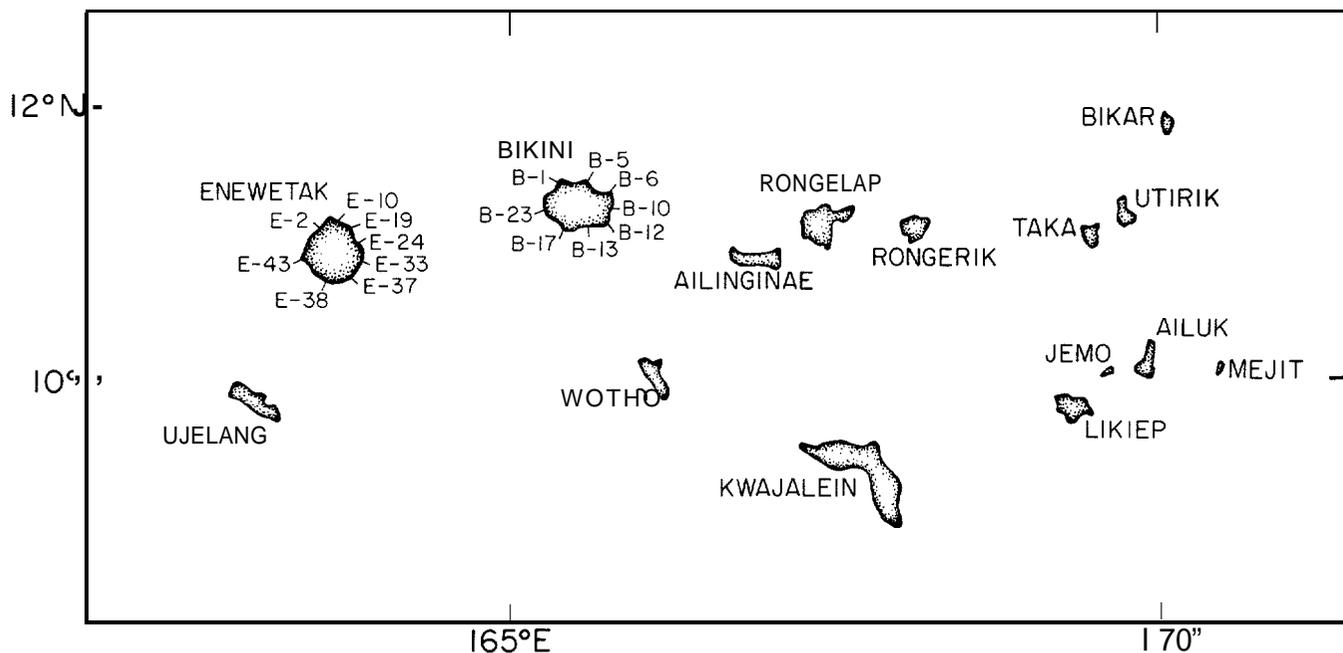


Figure 14.1. Locations of Enewetak, Bikini, and several other atolls in the Marshall Islands.

During the past few years we have been conducting studies at Enewetak and Bikini to better define the physical, chemical, and biological transport mechanisms as well as the fate of the transuranic elements and other long-lived radionuclides in the aquatic environment. Additional studies have been conducted at other atolls in the Marshall Islands and in the equatorial Pacific water outside of the atolls. These radionuclides are studied mainly to evaluate their impact on critical processes essential for the establishment and continuity of life at the atolls and because these studies can provide important data for understanding mobilization and migration processes of transuranic elements.

## 14.2.2. Experimental Studies

### 14.2.2a. Seawater-sample collections

Large-volume (50-200 liters) seawater samples obtained for analysis were collected by several methods. Within the lagoon of any atoll, filtered water samples from different depths and locations were collected aboard ship with a pump and hose fitted with an in-line filter. A 1- $\mu\text{m}$  Micro-Wynde II@ DCCPY (AMF, Cuno Division, Meriden, Connecticut) filter cartridge was used to remove particulate matter from the majority of the water samples. We have demonstrated that this filter is

as efficient in removing suspended particulate matter from the lagoon water as is a 0.2- to 0.3- $\mu\text{m}$  filter (Noshkin et al., 1974; Wong et al., 1980). Therefore, unless otherwise stated, the soluble concentrations discussed in this chapter refer to the quantity passing through a 1- $\mu\text{m}$  filter. Outside the atolls, water samples were collected at various depths by using a large-volume sampler. Plutonium and Am were either preconcentrated from the filtered water in the field by a coprecipitation technique described by Wong et al. (1978) and retained on filters or collected in 60-liter containers and returned to Lawrence Livermore National Laboratory for processing. When measurements of plutonium oxidation states were made in the field,  $^{236}\text{Pu}$  (VI) and  $^{242}\text{Pu}$  (IV) were used as yield tracers.

### 14.2.2b. Analysis

Plutonium was separated from the ashed filters, which contained either particulate matter or the preconcentrated soluble fraction of Pu, by the method described by Wong (1971). The  $^{241}\text{Am}$  was isolated and purified by using a modification of the procedure described by Bojanowski et al. (1975). Aliquots of  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  were used as yield tracers except when plutonium oxidation states were determined. Finally, Pu

and Am were electroplated onto stainless-steel disks and measured by  $\alpha$ -spectrometry. Some samples of sediment and filtered particulate matter from Bikini and Enewetak contained sufficiently high concentrations of  $^{241}\text{Am}$  to be determined directly by  $\gamma$ -spectrometry by using Ge(Li) detectors. Duplicates, blanks, and standards were routinely intermingled and processed along with the samples as part of our quality-assurance program.

### 14.3. RESULTS AND DISCUSSION

#### 14.3.1. Plutonium Concentrations in Lagoon Seawater

Tables 14.1 and 14.2 show the variation of  $^{239+240}\text{Pu}$  activity in filtered samples of seawater collected from several locations during different seasons at Enewetak and Bikini. Fallout levels of  $^{239+240}\text{Pu}$  in the surface waters of the northern equatorial Pacific have averaged  $15 \pm 7 \mu\text{Bq liter}^{-1}$  over the last 10 y (Noshkin et al., 1981b). Of this total concentration,  $16 \pm 7\%$  is associated with the filterable particulate material. Concentrations of  $^{239+240}\text{Pu}$  greater than background concentrations from global fallout were found in the water sampled from all locations throughout the lagoons. This is a direct indication that  $^{239+240}\text{Pu}$  has been continuously mobilized over the years into solution from the solid phases in these environments.

Ocean water with concentrations of Pu from global

fallout flows over the eastern and northern reefs and through the southern channels of the atolls. This water mixes with the labeled lagoon water, producing complex concentration gradients within the lagoons. Significant differences were noted in the concentration of  $^{239+240}\text{Pu}$  with the year during which it was sampled at some stations (Tables 14.1 and 14.2). It is not possible with the data available to discern any consistent trend in the change of concentration with time by comparing the results at any single station. Different seasonal, and even daily, mixing processes influence the concentration at some locations. For example, it has been previously noted that even changes in daily tidal currents affect concentrations of dissolved Pu at specific locations (Noshkin et al., 1974).

One objective was to estimate the fraction of the lagoon inventory transferred to the water column. In order to do so, it was necessary to assume that a reasonable average concentration for the entire lagoon could be determined during periods when sufficient samples were obtained for analysis. Shown in Table 14.3 are the average concentrations of soluble and particulate  $^{239+240}\text{Pu}$  estimated for Enewetak and Bikini lagoons during the periods indicated. The differences in the average concentration of soluble  $^{239+240}\text{Pu}$  determined from samples obtained during the periods indicated are not considered significant, and the assumption is made that the average amount of Pu in the water mass of the lagoon is constant. Future results from the lagoons may, however, show this to be a false premise.

**Table 14.1. Concentration of Soluble  $^{239+240}\text{Pu}$  ( $\text{mBq liter}^{-1}$ ) in Seawater Samples Collected at Specific Stations in Enewetak Lagoon**

Station Designation	October-December 1972 <sup>b</sup>	July-August 1974	May 1976	May-June 1982
5-8-4	0.51		0.84	0.44
5-8-2	0.61		1.15	0.46
5-8-1	1.20	0.77	1.06	0.77
5-7-1	0.25	1.85	0.97	0.57
5-6-6	1.63	1.74	0.77	0.72
5-6-3	0.56	1.22	0.26	0.53
5-6-2	0.21	—	0.05	0.68
5-5-4	2.44	0.08	0.17	1.41
5-5-3	0.48	0.70	0.13	0.37
5-9-4		0.32	0.57	0.27
5-9-3	0.36		0.85	0.49
5-9-2	0.42	0.26	0.29	0.51

<sup>a</sup>The 1- $\sigma$  counting error is less than 10% of listed value. A dash indicates that a sample was not taken.

<sup>b</sup>The 1972 Enewetak water samples were unfiltered. All other concentrations were determined in water sample filtered through 1- $\mu\text{m}$  filters.

**Table 14.2. Concentration of Soluble  $^{239+240}\text{Pu}$  (mBq liter $^{-1}$ ) in Sea-water Samples Collected at Specific Stations in Bikini Lagoon**

Station Designation <sup>b</sup>	December 1972	January-February 1977	September 1982
B- 15 Surface	2.26	1.00	—
B-15 Bottom	2.15	1.11	—
B-19	1.41	1.18	1.41
B-20	1.41	2.04	1.15
B-23 Surface	0.74	<b>1.63</b>	1.33
B-23 Bottom	0.32	0.49	—
B-25	2.56	2.07	—
B-2 Surface	3.44	2.74	—
B-2 Bottom	2.92	3.85	—

<sup>a</sup>The I-o counting error is less than 10% of listed value.

<sup>b</sup>A dash indicates a sample was not taken.

Since 1972, the average “soluble”  $^{239+240}\text{Pu}$  at Enewetak has been 0.78 mBq liter $^{-1}$ . At Bikini, a mean value of 1.70 mBq liter $^{-1}$  has been determined from the 1972 and 1977 collections. Taking into account the dimensions for each lagoon, these mean concentrations convert to standing inventories of 36 and 48 GBq in the lagoons at Enewetak and Bikini, respectively. These quantities, which exclude  $^{239+240}\text{Pu}$  associated with suspended particles, represent 0.08 and 0.09%, respectively, of the sediment inventories to a depth of 16 cm. The average quantity of  $^{239+240}\text{Pu}$  mobilized and found in solution at any time represents a small fraction of the

inventory associated with the major reservoir of the atolls.

#### 14.3.2. Other Evidence of $^{239+240}\text{Pu}$ Mobilization in the Central Pacific Atolls

Water and sediment samples were collected from regions of several atolls in the Marshall Islands east of Enewetak and Bikini (Fig. 14.1) and from Johnston Atoll, located at 16°44'33" N, 169°30'59" W, 1160 km

**Table 14.3. The Average Concentrations (mBq liter $^{-1}$ ) of  $^{239+240}\text{Pu}$  in Lagoon Water<sup>a</sup>**

Date of Samples	Number of Samples	Soluble	Particulate	Total
Enewetak Lagoon (Area: 933 km $^2$ ; Average Depth: 49 m)				
October-December 1972	35	0.81	0.37	1.18
July 1974	71	0.93	0.70	<b>1.63</b>
May 1976	29	0.59	0.48	1.07
May 1982	23	0.63	— <sup>b</sup>	— <sup>b</sup>
Bikini Lagoon (Area: 629 km $^2$ ; Average Depth: 45 m)				
December 1972	17	1.55	0.48	2.04
January-February 1977	26	1.81	— <sup>b</sup>	— <sup>c</sup>
September 1982 <sup>d</sup>	5	2.04	— <sup>b</sup>	— <sup>c</sup>

<sup>a</sup>Arithmetic mean values.

<sup>b</sup>Atoll not sampled.

<sup>c</sup>Not applicable.

<sup>d</sup>Incomplete results. The value shown represents an average from only 20% of the total samples obtained.

west-southwest of Hawaii. On 23 July 1962, a missile containing Pu was destroyed while still on the launch pad at Johnston Atoll. The aborted missile dispersed quantities of Pu into the surrounding shallow reef. A variety of samples have recently been collected from the marine environment of Johnston Atoll to assess the concentrations of Pu.

Average concentrations of  $^{239+240}\text{Pu}$  in the lagoon water and surface sediments from several of the northern atolls in the Marshall Islands are presented in Table 14.4, along with the range in concentrations detected at 13 stations sampled at Johnston Atoll. Samples of filtered lagoon water from several of the Marshall Islands contaminated by intermediate-range fallout and from Johnston atoll contained quantities of  $^{239+240}\text{Pu}$  in excess of the mean fallout level in the northern equatorial surface water outside the lagoon (Table 14.4). At Rongelap, the higher concentrations in the lagoon water noted in 1978 were verified in 1981, when a more extensive sampling program was conducted; therefore, mobilization of  $^{239+240}\text{Pu}$  from the sediments to the water column was evident at some of these atolls as well.

It has been noted that in shallow basins such as the Great Lakes and the Irish Sea a large fraction of introduced Pu becomes attached to sedimentary particles and is transferred rapidly to the bottom sediments (Edgington, 1981). One might, therefore, anticipate observing substantial reductions in the concentration of Pu in the

water of the shallow lagoons of the lesser-contaminated atolls such as Ailuk, Likiep, Utirik, or Wotho. The exchange rate of the lagoon water at these atolls is not accurately known, but we estimated the rate to be  $\geq 40$  d. This period is sufficiently long to permit most (95%) of the Pu from global fallout entering the lagoon to be effectively scavenged by the suspended materials during passage of water across the shallow reef. The mean concentration of  $^{239+240}\text{Pu}$  within these lagoons (Table 14.4) is not, however, distinguishable from the concentration from the average global fallout in the surface water outside the lagoon. This suggests that an equilibrium has been established at these locations between stabilized forms of fallout  $^{239+240}\text{Pu}$  in the surface seawater and in the sediments.

### 14.3.3. Oxidation States of Mobilized Plutonium in Lagoon Water

Samples of water from Bikini and Enewetak were collected and immediately processed aboard ship to determine the oxidation state(s) of the mobilized Pu in solution. Results from these analyses for both lagoons are shown in Tables 14.5 and 14.6, along with several replicate results in Table 14.6. The reproducibility among replicate analyses is considered satisfactory. The procedure used to separate reduced  $^{239+240}\text{Pu}$  (III and IV) from oxidized  $^{239+240}\text{Pu}$  (V and VI) was that described by Lovett and Nelson (1981), modified as described by Wong et al. (1985) for our use with water

Table 14.4. The Mean Water and Sediment Concentrations of  $^{239+240}\text{Pu}$  at Several Atolls in the Marshall Islands and Johnston Atoll<sup>a</sup>

Atoll	Year Collected	Surface <sup>b</sup> Sediment (Bq kg <sup>-1</sup> )	Concentration of $^{239+240}\text{Pu}$ in Water ( $\mu\text{Bq liter}^{-1}$ )		
			Soluble	Particulate	Total
Ailuk	1978	0.30	21	1.5	23
Likiep	1978	0.29	21	8.9	30
Utirik	1978	0.59	10	5.2	15
Wotho	1978	0.35	16	1.1	17
Rongelap	1978	10.32	48	49.0	98
Rongelap	1981		42	—	
Rongerik	1978	3.03	44	5.6	50
Johnston	1980	0.13-61.05	15-574	3.7-326	—
Northern equatorial Pacific surface water	1972-1982	—			15 ± 7

<sup>a</sup>A dash indicates sample not analyzed.

<sup>b</sup>Surface sediment refers to the top 3-cm layer.

**Table 14.5. The Concentration (mBq liter<sup>-1</sup>) of <sup>239+240</sup>Pu Oxidation States in Filtered Seawater at Bikini Atoll**

Station Number	Date	Depth	Reduced (III and IV)	Oxidized (V and VI)	Total	Percent Oxidized
B-1	2/81	Surface	0.33 ± 0.01	0.43 ± 0.02	0.76 ± 0.03	57 ± 3
B-1	2/81	10 m	0.49 ± 0.02	0.44 ± 0.03	0.93 ± 0.04	46 ± 4
B-1	2/81	25 m	0.49 ± 0.02	0.60 ± 0.06	1.08 ± 0.12	55 ± 7
B-5 Reef	2/81	Surface	0.98 ± 0.08	2.45 ± 0.23	3.43 ± 0.31	71 ± 10
B-6 Reef	2/81	Surface	0.21 ± 0.01	1.15 ± 0.04	1.37 ± 0.07	85 ± 6
B-20 Reef	2/81	Surface	0.14 ± 0.01	0.72 ± 0.07	0.86 ± 0.10	84 ± 12
B-1 Reef	2/81	Surface	0.21 ± 0.01	0.23 ± 0.02	0.44 ± 0.03	52 ± 4
B-19	9/82	Surface	0.22 ± 0.40	1.18 ± 0.08	1.40 ± 0.13	84 ± 4
B-18	9/82	Surface	< 0.02	1.98 ± 0.14	0.20 ± 0.14	99 ± 7
B-18	9/82	29 m	1.52 ± 0.09	2.89 ± 0.11	4.40 ± 0.22	66 ± 4
B-26	9/82	Surface	< 0.02	1.79 ± 0.07	1.81 ± 0.07	99 ± 3
B-26	9/82	48 m	0.15 ± 0.02	0.53 ± 0.04	0.64 ± 0.06	80 ± 9

**Table 14.6. The concentration (mBq liter<sup>-1</sup>) of <sup>239+240</sup>Pu Oxidation States in Filtered Seawater at Enewetak Atoll**

Station Number	Date	Depth	Reduced (III and IV)	Oxidized (V and VI)	Total	Percent Oxidized
E-24	10/79	Surface	0.17 ± 0.04	0.38 ± 0.03	0.56 ± 0.06	69 ± 9
E-24	10/79	Replicate	0.17 ± 0.04	0.48 ± 0.06	0.65 ± 0.10	74 ± 14
E-24	10/79	10 m	0.28 ± 0.04	0.85 ± 0.05	1.13 ± 0.09	75 ± 8
E-24	10/79	25 m	0.30 ± 0.05	1.01 ± 0.10	1.31 ± 0.13	77 ± 11
E-10	10/79	Surface	0.03 ± 0.01	0.32 ± 0.06	0.36 ± 0.07	91 ± 26
E-10	10/79	Replicate	0.04 ± 0.01	0.24 ± 0.03	0.28 ± 0.04	85 ± 16
5-6-1	10/79	Surface	0.19 ± 0.01	0.74 ± 0.05	0.93 ± 0.07	79 ± 8
E-10	6/82	Surface	0.05 ± 0.01	0.20 ± 0.01	0.24 ± 0.01	80 ± 6
6-2-1	6/82	Surface	0.46 ± 0.03	1.00 ± 0.05	1.45 ± 0.09	69 ± 5
6-2-1	6/82	Replicate	0.46 ± 0.04	0.93 ± 0.07	1.39 ± 0.08	67 ± 6
6-2-1	6/82	Replicate	—	—	1.41 ± 0.04	—
6-2-5	6/82	Surface	0.11 ± 0.01	0.48 ± 0.03	0.59 ± 0.05	82 ± 9
6-2-5	6/82	Replicate	—	—	0.55 ± 0.01	—
6-2-5	6/82	22 m	0.10 ± 0.01	0.40 ± 0.03	0.50 ± 0.04	80 ± 8
6-2-5	6/82	Replicate	—	—	0.47 ± 0.01	—
6-1-3	6/82	Surface	0.09 ± 0.01	0.44 ± 0.03	0.53 ± 0.04	83 ± 8
6-1-3	6/82	Replicate	—	—	0.51 ± 0.01	—
5-31-7	6/82	Surface	0.07 ± 0.01	0.38 ± 0.03	0.45 ± 0.04	85 ± 7
5-31-7	6/82	Replicate	0.06 ± 0.01	0.32 ± 0.02	0.38 ± 0.03	84 ± 7
5-31-7	6/82	Replicate	—	—	0.39 ± 0.01	—

samples larger than 50 liters. Both the reduced and the oxidized forms of <sup>239+240</sup>Pu coexisted in the lagoon water, with oxidized forms generally dominating. On the average, 78% of the total Pu in solution at both atolls was in the oxidized state.

It is difficult to identify any clear regularities or trends in the results, but, in some cases, samples from stations near the reef and near the sediment-water interface contained relatively larger fractions of reduced

Pu in solution than was found in mid-lagoon surface samples. Over 90% of the <sup>239+240</sup>Pu found associated with sedimentary or particulate material in the lagoon was in the reduced state (see footnote *b* in Table 14.7); therefore, the near-bottom or reef water would be expected to contain relatively higher concentrations of recently exchanged, reduced Pu. After desorption of reduced and oxidized species, the (III and IV) states disappear from the solution either by oxidation to the higher state or loss by adsorption onto newly exposed

Table 14.7. The concentration of  $^{239+240}\text{Pu}$  Oxidation States Released into Seawater and  $K_d$  Values after Mixing Lagoon Sediments from Enewetak off Station E-2<sup>a</sup>

Sample ID	Mixing Time (h)	Sediment* Concentration ( $\text{Bq g}^{-1}$ )	Reduced (III and IV) ( $\text{mBq liter}^{-1}$ )	Oxidized (V and VI) ( $\text{mBq liter}^{-1}$ )	$K_d \times 10^5$ <sup>c</sup>		
					Apparent	Reduced	Oxidized
<u>Fine Fraction (&lt; 0.5 mm)</u>							
439/440	3.5	0.74 (2)	1.89 (14)	2.44 (12)	1.7	3.4	0.12
443/444	3.5	0.65 (2)	2.63 (17)	1.78 (17)	1.5	2.4	0.15
399/400	24	0.63 (2)	0.85 (22)	2.00 (9)	2.2	7.1	0.13
411/412	24	0.70 (2)	0.52 (41)	2.48 (14)	2.3	13.0	0.11
427/426	74	0.72 (2)	0.44 (23)	2.96 (8)	2.1	15.6	0.10
<u>Coarse Fraction (&gt; 0.5 mm)</u>							
379/380	26	0.092 (4)	0.26 (54)	0.48 (26)	1.2	3.4	0.08
383/384	26	0.107 (5)	0.13 (38)	1.04 (13)	0.9	7.9	0.04
391/392	81	0.018 (3)	< 0.01	1.18 (11)	0.9	> 10	0.04

<sup>a</sup>Values in parentheses are the 1- $\sigma$  counting error expressed as percent of the value listed.

<sup>b</sup> $96 \pm 2\%$  of the total  $^{239+240}\text{Pu}$  associated with sediments was in the reduced state. There was 3.3-9.2 g of sediment mixed with 0.95 liters of filtered seawater.

<sup>c</sup>Apparent  $K_d$  = total concentration of  $^{239+240}\text{Pu}$  in dry sediment ( $\text{Bq kg}^{-1}$ ) / total concentration of  $^{239+240}\text{Pu}$  in solution ( $\text{Bq liter}^{-1}$ ). Reduced  $K_d$  = 96% of the total concentration in dry sediment/reduced concentration in solution. Oxidized  $K_d$  = 4% of the total concentration in dry sediment/oxidized concentration in solution.

surfaces. Laboratory experiments discussed in the next section provide results that support the former possibility. In either case, the oxidized forms of Pu become the dominant species in older water with longer residence times in the lagoons (stations B-18, B-26, and E-10 in Fig. 14.1) and probably persist as a complexed, unreactive species. Since the reduced forms of Pu are ubiquitous in all but a few samples, however, it is possible that the reduced Pu may also be stabilized by complexation to some degree, but that the stability of the complex may change with time.

#### 14.3.4. Exchange of Plutonium between Sediments and Seawater

At any location within Enewetak and Bikini lagoons, bottom sediments consist of different quantities of fine- and coarse-grained carbonate material, shell, foraminifera tests, coral fragments, and *Halimeda* debris. All of these components have different surface areas, and, therefore, different sorptive characteristics. Transuranic elements are associated with all components of the benthic environment (Noshkin, 1980), and their rate of desorption into solution may relate to the composition of the sediment.

To mimic the desorption characteristics of  $^{239+240}\text{Pu}$

from the sediments to solution observed in the environment, we conducted experiments in the laboratory (or aboard ship) with freshly collected sediments to arrive at a value for the distribution coefficient ( $K_d$ ) for plutonium. We placed quantities of sedimentary material in plastic containers and added volumes of filtered, equatorial Pacific surface seawater with very low concentrations of dissolved Pu ( $15 \mu\text{Bq liter}^{-1}$ ). The containers were shaken over a 3-d period to mix the contents. The water was then separated from the sediments by filtration through  $0.2\text{-}\mu\text{m}$  filters. Tracers were added to the solution phase, and Pu was separated and analyzed by the procedures described. Sediments were dried, dissolved, and analyzed for Pu. The range in the apparent  $K_d$  values [total  $^{239+240}\text{Pu}$  on sediments (in  $\text{Bq kg}^{-1}$ ) divided by total  $^{239+240}\text{Pu}$  in solution (in  $\text{Bq liter}^{-1}$ )] based on the analyses of 18 different lagoon sediments was between  $0.5$  and  $5.2 \times 10^5$ , with an average  $K_d$  for  $^{239+240}\text{Pu}$  of  $2.3 \times 10^5$  (Noshkin and Wong, 1980).

With the sediment inventory values and a  $K_d$  value of  $2.3 \times 10^5$  for Pu, one can construct a simple model to predict average concentrations expected in the lagoon water by assuming that the Pu in solution at any time is in equilibrium with that in the sediments. At any time, the amount of Pu in solution is limited by the saturation

of the solution under equilibrium conditions. The rate at which water and its dissolved Pu is flushed from the lagoon is balanced by input of the lesser-contaminated oceanic water that is rapidly equilibrated with remobilized Pu from the sediments. Assuming that this steady-state condition can be achieved, the mean Pu inventory and concentration of Pu in lagoon water computed from a  $K_d$  of  $2.3 \times 10^5$  as defined above was 0.04 TBq (0.85 mBq liter<sup>-1</sup>) at Enewetak and 0.05 TBq (1.51 mBq liter<sup>-1</sup>) at Bikini. There is good agreement between the average quantities of <sup>239+240</sup>Pu predicted and the average values shown in Table 14.3. The agreement between the calculated and the measured average concentrations, where one would accept a factor of 5 as being good agreement because of the range of  $K_d$  values determined, supports the contention of a steady-state condition and demonstrates the general usefulness of this simple model in predicting long-term average concentrations in the lagoon water.

Additional time-dependent experiments and oxidation-state determinations were conducted in the laboratory with contaminated lagoon sediments. Results for the different oxidation states released into seawater from fine- and coarse-sediment fractions obtained from two locations in Enewetak Lagoon are shown in Tables 14.7 and 14.8. Of the total <sup>239+240</sup>Pu associated with the sediments used to generate these results,  $96 \pm 2\%$  was in the reduced state. When fresh seawater initially contacted the fine- and coarse-sediment fractions shown in Table 14.7, there was a rapid release of both oxidized and reduced forms of <sup>239+240</sup>Pu into solution. As the contact time with the

sediment increased, the  $K_d$  for reduced Pu increased, indicating a disappearance of the reduced forms from solution. Concurrently, the  $K_d$  determined for the oxidized forms of Pu decreased slightly, showing that the oxidized forms of <sup>239+240</sup>Pu in solution increased over the same period. This increase of oxidized forms of Pu can be accounted for by assuming that the reduced forms initially mobilized are slowly oxidized when in solution. These results confirm the field observations in which both oxidized and reduced species were initially mobilized to bottom water in the lagoon. The concentration of reduced Pu decreased with time as a result of redox reactions, leaving the oxidized forms of Pu as the dominant dissolved species in solution.

Results in Table 14.8 also show rapid mobilization of both forms into solution, followed, however, by no apparent change in concentration of either species as the contact time with the E-24 sediments increased. After 94 h, the  $K_d$  values both for the reduced and for the oxidized forms of <sup>239+240</sup>Pu from the experiment with the fine-sediment fraction were less than the values after 74 h of contact with sediments from station E-2 (Table 14.7). The reasons for the different behavior of the E-2 and E-24 sediments is unknown, and we can only speculate that both mobilized species were stabilized in solution, possibly by complexing agents derived from materials present in the sediments at station E-24 but absent at station E-2. For whatever the reasons, the field measurements suggest that the reduced forms of <sup>239+240</sup>Pu mobilized into solution from the region of station E-24 were capable of remaining in a dissolved state for longer periods of time. Plutonium mobilized

**Table 14.8. The <sup>239+240</sup>Pu Oxidation States Released into Seawater and  $K_d$  Values after Periods of Mixing with Lagoon Sediments from Enewetak off E-24<sup>a</sup>**

Sample ID	Mixing Time (h)	Sediment Concentration (Bq g <sup>-1</sup> )	Reduced (III and IV) (Bq liter <sup>-1</sup> )	Oxidized (V and VI) (Bq liter <sup>-1</sup> )	$K_d \times 10^5$		
					Apparent	Reduced	Oxidized
Fine Fraction (< 0.5 mm)							
359/360	24	0.53 (3)	0.85 (22)	8.21 (6)	0.6	6.0	0.03
363/364	24	0.54 (2)	2.07 (19)	6.70 (7)	0.6	2.5	0.03
367/364	94	0.63 (3)	1.48 (14)	9.03 (8)	0.6	4.1	0.03
371/372	94	0.63 (3)	1.96 (15)	8.81 (7)	0.6	3.1	0.03
377/620	2880	0.65 (3)	2.15 (15)	8.14 (6)	0.6	2.6	0.03
Coarse Fraction (> 0.5 mm)							
339/340	23	0.22 (5)	0.56 (19)	1.55 (10)	1.1	3.9	0.06
343/344	23	0.22 (5)	0.56 (21)	1.74 (13)	0.9	3.7	0.05

<sup>a</sup> See footnotes in Table 14.7.

into solution from any region of either lagoon could be expected to behave in a manner between that of the examples in Tables 14.7 and 14.8.

Once the reduced Pu is oxidized and in solution, the process of readsorption of  $^{239+240}\text{Pu}$  onto the sediment particles appears to be determined by an accumulation factor different than the value obtained from the desorptive experiments. Table 14.9 shows two examples in which contaminated water from Enewetak Lagoon was equilibrated with quantities of relatively uncontaminated sediment from Kwajalein Atoll. (The oxidation states of Pu associated with these sediments were not determined.) The first example shows the initial and the final  $^{239+240}\text{Pu}$  concentrations in seawater from station E-24 after mixing with sediments for 22 h. There was no difference noted between the initial and the final concentrations either of reduced or of oxidized forms of Pu in solution. The computed apparent  $K_d$ , determined by comparing the final total water concentrations with the sediment concentrations, is significantly less than are the desorption values in Tables 14.7 and 14.8, which were determined after 24 h of mixing contaminated sediment with uncontaminated water.

The second set of results was generated by using aliquots of seawater in contact with sediments for longer periods of time. Unfortunately, the water selected was not as highly labeled with  $^{239+240}\text{Pu}$  as had been anticipated, and therefore the errors associated with the determinations are large. The results, however, show a complete disappearance of reduced  $^{239+240}\text{Pu}$  from solution after 72 h, but it is impossible to assess if this loss resulted from the operation of the redox equilibrium or from adsorption onto the sediment. There was a definite loss of the oxidized state of  $^{239+240}\text{Pu}$  by adsorption

onto the sediment: the concentrations in the sediment increased from  $0.030 \pm 0.11$  to  $0.56 \pm 0.67 \text{ mBq g}^{-1}$  after equilibration. Each of the sediment samples in contact with the water for 24, 72, and 3000 h gained, on the average,  $1.1 \pm 0.03 \text{ mBq}$ , whereas  $1.2 \pm 0.03 \text{ mBq}$ , on the average, was lost from solution. The Pu lost from solution can be accounted for by the gain onto the sediments. The apparent  $K_d$  computed in Table 14.9 is the value for total Pu in solution divided by total Pu in the sediments. The adsorption in each timed experiment was rapid in that there was no further change in the concentration of oxidized forms of Pu remaining in solution after 24 h of equilibration.

While it appears possible to predict the desorption of  $^{239+240}\text{Pu}$  by using a  $K_d$  of approximately  $2.3 \times 10^5$ , the readsorption process of mobilized Pu resulted in lower accumulation factors and was more complex than predicted by the simple partitioning between solution and solid phases.

#### 14.3.5. Relationships between $^{241}\text{Am}$ and $^{239+240}\text{Pu}$

Concentration profiles to a depth of 1000 m in the equatorial Pacific, 27 km west of Bikini (station WBO) indicate that  $^{241}\text{Am}$  in the ocean is more strongly associated with particles than is  $^{239+240}\text{Pu}$  (Table 14.10). Some data from the water column 10 km from Johnston Atoll (station JAO) are provided in Table 14.11 to highlight certain features of the results at station WBO. The fact that Pu concentrations were more than ten times higher in the surface waters at station WBO as compared with the global fallout concentrations in the surface layers at station JAO indicates that mobilized

Table 14.9. Equilibration of  $^{239+240}\text{Pu}$ -Labeled Seawater with Lesser-Contaminated Sediments<sup>a</sup>

Contact Time (h)	Sediment Concentration ( $\text{mBq g}^{-1}$ )	Concentration of $^{239+240}\text{Pu}$ ( $\text{mBq liter}^{-1}$ )			$K_d \times 10^3$
		Reduced	Oxidized	Total	
0	—	0.14 (11)	0.72 (10)	0.86 (11)	—
22	0.17 (21)	0.20 (8)	0.75 (5)	0.96 (6)	0.2
0	— <sup>b</sup>	0.04 (54)	0.32 (19)	0.36 (18)	—
24	0.67 (12)	0.04 (75)	0.19 (27)	0.24 (26)	2.8
72	0.56 (15)	0.03 (40)	0.13 (14)	0.15 (13)	3.7
3000	0.63 (15)	< 0.01	0.16 (19)	0.16 (19)	3.9

<sup>a</sup>Values in parentheses are the I-a counting error expressed as percent of the value listed.

<sup>b</sup>Initial concentration in the sediment was  $0.30 (37) \text{ mBq g}^{-1}$ ; 3.84, 2.90, and 3.3 g of sediment were used in the three equilibrium equation experiments, respectively. The volume of seawater used was 1 liter.

**Table 14.10. Concentrations of Two Transuranic Elements in the water Column at Station WBO and inventory to a Depth of 1000 m<sup>a</sup>**

Depth (m)	<sup>239+240</sup> Pu (μBq liter <sup>-1</sup> )		<sup>241</sup> Am (μBq liter <sup>-1</sup> )		<sup>241</sup> Am: <sup>239+240</sup> Pu	
	Prefiltered	Solution	Prefiltered	Solution	Prefiltered	Solution
Surface	lost	170.0 (4)	lost	lost	—	—
100	1.5 (22)	18.9 (11)	lost	6.3 (45)	—	0.33 (46)
200	7.4 (15)	28.1 (11)	lost	8.1 (26)	—	0.29 (29)
300	17.0 (11)	32.9 (15)	20.0 (47)	7.0 (50)	1.2 (48)	0.21 (52)
400	18.1 (11)	55.5 (9)	22.6 (23)	< 1.0	1.2 (25)	< 0.02
500	7.8 (25)	70.3 (7)	29.2 (20)	4.1 (40)	3.8 (32)	0.06 (40)
600	1.1 (60)	59.2 (7)	14.1 (28)	6.7 (50)	12.0 (65)	0.11 (50)
700	4.4 (30)	59.2 (7)	28.5 (16)	19.2 (37)	6.4 (34)	0.32 (38)
800	4.4 (36)	81.4 (6)	24.1 (25)	13.0 (35)	5.4 (44)	0.16 (36)
900	11.5 (27)	74.0 (9)	26.6 (18)	10.0 (30)	2.3 (32)	0.14 (31)
1000	15.2 (28)	66.6 (7)	26.6 (27)	< 4.0	1.8 (39)	< 0.07
Inventory (MBq km <sup>-2</sup> ) at a depth of 1000 m	8.1	51.8	20.0	8.1	2.4	0.39

<sup>a</sup>Measured in September 1980. Values in parentheses are the I-a counting error expressed as percent of the listed value. The  $K_d$  ratio of <sup>239+240</sup>Pu:<sup>241</sup>Am to 1000 m = the ratio of inventories  $\frac{{}^{239+240}\text{Pu prefiltered/solution}}{{}^{241}\text{Am prefiltered/solution}} = 0.06$ .

**Table 14.11. Transuranic Elements in the Water Column at Station JAO and inventory to a Depth of 1000 m<sup>a</sup>**

Depth (m)	<sup>239+240</sup> Pu (μBq liter <sup>-1</sup> )		<sup>241</sup> Am (μBq liter <sup>-1</sup> )		<sup>241</sup> Am: <sup>239+240</sup> Pu	
	Prefiltered	Solution	Prefiltered <sup>b</sup>	Solution	Prefiltered <sup>b</sup>	Solution
Surface	< 4	4.8 (37)	—	< 1	—	< 0.2
100	0.7 (50)	< 4	—	4.1 (50)	—	lost
200	< 0.4	7.0 (26)	—	2.6 (20)	—	0.34 (33)
300	< 4	5.6 (8)	—	10.7 (25)	—	0.26 (26)
400	2.2 (45)	40.3 (9)	—	2.6 (60)	—	0.06 (60)
500	5.6 (23)	38.5 (12)	—	7.4 (37)	—	0.19 (39)
600	2.2 (60)	43.3 (11)	—	8.9 (30)	—	0.20 (30)
700	11.1 (25)	34.1 (9)	—	13.3 (47)	—	0.39 (48)
800	5.6 (28)	40.7 (35)	—	< 7	—	< 0.2
900	9.3 (27)	26.3 (14)	—	6.3 (30)	—	0.24 (33)
1000	8.9 (27)	30.0 (2)	—	7.8 (30)	—	0.24 (32)
Inventory (MBq km <sup>-2</sup> ) at a depth of 1000 m	4.8	29.2	—	6.7	—	0.23

<sup>a</sup>Values in parentheses are the I-o counting error expressed as the percent of the listed value.

<sup>b</sup>Samples not analyzed.

forms of <sup>239+240</sup>Pu are passed from the lagoon to the water mass of the northern equatorial Pacific. The concentrations throughout the upper 1000 m at station WBO originate from Bikini and are supplemented by global fallout concentrations typical for this region.

Whereas the <sup>239+240</sup>Pu concentration in solution from all depths sampled at station WBO exceeded that for the particulate materials filtered, the opposite was true for <sup>241</sup>Am. The concentration ratios show different but substantial enrichment of <sup>241</sup>Am over <sup>239+240</sup>Pu on

the particulate fraction throughout the water column. At stations WBO and JAO, 14% of the total Pu inventory in the water column to a depth of 1000 m was associated with particulate matter, whereas 71% of the total  $^{241}\text{Am}$  inventory at station WBO was bound to particles. This partitioning between  $^{241}\text{Am}$  and  $^{239+240}\text{Pu}$  in the ocean is not a feature related to the source term for the radionuclides.

Pentreath et al. (1980) report that the  $K_d$  values of  $^{241}\text{Am}$ , determined for particulate material in the surface of the seawater within and outside the Irish Sea, are from 2.5 to 7.8 times greater than are the respective values for  $^{239+240}\text{Pu}$ . Beasley and Cross (1980) show results from the Mediterranean, where an average of 10% of  $^{241}\text{Am}$  from fallout is retained on filters, as compared to only 3.8% of the  $^{239+240}\text{Pu}$ .

Results from our laboratory experiments using different sediments from Enewetak indicate that  $^{241}\text{Am}$  was more strongly associated with lagoon sediments than was  $^{239+240}\text{Pu}$  (Table 14.12). The  $K_d$  values for  $^{241}\text{Am}$  were 3.3-18 times greater than were those for  $^{239+240}\text{Pu}$  for the set of samples tested. Our laboratory results suggest there is a lesser, if any, tendency for  $^{241}\text{Am}$  to be mobilized either from sedimentary or from particulate material into solution as a dissolved species.

Table 14.13 compares the  $^{239+240}\text{Pu}$ : $^{241}\text{Am}$  concentrations in solution and in association with particulate material at Enewetak and Bikini lagoons. Although the concentrations of  $^{241}\text{Am}$  in solution within the lagoons were small, they were nevertheless an order of magnitude greater than were the global fallout concentrations in the surface waters of the northern equatorial Pacific. All results have been corrected for any increase in

$^{241}\text{Am}$  from  $^{241}\text{Pu}$  decay between the time of collection and separation. Small but measurable amounts of  $^{241}\text{Am}$  were also capable of mobilizing from sedimentary deposits into solution.

The mean activity ratio of  $^{241}\text{Am}$ : $^{239+240}\text{Pu}$  associated with the particulate material is essentially identical to the mean ratio of the sediment inventory at each atoll (Section 14.2.1). There is a large reduction in this ratio for the radionuclides in solution compared with the values associated with the particulate matter and, by analogy, the sediments. The  $^{241}\text{Am}$  is strongly bound to the solid phases and is therefore less likely to desorb into solution than is Pu.

In the final column of Table 14.13, the prefiltered: solution concentrations of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$ , have been converted to the ratio of the  $K_d$  for the two transuranic elements. The mean  $K_d$  ratio of 0.13 agrees well with the average ratio of 0.11 for values determined in the laboratory experiments (Table 14.12). The value of the mean ratio determined from the inventories in the water column at station WBO (Table 14.10) is 0.06. This is roughly half of the value for the ratio determined from the lagoon water, and it suggests that a larger fraction of the total dissolved Pu found in the water column outside the lagoons is in the oxidized state, as compared to the average (78%) for oxidized forms in solution within the lagoons.

#### 14.3.6. Residence Time of $^{239+240}\text{Pu}$ and $^{241}\text{Am}$ in the Lagoons

Results from biological indicators (Noshkin, 1980) and from the direct measurements of the mean concentra-

Table 14.12. Comparative  $K_d$  Values for  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$ <sup>a</sup>

ID Number	$^{239+240}\text{Pu}$			$^{241}\text{Am}$		
	Solution (mBq liter <sup>-1</sup> )	Solid (Bq g <sup>-1</sup> )	$K_d$ <sup>b</sup>	Solution (mBq liter <sup>-1</sup> )	Solid (Bq g <sup>-1</sup> )	$K_d$
224	2.07 ± 0.07	1.01 ± 0.02	4.8 × 10 <sup>5</sup>	0.25 ± 0.10	1.06 ± 0.07	4.3 × 10 <sup>6</sup>
226	1.52 ± 0.7	0.79 ± 0.01	5.2 × 10 <sup>5</sup>	0.11 ± 0.11	0.63 ± 0.03	5.4 × 10 <sup>6</sup>
228	4.04 ± 1.0	1.31 ± 0.01	3.3 × 10 <sup>5</sup>	0.11 ± 0.07	0.52 ± 0.03	4.7 × 10 <sup>6</sup>
230	3.07 ± 0.07	1.21 ± 0.01	3.9 × 10 <sup>5</sup>	0.28 ± 0.12	0.34 ± 0.04	1.3 × 10 <sup>6</sup>
236	6.41 ± 0.10	0.73 ± 0.01	1.1 × 10 <sup>5</sup>	0.08 ± 0.07	0.16 ± 0.02	2.0 × 10 <sup>6</sup>
Mean			(3.7 ± 1.6) × 10 <sup>5</sup>			(3.5 ± 1.8) × 10 <sup>6</sup>

<sup>a</sup>Determined from grab samples of sediment and seawater collected at Enewetak and transferred to containers and mixed during a two-month storage period; mixed-size range of solids. Seawater filtered through 0.45- $\mu\text{m}$  filter prior to analysis.

$$^b K_d = \frac{(\text{Bq per kg of dry solids})}{(\text{Bq per kg of water})}$$

Table 14.13. The  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  Concentrations in Seawater and Particulate Matter in Two Lagoons<sup>a</sup>

Location	Date Sampled	$^{239+240}\text{Pu}$ (mBq liter <sup>-1</sup> )		$^{241}\text{Am}$ (mBq liter <sup>-1</sup> )		$^{241}\text{Am} : ^{239+240}\text{Pu}$		$K_d$ ( $^{239+240}\text{Pu} : ^{241}\text{Am}$ ) <sup>b</sup>	
		Prefiltered	Solution	Prefiltered	Solution	Prefiltered	Solution		
Enewetak									
Mid-lagoon	8/74	—	1.11 (5)	—	—	—	0.06 (39)	—	
Mid-lagoon	4/79	0.16 (5)	—	0.036 (13)	0.067 (39)	0.24 (13)	—	—	
Mid-lagoon	4/79	0.13 (5)	—	0.028 (12)	—	0.21 (13)	—	—	
Mid-lagoon	10/79	0.12 (5)	—	0.054 (6)	—	0.46 (8)	—	—	
Mid-lagoon	10/79	0.19 (3)	—	0.060 (4)	—	0.31 (5)	—	—	
E-24 Lagoon	10/79	0.75 (2)	0.84 (2)	0.122 (7)	—	0.16 (7)	0.05 (26)	0.31	
E-24 Reef	10/79	2.81 (2)	2.15 (3)	0.322 (9)	0.041 (26)	0.11 (9)	0.02 (25)	0.18	
E-10 Reef	10/79	8.95 (3)	0.16 (5)	5.59 (3)	0.041 (26)	0.62 (4)	0.10 (30)	0.16	
E-24 Reef	10/79	0.98 (1)	2.33 (2)	0.50 (5)	0.017 (17)	0.51 (5)	0.027 (17)	0.05	
E-24 Reef	11/80	—	1.37 (3)	—	0.024 (35)	—	0.018 (35)	—	
E-24 Reef	1/81	—	1.63 (2)	—	0.016 (38)	—	0.008 (38)	—	
E-24 Reef	7/81	—	1.07 (2)	—	0.024 (20)	—	0.023 (20)	—	
Mean	—	—	—	—	—	0.33 (55)	0.038 (79)	—	
Bikini									
B-10	11/78	0.11 (9)	0.28 (4)	0.087 (8)	0.018 (50)	0.78 (9)	0.063 (50)	0.08	
B-2	11/78	1.99 (5)	1.78 (2)	1.58 (5)	0.122 (30)	0.79 (7)	0.068 (30)	0.09	
B-6	11/78	3.63 (4)	0.85 (3)	3.26 (4)	0.022 (65)	0.90 (6)	0.026 (65)	0.03	
B-13	11/78	0.25 (7)	1.45 (2)	0.211 (6)	0.043 (45)	0.82 (9)	0.029 (45)	0.04	
Mean	—	—	—	—	—	0.82 (7)	0.046 (48)	—	
Mean	—	—	—	—	—	—	—	0.13	
Equatorial Pacific									
surface water <sup>c</sup>	6-1 1/78	$1.5 \times 10^{-3}$ (44)	$10.4 \times 10^{-3}$ (44)	$2.2 \times 10^{-3}$ (51)	$4.8 \times 10^{-3}$ (75)	—	—	—	

<sup>a</sup>The 1- $\sigma$  counting error in parentheses is expressed as percent of the listed value. A dash denotes the absence of data.

<sup>b</sup> $K_d$  ratio =  $^{239+240}\text{Pu}$  (prefiltered/solution) :  $^{241}\text{Am}$  (prefiltered/solution).

<sup>c</sup>The average of 18 samples.

tions of the two transuranic elements in the lagoons described in this chapter indicate that the average amount of  $^{239+240}\text{Pu}$  in solution has been constant since at least 1965. Mobilized Pu has come from a sufficiently large reservoir that the amount lost to solution over the years has not substantially depleted the sedimentary inventory. A fraction of the  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  in the water (Tables 14.3 and 14.13) is associated with particulate matter, some of which is resuspended from the bottom sediments. Very little sedimentary material escapes from the lagoon, and resuspended bottom material probably settles out onto the lagoon floor: therefore, no  $^{239+240}\text{Pu}$  or  $^{241}\text{Am}$  associated with particulate matter is assumed to be lost from the lagoon.

Physical circulation data accumulated at Enewetak by Atkinson et al. (1981) indicate that the mean exchange rate for the lagoon water with the ocean is approximately one month. The authors point out, however, that water entering the northern portion of the atoll, where sediments have the highest concentrations

of Pu, takes about four months to exit the lagoon. Previously, von Arx (1948) estimated that the water in Bikini Lagoon exchanges seven times annually with the ocean. Rates between 30 and 50 d are substantially faster than the mean exchange rate of (140 d) estimated for  $^{239+240}\text{Pu}$  from radiological data associated with several biological indicators (Noshkin, 1980). Noshkin and Wong. (1980) have used this 140-d residence time along with the average inventory of soluble  $^{239+240}\text{Pu}$  (36 GBq) in lagoon water, and they estimate that the soluble inventory represents 0.08% of the inventory in the sediment (to a depth of 16 cm) to calculate a mean life of 435 y (half-residence time of 330 y) for Pu in the Enewetak sediment. Loss of  $^{239+240}\text{Pu}$  by radiological decay was neglected in the above and in subsequent calculations. At Bikini, the computed mean life for  $^{239+240}\text{Pu}$  in the sediment (to a depth of 16 cm) column was 460 y.

The average  $^{241}\text{Am} : ^{239+240}\text{Pu}$  ratios of concentrations in solution are 0.038 and 0.046 at Enewetak and Bikini,

respectively (Table 14.13). Multiplying these values by the average inventories of  $^{239+240}\text{Pu}$  in solution provides average inventories of 1.3 and 2.2 GBq as the quantities of  $^{241}\text{Am}$  in solution at Enewetak and Bikini atolls, respectively. Using a water residence time of 140 d, we calculate that 3.3 and 5.9 GBq of  $^{241}\text{Am}$  are lost annually from Enewetak and Bikini. Assuming again that the inventory to a depth of 16 cm in the sediment is the reservoir for the mobilized  $^{241}\text{Am}$ , the mean life, neglecting radioactive decay, exceeds 4000 y. Since the mean life of  $^{241}\text{Am}$  is 625 y (with a half-life of 433 y), the effective mean lifetime for  $^{241}\text{Am}$  in the sedimentary reservoir is 555 y. Taking into account the exchange rates and inventory values discussed in this chapter,  $^{241}\text{Am}$  will be depleted in the sedimentary reservoirs of the atolls primarily by radioactive decay, whereas most of the  $^{239+240}\text{Pu}$  will be lost by mobilization and exchange with the open ocean, assuming that the mobilization process continues at the same rate in subsequent years.

The assessments discussed thus far in this chapter were made by using an exchange rate of 140 d and a sedimentary reservoir extending from the sediment-water interface to a depth of 16 cm. The depletion rate of Pu and Am from the lagoons clearly depends on the exchange rate of water between the lagoon and the ocean, and the size and depth of the reservoir from which the mobilized  $^{239+240}\text{Pu}$  or  $^{241}\text{Am}$  is derived. The evidence provided by von Arx (1948) and Atkinson et al. (1981), indicating that the exchange rate of water and its dissolved constituents between the lagoon and ocean is more rapid than 140 d, cannot be dismissed. There is some evidence that Pu contained in subsurface sediments is lost to the overlying water by vertical movement of the interstitial water. We do not know, however, the active depth in the sediment column through which Pu can move as a result of advection or diffusion along concentration gradients. In addition, we have not assessed the importance of this mechanism relative to other physical, biological, or chemical disturbances that may result in resuspension of sediment to the water column followed by Pu mobilization into solution. If it is assumed that the water and its dissolved constituents exchange between Enewetak Lagoon and the ocean every 30 d, for example, and that the principal reservoir for Pu is only the surface 2.5-cm layer of the sediment, then the mean and the half-residence times for  $^{239+240}\text{Pu}$  in this reservoir are only 21 and 15 y, respectively, and the mean and half-residence times for  $^{241}\text{Am}$  computed for these conditions are 416 and 289 y, respectively.

This computation shows that the mean quantity of

plutonium mobilized into solution during 1982 should be half the average amount it was 15 y ago. The  $^{241}\text{Am}$  levels would remain essentially unchanged during this period. Our measurements do not agree with this rapid a rate of Pu disappearance from the lagoon. Either the residence time for the lagoon water is substantially longer than 30 d, or the size of the active sedimentary reservoir extends deeper than 2.5 cm. Using an exchange rate of one month at Enewetak and the quantity of Pu contained in the reservoir to a depth of 16 cm, the mean and the half-residence times of  $^{239+240}\text{Pu}$  are 103 and 71 y, respectively, and the mean and half-residence times for  $^{241}\text{Am}$  are, respectively, 400 and 277 y. For this example, the measurements of mean lagoon concentrations presented in this chapter lack the degree of precision necessary to distinguish whether this rate is reasonable.

Work to resolve the correct rates of Pu and Am loss from both lagoons is currently a high-priority program. The rate of Pu disappearance from the sediments could be much more rapid than previously estimated.

#### 14.4. CONCLUSIONS

Little reliable information is available to predict the fate of transuranic elements in the deep sea. Only from the accumulation and comparison of results from different sources in the environment can a clearer understanding of the behavior of transuranic elements in the ocean be developed and universal characteristics identified.

Strong association both of  $^{239+240}\text{Pu}$  and of  $^{241}\text{Am}$  is found with the sediments, but we found that  $^{239+240}\text{Pu}$  is less firmly bound and is capable of more rapid mobilization from the sediments at Bikini and Enewetak atolls. Small amounts of  $^{241}\text{Am}$  are also capable of dissociating from marine sediments. The partitioning of  $^{241}\text{Am}$  between sediments and water is controlled by the law of mass action, and the mechanism can be considered reversible. The amount of  $^{239+240}\text{Pu}$  mobilized into solution at the atolls can be reasonably predicted using a  $K_d$  of approximately  $2.3 \times 10^5$  and the mean concentrations in the sediment. This value also provides reasonable estimates of the quantities mobilized into solution at Rongelap Atoll, Johnston Atoll, and from sedimentary deposits at San Clemente Island, California (Noshkin et al., 19X1a).

The mobilized  $^{239+240}\text{Pu}$  at Enewetak and Bikini has solute-like characteristics, and different valence states coexist in solution. The largest fraction of the soluble Pu is in an oxidized form (V or VI). Quantities asso-

ciated with suspended particulate material and sediments are predominantly in the reduced state (III or IV). The sorption-desorption process is not completely reversible because of changes that occur in the relative amounts of the mixed oxidation states in solution with time. The oxidized forms of  $^{239+240}\text{Pu}$  in solution have a lesser tendency to associate with sedimentary or particulate material than does reduced Pu. Complexation after mobilization also affects the resorption rate. Therefore, any characteristics of  $^{239+240}\text{Pu}$  described at a point of reference may not necessarily be relevant in explaining behavior after mobilization and migration into solution.

Water profiles to a depth of 1000 m in the equatorial Pacific show that  $^{241}\text{Am}$ : $^{239+240}\text{Pu}$  ratios are more than two times higher in the particulate phase than in the soluble phase. This separation is mediated by the higher solubility of Pu relative to Am. Since  $^{241}\text{Am}$  and  $^{239+240}\text{Pu}$  associated with particulate matter should move vertically in the water column more rapidly than would the species in solution, the rate of vertical transport of  $^{241}\text{Am}$  to deep bottom sediments can be assumed to be more rapid than that for  $^{239+240}\text{Pu}$ . As the lagoon studies show, once in the sediment,  $^{241}\text{Am}$  will be remobilized into solution at a slower rate than will  $^{239+240}\text{Pu}$ . Some fraction of  $^{239+240}\text{Pu}$  placed on the surface of the seafloor should, in time, disperse into the overlying water mass and migrate from its original site. The  $^{241}\text{Am}$  should remain more firmly fixed to the sedimentary material near the point of introduction. The rate of disappearance of the two radionuclides will depend on the physical, biological, and chemical characteristics of the sedimentary deposits and the rate of water movement into and out of the contaminated region. The relative amounts of  $^{241}\text{Am}$  to  $^{239+240}\text{Pu}$  in the sedimentary deposits at Enewetak and Bikini will be altered in the future as a result of Pu mobilization and the radiological decay of  $^{241}\text{Am}$ .

It is not yet possible to make long-term predictions of the relative quantities remaining in the atolls' sediments. These predictions rely on accurately knowing the size of the sedimentary reservoir capable of continuously supplying plutonium to the overlying water and the mean residence time for the dissolved Pu in the lagoon's water mass, and these parameters are not yet well enough known.

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