

## Plutonium in the Ocean Environment: Its Distributions and Behavior

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Marine environments have been extensively contaminated by plutonium as a result of global fallout due to atmospheric nuclear-weapons testing. Knowledge of the levels and behavior of plutonium in marine environments is necessary to assess the radiological and ecological effects of plutonium. Such analytical techniques as radiochemical analysis,  $\alpha$ -spectrometry, and mass spectrometry have been developed to analyze the plutonium in seawater over the past five decades. Because of complex chemical properties (e.g. high reactivity to particles), plutonium in the ocean exhibits more complicated behavior than other long-lived anthropogenic radionuclides, such as  $^{137}\text{Cs}$ . In the present study, I reviewed the research history of plutonium in the ocean, including spatial and temporal changes of plutonium levels and distributions, and its oceanographic behavior.

### 1. Introduction

The first global contamination by plutonium, which occurred following nuclear explosions at Aramogode, Hiroshima, and Nagasaki in August 1945, was recorded in the ice core of Arctic Canada.<sup>1</sup> Plutonium released from atmospheric nuclear tests, serious nuclear reactor accidents, and other sources are almost globally detectable in the atmosphere, ocean, and terrestrial environment. Most originated from atmospheric nuclear-weapons testing in the early 1960s.<sup>2-4</sup> The cumulative deposition of bomb-derived  $^{239,240}\text{Pu}$  on the Earth's surface was estimated to be  $11 \times 10^{15}$  Bq, whereas the cumulative depositions of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ , typical long-lived fission products, were  $948 \times 10^{15}$  and  $622 \times 10^{15}$  Bq.<sup>5</sup> In 1964,  $1.3 \times 10^{15}$  Bq of  $^{238}\text{Pu}$  was injected into the upper atmosphere of the southern hemisphere as a result of a US satellite burnup.<sup>6</sup> Additionally, local and regional contamination of plutonium in the environment have resulted from nuclear waste discharge from the nuclear fuel reprocessing plants in the UK and France and from ocean dumping of nuclear wastes. For example, the Sellafield reprocessing plant in the UK released  $0.68 \times 10^{15}$  Bq of  $^{239,240}\text{Pu}$  into the Irish Sea.<sup>7</sup> In the mid-1950s, a substantial amount of plutonium was injected into the western North Pacific surface waters by close-in fallout from the US nuclear explosions conducted at the Pacific Proving Grounds in the Marshall Islands<sup>8,9</sup>; the estimated total burden of close-in fallout plutonium was  $3.8$  to  $6.3 \times 10^{15}$  Bq. The 1986 Chernobyl nuclear reactor accident resulted in atmospheric release of  $0.06 \times 10^{15}$  Bq of  $^{239,240}\text{Pu}$ ; and ten days after the explosion,  $38 \times 10^{15}$  of  $^{137}\text{Cs}$  and  $8 \times 10^{15}$  Bq of  $^{90}\text{Sr}$  were released into the environment.<sup>10</sup> The effect of the Chernobyl fallout on the ocean was very limited, since most of the Chernobyl plutonium contaminated the land near Chernobyl; the Chernobyl-derived contribution of plutonium deposition in the Baltic Sea was estimated to be 10% of the total plutonium deposition.<sup>11</sup> Although no information is available on the environmental effects of accidental plutonium in the ocean, the potential sources of plutonium in marine environments are nuclear weapons accidents.<sup>12</sup> First, in 1965, an attack aircraft loaded with one B43 nuclear weapon rolled off the deck of the *USS Ticonderoga*, and the nuclear weapon was never found. Second, a former USSR missile submarine with

three nuclear-armed ballistic missiles sank 750 miles northwest of the island of Oahu.

The major sinks of plutonium released in the environment are the ocean and land. Knowledge of the levels and behavior of plutonium in marine environments is important for assessing the ecological effects of plutonium, due to high public concern about the chemical and radiotoxicity of plutonium. Since the first report of plutonium concentrations in seawater was published in 1964,<sup>13</sup> many researchers have determined plutonium concentrations in the ocean and studied oceanographic behavior of plutonium. The data of oceanic plutonium concentrations have been compiled in a database.<sup>14,15</sup>

Plutonium in the ocean is transported by physical and biogeochemical processes. During the past four decades, plutonium concentrations in the surface waters of the open ocean have decreased with sea-area-dependent residence time, which is generally shorter than that of the corresponding surface  $^{137}\text{Cs}$ .<sup>16,17</sup> Plutonium, which is a typical particle-reactive radionuclide in contrast to  $^{137}\text{Cs}$ , moves vertically with sinking biogenic particles<sup>18,19</sup> and is regenerated in deep waters as a result of microbial decomposition of particles. Biogeochemical models have reproduced the vertical profile of plutonium with surface minimum, mid-depth maximum, and decrease with depth.<sup>20-22</sup> However, plutonium behavior in oceanic water is more complicated because of such physical processes as advection and upwelling.<sup>23</sup> For example, the observation that the plutonium maximum layer in the mid-latitude region of the North Pacific deepened with time<sup>9</sup> has been explained by a simple one-dimensional biogeochemical model<sup>20</sup>; however, biogeochemical processes alone cannot be used to explain a decrease of inventory in the corresponding site, where advection may play a significant role. The North Pacific deep waters (more than 2000 m depth) contain a significant amount of plutonium,<sup>8</sup> the input processes of which are still unknown.

Plutonium in the environment consists of a number of different isotopes ( $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{241}\text{Pu}$ ): the most abundant are  $^{239}\text{Pu}$ , which has radioactive half-life of 24,110 years; and  $^{240}\text{Pu}$ , which has radioactive half-life of 6,563 years. Although they have lower atom concentrations,  $^{238}\text{Pu}$  (with a radioactive half-life of 87.7 years) and  $^{241}\text{Pu}$  (with a radioactive half-life of 14.1 years) are also important isotopes of plutonium. All plutonium isotopes except  $^{241}\text{Pu}$  are  $\alpha$ -emitters. The  $\alpha$  particle energy of  $^{238}\text{Pu}$  is 5.49 MeV; that of  $^{239}\text{Pu}$  is 5.10 MeV; and that of  $^{240}\text{Pu}$  is 5.15 MeV. The  $\beta$ -particle energy of  $^{241}\text{Pu}$  is 5.2 keV.

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Therefore,  $\alpha$ -spectrometry is effective in determining plutonium concentrations in seawater. However, the sum of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  activities has been used as a measure of plutonium concentration because the separation of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  is difficult using  $\alpha$ -spectrometry, due to their similar energy range of  $\alpha$  particles. Plutonium isotope ratios depend on their sources; for example, the average global fallout  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio is 0.18,<sup>24-27</sup> whereas an elevated ratio was reported for fallout from US nuclear tests in the 1950s.<sup>28,29</sup> The plutonium isotope signature is therefore a useful tool for identifying the sources of plutonium and for clarifying their behavior in marine environments.

In this study, I review the research history of plutonium in marine environments, including distributions of plutonium in the ocean, long-term trends of plutonium concentrations, plutonium inventories in the water column, speciation, and isotope ratios.

## 2. Plutonium analysis

I simply reviewed methods of analyzing plutonium in seawater. Concentrations of plutonium in seawater are usually extremely low ( $<50\text{ mBq m}^{-3}$ ) except in highly contaminated areas, and most of its isotopes emit  $\alpha$  particles. Therefore, plutonium contents have been determined by  $\alpha$  spectrometry, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and Accelerator Mass Spectrometry (AMS), after longer radiochemical processes (e.g., preconcentration from large-volume samples, radiochemical separation and purification, and electrodeposition).

**2.1. Sampling.** Large volumes (50 to 500 L) of seawater are required for the assay of plutonium and americium because of the extremely low plutonium concentrations in open ocean water. Surface water samples of 100 to 500 L were usually collected with submersible pumping systems on board. Deep water samples were collected with a 100 L GoFlo sampler or CTD-rosette sampler. All water samples were filtered through a fine membrane filter (Millipore HA,  $0.45\mu\text{m}$  pore size) immediately after sampling.

**2.2 Preconcentration of Pu.** Coprecipitation is generally used for extracting trace amounts of Pu from large volumes of seawater, and this process is usually performed on board. In the early stage, Pu was coprecipitated with ferric hydroxide or bismuth phosphate.<sup>30,31</sup> However, low and erratic recoveries of trace Pu occurred in the environmental samples. A proposed simple concentration method included the partial precipitation of (Mg, Ca) hydroxides/carbonates by adding small amounts of sodium hydroxide.<sup>32,33</sup> Recently, coprecipitation with  $\text{MnO}_2$  was proposed as a method of preconcentrating Pu in seawater.<sup>34,35</sup> First, after the seawater sample was acidified,  $^{242}\text{Pu}$  was added as a yield tracer, and  $\text{KMnO}_4$  was added to change the chemical form of Pu to a dissolved form (Pu(VI)). Next, after NaOH and  $\text{MnCl}_2$  were added to the solution, Pu coprecipitated with the bulky manganese dioxide at pH 9. Finally, the settled  $\text{MnO}_2$  precipitation was collected. Another method of preconcentrating Pu<sup>36</sup> involved acidifying a 200 L seawater sample to pH 2 with 12 M HCl (200 mL). Ferric chloride (2 g), a known amount of tracer ( $^{242}\text{Pu}$ ), and  $\text{K}_2\text{S}_2\text{O}_5$  (100 g) were then added, and the solution was stirred for 1 h, so that all the Pu species in the solution was reduced to Pu(III). Finally, Pu was coprecipitated with ferric hydroxide at pH 10 by adding diluted NaOH solution (0.5 to 1 M).

**2.3. Radiochemical separation.** Relatively large amounts of precipitates were obtained at the preconcentration stage. Although precipitate reduction is usually required, a simple separation method using anion exchange resin with a large column was proposed.<sup>32,33</sup> In order to remove large amounts of  $\text{MnO}_2$  or  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ , additional coprecipitation was performed.<sup>34</sup> The  $\text{MnO}_2$  precipitates were separated and

dissolved in 2 M HCl with excess  $\text{NH}_2\text{OH HCl}$  to reduce it to Mn(II). To scavenge Pu with ferric hydroxide, 50 mg of Fe(III) was added in the solution and oxidized from Pu(III) to Pu(IV) with  $\text{NaNO}_2$ . Ammonium hydroxide was added to form the  $\text{Fe}(\text{OH})_3$  precipitate at a pH of 8 to 9. The solution was briefly boiled, and then the pH in the solution was adjusted to 6 or 7, in which residual amounts of  $\text{MnO}_2$  changed to Mn(II). The  $\text{Fe}(\text{OH})_3$  precipitates were separated from the supernatant solution by centrifugation. The precipitate was dissolved with 14 M  $\text{HNO}_3$ . Finally, the acid concentration of the solution was adjusted to 8 M  $\text{HNO}_3$ . The solution was passed through the anion exchange column (Dowex 1-X8,  $\text{NO}_3$  form), in which Pu and Th were adsorbed onto resin, whereas Am, U, and Fe remained in the effluent. The column was washed with 8M  $\text{HNO}_3$ , and the Th fraction was eluted with 10 M HCl. The Pu fraction was eluted with 9 M HCl solution containing 0.1 M  $\text{NH}_4\text{I}$ . The chemical recoveries were 40 to 60%.

Recently, new types of extraction chromatographic resin have been proposed for radiochemical separation and purification of actinides instead of anion exchange resin.<sup>37</sup> TRU Resin<sup>TM</sup> (comprised of 0.75 M solution bifunctional organophosphorus extractant octylphenyl-*N,N*-di-isobutyl carbamoylphosphine oxide in tri-*n*-butyl phosphate immobilized on inert porous polymeric resin) was used for separating actinides.<sup>34,35,37-39</sup> Kim et al<sup>46</sup> developed analytical techniques for determining Pu in seawater using sector field ICP-MS (SF-ICP-MS), with a sequential flow injection system including a TEVA-Spec (Eichrom Industries) column for the radiochemical separation of Pu.

**2.4. Radiochemical separation of plutonium in particulate matter.** Filtered samples (100 to 1000 L) were digested with 14 M  $\text{HNO}_3$  and 12 M HCl in an appropriate beaker on a hot plate.<sup>33</sup> Next,  $^{242}\text{Pu}$  was added as a tracer of the chemical yield. The solution was evaporated to dryness on a hot plate. The residue was then dissolved with 8 M  $\text{HNO}_3$  and  $\text{NaNO}_2$  was added on a hot plate. After the filtration of the filter paper, the solution was passed through an anion exchange column. The column was successively washed with 20 mL of 8 M  $\text{HNO}_3$  and 50 mL of 9 M HCl. The Pu fraction was eluted with 100 mL of 1.2 M HCl including 1 mL of 30%  $\text{H}_2\text{O}_2$ . The chemical yield exceeded 90%.

**2.5. Electrodeposition.** Pu samples are usually electroplated onto a stainless steel disk for  $\alpha$  counting. The disk diameter depends on the active surface area of the detectors. In this study, electrodeposition was performed using an electrolysis apparatus with an electrodeposition cell consisting of a Teflon cylinder, a platinum cathode electrode, and a stainless steel disk anode. Pu was electrodeposited under two conditions (aqueous sulfuric acid media<sup>40</sup> and ethanol media<sup>33</sup>). To establish homogeneous plating onto the disk, the disk surface had to be cleaned by appropriate washing processes.

**2.6.  $\alpha$ -spectrometry.** The  $\alpha$ -spectrometer consisted of several vacuum chambers, including a solid-state detector, a pulse-height analyzer, and a computer system. The detector, which was a silicone surface barrier type (PIPS, energy resolution  $<25\text{ keV}$  full width at half maximum (FWHM), counting efficiency: 15 to 25%), had an active surface area of 450 to 600  $\text{mm}^2$  and a minimum depletion thickness of 100  $\mu\text{m}$ . The vacuum condition in the chamber was reduced to less than 200 mTorr using a vacuum pump, and the counting time was more than 80000 s.

**2.7. Mass spectrometry.** Thermal Ionization Mass Spectrometry (TIMS),<sup>41-43</sup> Resonance Ionization Mass Spectrometry (RIMS),<sup>44</sup> ICP-MS, and AMS<sup>45</sup> have been used for determining plutonium isotopes. The recent development of SF-ICP-MS allowed us to collect more data of  $^{239}\text{Pu}$  concentrations and  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in marine samples.<sup>46-54</sup> Since ICP-MS detection limits of plutonium were in the sub-femtogram range, I could reduce the sample volumes of several

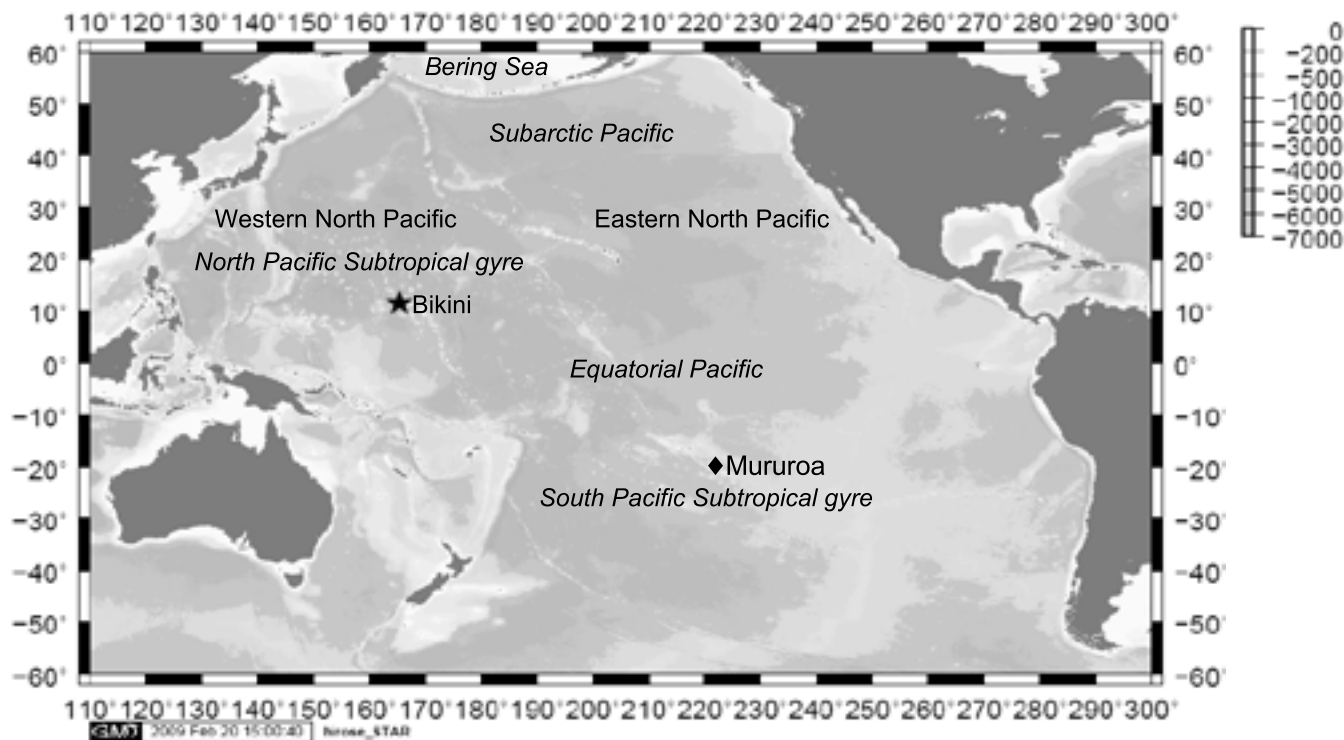


Figure 1. Map of the Pacific Ocean.

tens of liters. In order to obtain high-quality data of plutonium isotopes, however, it was necessary to develop simpler purification techniques to remove interference elements. The MS techniques, which provided information on  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in the seawater samples, were useful tools for identifying sources of plutonium in marine environments.

### 3. Plutonium in the Ocean: Distribution and Behavior

**3.1. Surface  $^{239,240}\text{Pu}$  concentrations.** Although  $^{239,240}\text{Pu}$  concentrations in surface waters were determined in the 1960s,<sup>13,55</sup> the first geographical distribution of surface  $^{239,240}\text{Pu}$  in the Pacific (Figure 1) in the early 1970s was depicted by Miyake and Sugimura,<sup>56</sup> who found higher  $^{239,240}\text{Pu}$  concentrations in the mid-latitude region of the North Pacific. The geographical distribution of surface  $^{239,240}\text{Pu}$  was governed by global fallout from the atmospheric nuclear testing conducted in the early 1960s. In the early 1980s, a similar geographical pattern of surface  $^{239,240}\text{Pu}$  was observed,<sup>57</sup> although the latitudinal gradient of surface  $^{239,240}\text{Pu}$  decreased, compared with that in the early 1970s. In the early 1990s, a geographic distribution of surface  $^{239,240}\text{Pu}$  in the Atlantic, Indian, and Pacific Oceans ranging from 0.6 to 11.5  $\text{mBq m}^{-3}$  was observed,<sup>58</sup> with higher concentration in the western North Pacific and North Atlantic, and a low concentration in the eastern North Pacific.

In the 2000s, the  $^{239,240}\text{Pu}$  concentrations in the surface waters of the world ocean were evaluated from comprehensive dataset based on the IAEA-MEL research program of Worldwide Marine Radioactivity Studies<sup>15,60,61</sup> and the HAM database constructed by Aoyama and Hirose.<sup>14</sup> The highest  $^{239,240}\text{Pu}$  concentration in the surface waters ( $>100 \text{ mBq m}^{-3}$ ) occurred in the Irish Sea, in which the effect of the Sellafield discharge<sup>7</sup> continued. A relatively high  $^{239,240}\text{Pu}$  concentration was observed in the surface waters (10 to 50  $\text{mBq m}^{-3}$ ) in the northern North Atlantic, the Barents Sea, the North Sea, the Mediterranean, and the English Channel. The  $^{239,240}\text{Pu}$  concentrations in the surface waters of the Pacific, Atlantic, and Indian Oceans ranged from 1 to 10  $\text{mBq m}^{-3}$ ; however, in the Antarctic Ocean, the concentration was less than 0.5  $\text{mBq m}^{-3}$ . Plutonium data in the surface water of the South Pacific were

still scant. Therefore, in 2003, the high-density longitudinal distribution of surface  $^{239,240}\text{Pu}$  along 32.5°S in the South Pacific was depicted,<sup>59</sup> with  $^{239,240}\text{Pu}$  concentrations ranging from 0.5 to 4.1  $\text{mBq m}^{-3}$ , which indicated a spatial distribution governed by oceanographic processes.

Temporal changes of surface  $^{239,240}\text{Pu}$  in the Pacific have been investigated.<sup>16,17,62</sup> Surface  $^{239,240}\text{Pu}$  decreased with time in all the oceans, due to the continuous decrease of fallout input after the end of the Chinese atmospheric nuclear test in 1980 and the subsequent decreasing stratospheric fallout.<sup>4</sup> The  $^{239,240}\text{Pu}$  concentration in the surface water has decreased exponentially since 1970, although decrease rates depend on the sea area. The decrease rates of the surface  $^{239,240}\text{Pu}$  concentrations in the ocean are generally faster than that of  $^{137}\text{Cs}$ , due to biogeochemical processes.

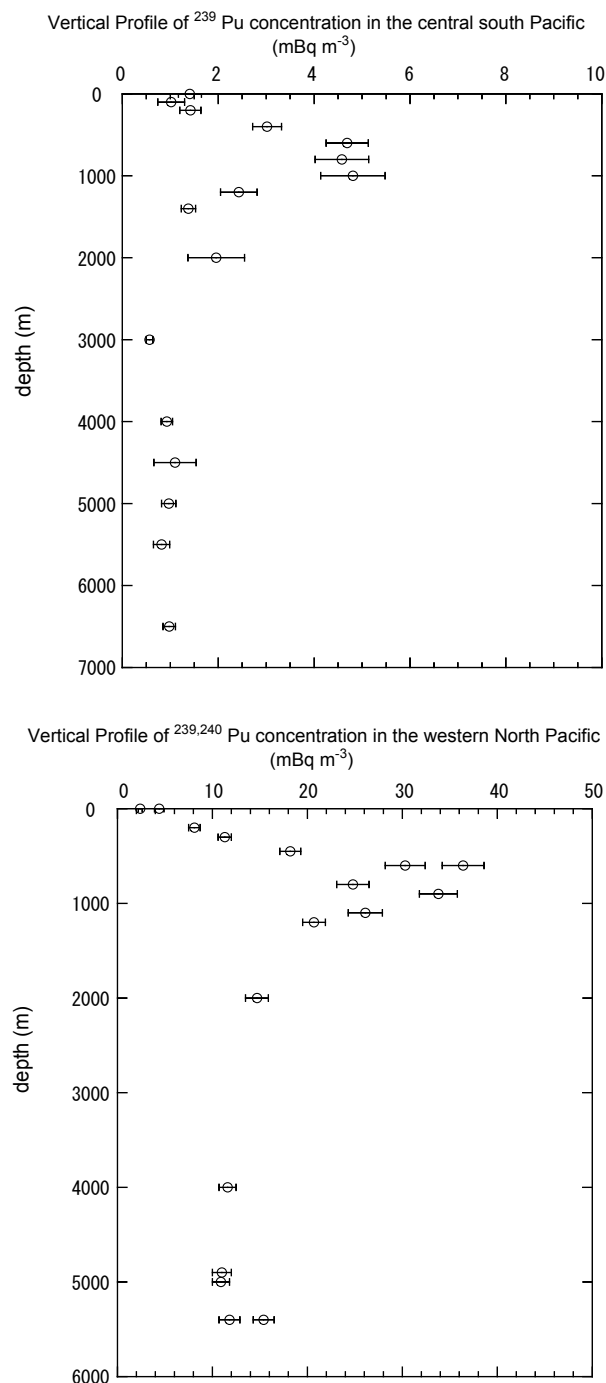
The  $^{239,240}\text{Pu}$  concentrations in the surface waters of the Pacific in 2000 were estimated to range from 0.3 to 2.7  $\text{mBq m}^{-3}$ , with a spatial variation larger than that of  $^{137}\text{Cs}$ .<sup>63</sup> Higher surface  $^{239,240}\text{Pu}$  concentrations appeared in the subarctic Pacific and the eastern equatorial Pacific. Higher surface  $^{239,240}\text{Pu}$  concentrations in the subarctic Pacific and the Sea of Japan could be explained by rapid recycling of scavenged  $^{239,240}\text{Pu}$  due to large vertical mixing in winter,<sup>64,65</sup> whereas surface  $^{239,240}\text{Pu}$  in the eastern equatorial Pacific was possibly maintained at a higher level by equatorial upwelling.<sup>66</sup> The lower values in the mid-latitude region of the eastern North Pacific were consistent with the higher decrease rate of  $^{137}\text{Cs}$  in the mid-latitude region of the eastern North Pacific. Estimated surface  $^{239,240}\text{Pu}$  concentrations in the subtropical region of the western North Pacific were higher than those in the subtropical region of the eastern North Pacific. Furthermore, the difference between the surface  $^{239,240}\text{Pu}$  concentration of the mid-latitude region of the Northern Hemisphere and that of the Southern Hemisphere was small, although its causes are still unknown. Therefore, in addition to the physical processes, the biogeochemical process is a significant factor controlling the current geographic distribution of the  $^{239,240}\text{Pu}$  concentration in the surface waters of the Pacific,<sup>8,9,18,20,62</sup> considering the relative short residence time of surface  $^{239,240}\text{Pu}$ .<sup>17</sup>

**3.2. Vertical profiles of  $^{239,240}\text{Pu}$  in the ocean.** The first

comprehensive data on vertical distributions of  $^{239,240}\text{Pu}$  in open ocean water columns were reported for GEOSECS stations,<sup>8,67</sup> although a preliminary measurement of deep  $^{239,240}\text{Pu}$  had been carried out by Bowen et al<sup>30</sup> and Miyake and Sugimura.<sup>56</sup> Figure 2 depicts vertical profiles of  $^{239,240}\text{Pu}$  observed in the subtropical regions of the North and South Pacific.<sup>68,69</sup> All vertical profiles of  $^{239,240}\text{Pu}$  in the ocean were characterized by a typical distribution pattern with surface minimum, subsurface maximum, and gradual decrease with increasing depth.<sup>8,9,16,70-75</sup> Maximum  $^{239,240}\text{Pu}$  concentrations in the water column appeared at depths of 500 to 1000 m.<sup>69</sup> The shape of  $^{239,240}\text{Pu}$  profiles depended on the sea area: a rather broad peak of  $^{239,240}\text{Pu}$  maximum was observed in the Sea of Japan<sup>23,76-80</sup> and in the Mediterranean Sea.<sup>81</sup> Furthermore, although a surface minimum of  $^{239,240}\text{Pu}$  was observed, definite profiles of  $^{239,240}\text{Pu}$  with a subsurface maximum (as in the Pacific) were not observed in the Arctic Atlantic Ocean.<sup>82,83</sup> The broad profiles of  $^{239,240}\text{Pu}$  in water columns may be explained by deep convection due to meteorological and oceanographic conditions related to each sea. The  $^{239,240}\text{Pu}$  maximum of the South Pacific was smaller than that of the North Pacific.<sup>68,84</sup> This pattern of vertical  $^{239,240}\text{Pu}$  profiles and their temporal change was demonstrated by particle-scavenging processes, which involved the removal of  $^{239,240}\text{Pu}$  by sinking particles following the regeneration of dissolved  $^{239,240}\text{Pu}$  due to the biological degradation of particles.<sup>18,20</sup>

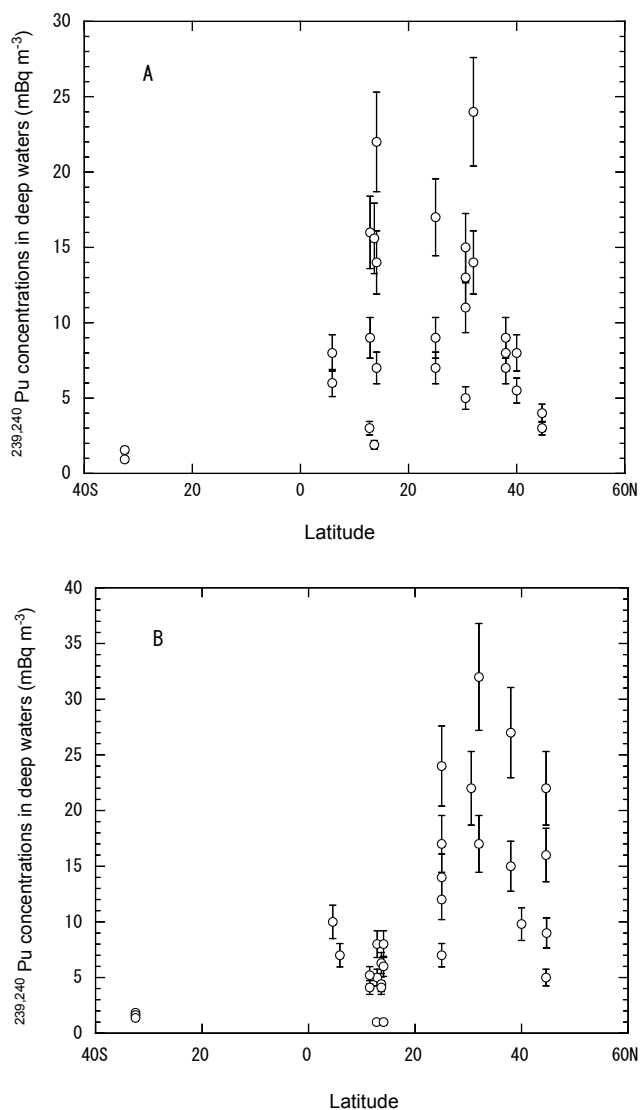
Temporal change of the  $^{239,240}\text{Pu}$  profile in the eastern North Pacific at the same site (31°23'N, 150°02'W) as the GEOSECS observation in 1973 was examined.<sup>85</sup> The  $^{239,240}\text{Pu}$  maximum in the mid-latitude region of the North Pacific moved to a deeper layer over time. The peak  $^{239,240}\text{Pu}$  concentration at a depth of 400 m markedly decreased over a 28-year period, whereas the  $^{239,240}\text{Pu}$  concentrations in deep waters (>1000 m depth) revealed no significant difference from GEOSECS data. Similar changes in the vertical distribution of  $^{239,240}\text{Pu}$  were observed in the western North Pacific mid-latitude region.<sup>9</sup> These findings suggested that the  $^{239,240}\text{Pu}$  concentrations in mid-depth (200 to 800 m) in the mid-latitude region of the North Pacific decreased over the past three decades. This change could not be explained by a simple biogeochemical process including only vertical transport, e.g. particle scavenging, because no marked increase of the  $^{239,240}\text{Pu}$  concentrations occurred in deeper water layers (>1000 m). Thus, it was likely that most of the  $^{239,240}\text{Pu}$  at mid-depth in the mid-latitude region of the North Pacific was transported by horizontal advection. On the other hand, when two sites in the equatorial North Pacific, location: 7°59'N, 164°54'E (Hirose et al<sup>85</sup>) and 5°53'N, 170°01'W (GEOSECS, 1973), were compared, no apparent change in the vertical  $^{239,240}\text{Pu}$  profile in the depth layers of the surface to 1000 m occurred over the past three decades.<sup>85</sup> A similar tendency was observed in the subtropical western North Pacific.<sup>9,69</sup> However a significant difference of  $^{239,240}\text{Pu}$  concentrations in deep waters (>1500 m depth) occurred between two sites: deep  $^{239,240}\text{Pu}$  concentrations in the station near the Pacific Proving Ground nuclear test sites (11°35'N, 165°23'E) were higher than those in the eastern station (GEOSECS site).

**3.3. Deep  $^{239,240}\text{Pu}$ .** The North Pacific deep waters contained substantial amounts of  $^{239,240}\text{Pu}$ ,<sup>8,71,85</sup> whereas plutonium concentrations in the South Pacific deep waters were 1 mBq m<sup>-3</sup>,<sup>68</sup> or one order of magnitude lower than that in the North Pacific. The Japan and Bonin trench waters (>6000 m depth) in the western North Pacific contained marked amounts of  $^{239,240}\text{Pu}$ .<sup>74,86</sup> The introduction of  $^{239,240}\text{Pu}$  in deep waters resulted in an increased interest in deep plutonium and how processes were related to the vertical transport of  $^{239,240}\text{Pu}$  in deep layers. Livingston et al<sup>9</sup> suggested that the  $^{239,240}\text{Pu}$  concentrations in deep water (more than 2000 m depth) were maintained at a nearly constant level during the past two decades. In order to clarify the present feature of deep  $^{239,240}\text{Pu}$ ,



**Figure 2.** Vertical profiles of plutonium concentrations in the North and South Pacific subtropical regions. The plots used data cited in Povinec et al (Ref.69) and Hirose et al (Ref.68).

latitudinal distributions of deep  $^{239,240}\text{Pu}$  at two different layers, upper (2000 to 3500 m) and lower (4000 to 6000 m), along 165°E and 180° longitudes were analyzed.<sup>85</sup> The latitudinal distribution of the  $^{239,240}\text{Pu}$  concentrations in the upper deep layer along 165°E longitude revealed two peaks, one in the mid-latitude region (30 to 40°N) corresponding to the latitudinal pattern of global fallout, and another in the south subtropical region (10 to 15°N), corresponding to close-in fallout due to the Pacific Ground nuclear test sites. The lower  $^{239,240}\text{Pu}$  concentrations in the upper deep layer occurred in the north subtropical (15 to 30°N) and equatorial (0 to 10°N) regions. The  $^{239,240}\text{Pu}$  concentrations in the lower deep layer were lower than those in the upper deep layer. For the latitudinal distribution of the  $^{239,240}\text{Pu}$  in deep water along 180° longitude (Figure. 3), a clear structure of the latitudinal distribution of the  $^{239,240}\text{Pu}$  concentrations was observed in the upper deep layer, with a high



**Figure 3.** Latitudinal distributions of  $^{239,240}\text{Pu}$  concentrations in deep waters along  $180^\circ$  in the Pacific. Depth range: A. 2000 to 3500 m, B. 4000 to 6000 m.

concentration in the North Pacific and a low concentration in the South Pacific. However, higher  $^{239,240}\text{Pu}$  concentrations in the North Pacific subtropical region were lower than those in the corresponding latitude along  $165^\circ\text{E}$ . The latitudinal distribution of the  $^{239,240}\text{Pu}$  concentrations in the lower deep layer was similar to that in the upper deep waters except for a different structure with a pronounced peak in the mid-latitude region ( $30^\circ$  to  $40^\circ\text{N}$ ); specifically, the  $^{239,240}\text{Pu}$  concentrations in the lower deep layer in the mid-latitude region were greater than those in the upper deep layer.

These findings suggest that the geographical structure of deep  $^{239,240}\text{Pu}$  concentrations with a larger latitudinal gradient than that of surface  $^{239,240}\text{Pu}$  exists in the Pacific: the high-concentration area is located in the western North Pacific and the low-concentration area is the South Pacific. The geographical distributions of deep  $^{239,240}\text{Pu}$  suggest little contribution of vertical transport of  $^{239,240}\text{Pu}$  and its mineralization in the North Pacific deep waters ( $>2000$  m). Model study<sup>21</sup> suggests less contribution of biogeochemical vertical transport to deep  $^{239,240}\text{Pu}$  ( $>2000$  m depth), although four decades have passed since surface injection of  $^{239,240}\text{Pu}$ . These findings suggest that some fallout  $^{239,240}\text{Pu}$ -bearing particles were rapidly transported to the deep layers and dissolved in deep waters. Therefore, it is likely that the geographical distributions of  $^{239,240}\text{Pu}$  in deep waters reflect spatial distributions of global fallout and close-in

fallout. Furthermore, detection of temporal change in deep  $^{239,240}\text{Pu}$  might provide important information on the thermohaline circulation of deep water in the Pacific.

**3.4. Residence times of surface Pu.** The residence time of plutonium in surface waters is an important factor for assessing the long-term ecological and radiological effects of plutonium, and for obtaining oceanographic information using plutonium as a tracer. The half-residence time (HRT) of plutonium in the surface layer was calculated from vertical flux data of a sediment trap experiment.<sup>19</sup> Hirose et al.<sup>62</sup> estimated the HRT of surface  $^{239,240}\text{Pu}$  from the temporal change of  $^{239,240}\text{Pu}/^{137}\text{Cs}$  ratios in the surface water of the western North Pacific. Since the residence times of plutonium in surface waters depend on the sea area, temporal changes of surface plutonium in the ocean were examined for different sea areas, whose division took into account the oceanographic and input conditions.<sup>16,17</sup> The  $^{239,240}\text{Pu}$  concentrations in the surface waters of each sea area decreased exponentially during the past three decades. With the assumption that the surface  $^{239,240}\text{Pu}$  exponentially decreased with time, curve fitting was carried out to determine the apparent residence time of  $^{239,240}\text{Pu}$  in the surface waters. In the mid-latitude region of the western North Pacific, the apparent residence time of surface  $^{239,240}\text{Pu}$  was calculated to be 7.5 years, which was the same order of magnitude as previous estimates.<sup>16</sup> The apparent residence time of surface  $^{239,240}\text{Pu}$  was longer than the residence time of  $^{239,240}\text{Pu}$  (four years), due to particle scavenging as determined by sediment traps<sup>19</sup> and  $^{239,240}\text{Pu}/^{137}\text{Cs}$  ratios.<sup>62</sup> This result suggested recycling processes of  $^{239,240}\text{Pu}$ , such as vertical mixing and upwelling of deep waters with higher  $^{239,240}\text{Pu}$  concentrations, and supply due to horizontal advection.

In the western North Pacific ( $10$  to  $20^\circ\text{N}$ ), surface  $^{239,240}\text{Pu}$  gradually decreased during the same period.<sup>83</sup> However, the apparent decrease rate of surface  $^{239,240}\text{Pu}$  was slower than that in the mid-latitudes. The apparent HRT of surface  $^{239,240}\text{Pu}$  was calculated to be 15 years. The longer apparent HRT of surface  $^{239,240}\text{Pu}$  in the subtropical North Pacific may be attributable to less particle scavenging due to low productivity in the oligotrophic ocean, in addition to recycling processes. In the equatorial Pacific and subarctic Pacific, a longer HRT of plutonium in surface waters occurred, although higher scavenging of  $^{239,240}\text{Pu}$  than in the oligotrophic ocean due to relatively high productivity was expected.<sup>17</sup> A relatively long HRT in the equatorial region was estimated for surface  $^{137}\text{Cs}$ .<sup>17,87</sup> A longer HRT of  $^{239,240}\text{Pu}$  in these sea areas may be explained by such physical processes as deep ventilation in the subarctic and equatorial upwelling. It must be noted that for surface  $^{239,240}\text{Pu}$  in the equatorial Pacific as well as subtropical North Pacific, there may be a contribution of outflow from potential sources of  $^{239,240}\text{Pu}$  at the Marshall Islands nuclear explosion sites.<sup>5</sup>

In the Mediterranean, the mean residence time of plutonium in the surface waters was estimated to be 15 years from the temporal change of surface  $^{239,240}\text{Pu}$  concentrations.<sup>88</sup>

**3.5. Chemical speciation of plutonium.** The chemistry of plutonium in natural waters is generally complicated because plutonium exhibits four valences (III, IV, V, and VI) and forms complexes with inorganic and organic ligands.<sup>89-91</sup> Choppin and Morgenstern<sup>92</sup> reviewed the chemical behavior of plutonium in an aqueous environment. The most important chemical property of plutonium in the marine environment is its oxidation state, because many chemical processes (e.g. solubility, hydrolysis, and complexation) are largely affected by valence. The oxidation state of plutonium affects its biogeochemical processes in the marine environments and radiochemical analyses of water samples (e.g. concentration and separation). The oxidation of plutonium depends on the pH of the solution: lower oxidation states are stabilized in acidic solution, whereas higher oxidation states are more stable in alkaline solution. The reactivity of Pu(IV) and Pu(III) is generally

greater than that of Pu(V) and Pu(VI) because Pu(V) exists as  $\text{PuO}_2^+$  and Pu(VI) exists as  $\text{PuO}_2^{2+}$ . However, it is difficult for Pu(IV) in natural aquatic conditions to form complexes with organic ligands such as humic acids because the free Pu(IV) ion concentration is extremely low as a result of strong hydrolysis.

Speciation studies<sup>33,93-95</sup> revealed that the dominant species of Pu dissolved in seawater is in oxidized form (V and/or VI). Orlandini et al<sup>96</sup> and Choppin<sup>97</sup> demonstrated that Pu(V) dominates in the oxidized fraction and that Pu(VI) is unstable in natural waters. In most natural systems, the significant oxidation states are Pu(IV) and Pu(V), while Pu(III) and Pu(VI) are generally insignificant. Taking into account hydrolysis and complexation with carbonate species,  $\text{PuO}_2^+$  is a dominant species of Pu(V) under the conditions of artificial seawater, whereas Pu(IV) exists as hydroxo complexes ( $\text{Pu}(\text{OH})_4$ ).<sup>92</sup>

In order to clarify the behavior of plutonium in the ocean, it is important to gain a better understanding of the interaction between plutonium and marine particulate matter. The portion of particulate  $^{239,240}\text{Pu}$  to total  $^{239,240}\text{Pu}$  was less than 10% in surface waters, including the North Pacific and Mediterranean,<sup>33,88,98-100</sup> whereas it was less than 2% in the Pacific deep waters.<sup>100</sup> Colloidal plutonium (<1 kD) and its isotope ratios were determined by cross-flow ultrafiltration (CFF) following TIMS measurements,<sup>43</sup> in which the majority of plutonium was found in the low molecular weight fraction. Sequential leaching experiments for particulate matter<sup>101</sup> suggested that a major chemical form of particulate  $^{239,240}\text{Pu}$  was an organic complex of Pu(IV), which was strongly supported by the relationship between particulate plutonium and ligand.<sup>102</sup>

**3.6. Plutonium isotope ratios.** Plutonium isotope ratios in seawater are useful tools for determining the sources of plutonium because these ratios depend on nuclear weapons design, test yields of nuclear explosions, and discharge from nuclear fuel processing plants. The  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio and  $^{238}\text{Pu}/^{239,240}\text{Pu}$  activity ratio in fallout that were affected from a kind of nuclear explosions and the SNAP9A satellite burnup were variable.<sup>4</sup> Recent development of ICP-MS techniques allowed us to determine plutonium isotopic ratios ( $^{240}\text{Pu}/^{239}\text{Pu}$ ) in environmental samples with high precision.<sup>38,46,50-52,54</sup> The global fallout average  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio was 0.18, based on aerosols, soil samples, and ice core data.<sup>24-27</sup> However, a different nuclear test series could be characterized by either higher or lower ratios. For example, generally lower  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios characterized the fallout from Nagasaki (average value of 0.042), the Nevada test site (average value of 0.035), and the Semipalatinsk test site (average value of 0.036)<sup>41,103-105</sup>; however, elevated  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios (0.21 to 0.36) were measured in soil samples from Bikini Atoll.<sup>28,29</sup>

The  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in water samples were determined in the North Pacific and marginal seas.<sup>41,48,50-52,85</sup> The  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in the North Pacific waters ranged from 0.164 to 0.28, and thus were in the range of the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of global fallout (0.18) and that of close-in fallout (0.3). The  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in the shallower layer of the North Pacific tended to be lower than that in deep waters.<sup>41</sup> The recent  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in deep waters were 0.25, supporting the results of Buessler.<sup>41</sup> Higher  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios were observed in the surface waters of the sea areas around the Japanese Islands, including the Sea of Japan.<sup>47,48,50-52</sup> The elevated  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios, compared with the ratio of global fallout, resulted in close-in fallout plutonium from the Pacific Proving Ground nuclear testing. However, significant low  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios occurred in shallower layers of the equatorial North Pacific (7°59'N, 165°03'E), which may indicate southward movement of subsurface waters including global fallout  $^{239,240}\text{Pu}$ .<sup>85</sup> It must be noted that the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in the western North Atlantic coastal waters<sup>43</sup> and French Polynesia deep water (500 to 1000 m depth; 15°S)<sup>84</sup>

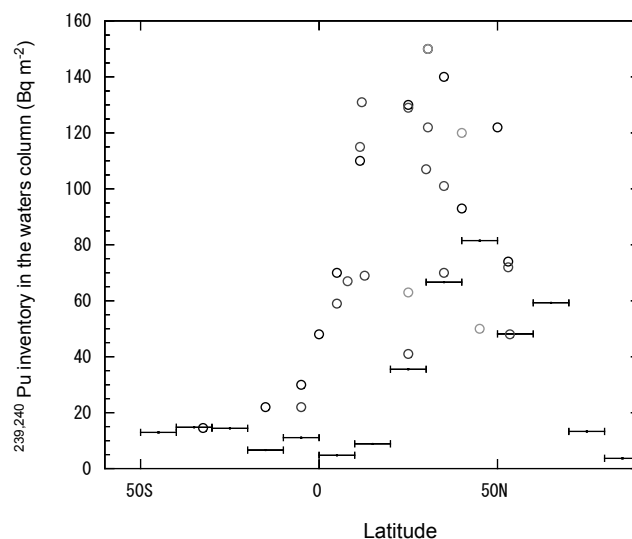
coincided with those in global fallout, although lower  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios (<0.05) due to the French nuclear tests were observed in the Mururoa lagoon waters.

Although data of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  activity ratios in the open ocean waters are limited, lower and higher  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratios than those in global fallout were observed in the subtropical western North Pacific,<sup>69</sup> and higher  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratios were observed in the eastern equatorial Pacific.<sup>58</sup>

A  $\beta$ -emitter with a half-life of 14.1 years,  $^{241}\text{Pu}$  is an important isotope because it is a parent nuclide of  $^{241}\text{Am}$ , an  $\alpha$ -emitter with a half-life of 433 years. Livingston et al<sup>106</sup> found that a typical value of the  $^{241}\text{Pu}/^{239,240}\text{Pu}$  activity ratio in global fallout samples was 13 to 14.

**3.7. Inventory of  $^{239,240}\text{Pu}$  in the water column.** The water column inventories of  $^{239,240}\text{Pu}$  in the Pacific were evaluated for the GEOSECS stations in the early 1970s.<sup>8</sup> The  $^{239,240}\text{Pu}$  inventory in the water columns of the open ocean was calculated by interpolating the  $^{239,240}\text{Pu}$  concentration measured at each depth.<sup>9</sup> A pronounced feature of latitudinal distribution of the  $^{239,240}\text{Pu}$  inventory (Figure. 4) was markedly high  $^{239,240}\text{Pu}$  inventories in the western North Pacific, compared with that of the latitudinal distribution of global fallout  $^{239,240}\text{Pu}$ .<sup>107</sup> The higher water column inventories of  $^{239,240}\text{Pu}$  in the western North Pacific (100 to 130  $\text{Bq m}^{-2}$ )<sup>69,74</sup> continued in the 1990s.<sup>9</sup> This finding suggested that a significant amount of the  $^{239,240}\text{Pu}$  inventory in the water column in the western North Pacific originated from sources other than global fallout, such as close-in fallout, consistent with the fact that close-in fallout from testing at the Pacific Proving Grounds is the most important source of plutonium in the North Pacific, according to a plutonium isotope study,<sup>41</sup> and that most of the close-in fallout  $^{239,240}\text{Pu}$  still remains in the western subtropical North Pacific.

It is probable that the present water column inventories of  $^{239,240}\text{Pu}$  are controlled by horizontal advection and bottom topography of the North Pacific instead of deposition due to global and close-in fallout, because the major deposition of  $^{239,240}\text{Pu}$  originating from atmospheric nuclear weapon testing occurred in the 1950s and early 1960s. It is also possible that the apparent inventories of plutonium depend on depth. Therefore, in order to gain a better understanding of surface processes including biogeochemical processes and surface input from unknown sources such as radioactive waste dumping by the former USSR,<sup>80</sup> 2300 m-depth inventories of  $^{239,240}\text{Pu}$  were introduced to clarify the characteristics of the spatial distribution of the  $^{239,240}\text{Pu}$  water column inventories.<sup>9,108</sup> The 2300



**Figure 4.** Latitudinal distribution of  $^{239,240}\text{Pu}$  water column inventories in the Pacific. Bar shows the latitudinal distribution of global fallout  $^{239,240}\text{Pu}$  (Ref.107) and open circle shows the  $^{239,240}\text{Pu}$  water column inventory.

m  $^{239,240}\text{Pu}$  inventories in the Sikoku Basin of the western North Pacific ( $\sim 70 \text{ Bq m}^{-2}$ )<sup>85,108</sup> seemed to be greater than those in mid-latitudes of the central North Pacific (35 to  $53 \text{ Bq m}^{-2}$ ) and of the same order of magnitude as in the sea area near Bikini and Enewetak Atolls observed in 1997 (61 and  $74 \text{ Bq m}^{-2}$ ).<sup>9</sup>

The  $^{239,240}\text{Pu}$  inventory in the mid-latitude region of the western North Pacific decreased, in comparison with that in GEOSECS.<sup>9,69</sup> A major part of the decrease of the  $^{239,240}\text{Pu}$  inventory in the mid-latitude region was attributable to the deficient upper layer (0 to 1000 m depth). A decrease of inventory in the water columns of the North Pacific mid-latitude region was observed for  $^{137}\text{Cs}$ .<sup>109</sup> However, no temporal decrease of the  $^{239,240}\text{Pu}$  inventories was observed in the subtropical and equatorial North Pacific water columns.<sup>9</sup>

The fallout plutonium originating from the Pacific Proving Ground testing (Bravo test) was characterized by a lower  $^{238}\text{Pu}/^{239,240}\text{Pu}$  activity ratio (0.001) and a higher  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio (0.33).<sup>103</sup> If plutonium in the water columns of the western North Pacific consisted of only two components (i.e. global fallout and close-in fallout (Bravo test)),  $^{239,240}\text{Pu}$  inventories derived from individual fallout could be estimated from plutonium isotope data based on a simple mixing model. The  $^{239,240}\text{Pu}$  water column inventory originating from global fallout for the use of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  activity ratios can be estimated by

$$I_{\text{WG},1} = (I_{\text{WT},2} - I_{\text{WT},1} R_B) / (R_G - R_B), \quad (1)$$

where  $I_{\text{WT},1}$  is the total inventory of  $^{239,240}\text{Pu}$  in the water column,  $I_{\text{WG},1}$  is the total inventory of  $^{239,240}\text{Pu}$  from global fallout,  $I_{\text{WT},2}$  is the total inventory of  $^{238}\text{Pu}$  in the water column, and  $I_{\text{WG},2}$  is the total inventory of  $^{238}\text{Pu}$  from global fallout. The value of  $R_G$  is the  $^{238}\text{Pu}/^{239,240}\text{Pu}$  activity ratio in global fallout (0.029), and that of  $R_B$  is the  $^{238}\text{Pu}/^{239,240}\text{Pu}$  activity ratio in close-in fallout from US nuclear explosions (0.001). As another estimation of close-in fallout plutonium, the  $^{239,240}\text{Pu}$  concentration derived from the Bikini nuclear explosion is calculated from  $^{240}\text{Pu}/^{240}\text{Pu}$  atom ratios by

$$A_B = A_O(1 + \lambda_R R_B) / [1 + \lambda_R R_B + (1 + \lambda_R R_G) Q] \quad (2)$$

and

$$Q = (R_O - R_B) / (R_G - R_O),$$

where  $A_B$  is the Bikini-derived  $^{239,240}\text{Pu}$  activity concentration,  $A_O$  is the observed  $^{239,240}\text{Pu}$  activity concentration,  $\lambda_R$  is the ratio of the radioactive decay constant of  $^{239}\text{Pu}$  to  $^{240}\text{Pu}$ ,  $R_B$  is the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio of the Bikini water sample,  $R_G$  is the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio of Bikini global fallout water sample, and  $R_O$  is the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio of the observed water sample. The Bikini-derived  $^{239,240}\text{Pu}$  inventory was calculated from the calculated Bikini-derived  $^{239,240}\text{Pu}$  concentrations at each depth. The results suggest that a significant amount of  $^{239,240}\text{Pu}$  derived from close-in fallout spread over the subtropical region of the western North Pacific,<sup>37-61</sup> and close-in fallout  $^{239,240}\text{Pu}$  accounted for 37–61 % of the current  $^{239,240}\text{Pu}$  inventory. A gap of the  $^{239,240}\text{Pu}$  inventory between the subtropical and equatorial North Pacific was resulted from the close-in fallout, since most of the close-in fallout due to the Pacific Proving ground nuclear explosion occurred in the northern sea area of Bikini and Enewetak Atolls.<sup>110</sup>

**3.8. Local contamination of plutonium.** Nuclear treatment sites; e.g. Bikini ( $11^\circ 35' \text{N}$ ,  $165^\circ 23' \text{E}$ ), Enewetak ( $11^\circ 30' \text{N}$ ,  $162^\circ 15' \text{E}$ ), and Mururoa Atolls ( $21^\circ 50' \text{S}$ ,  $138^\circ 50' \text{W}$ ) (Figure 1); produced hot spots of plutonium-contaminated areas in the marine environment. High  $^{239,240}\text{Pu}$  concentrations in lagoon waters (more than  $1 \text{ Bq m}^{-3}$  in Bikini in 1982,  $0.54 \text{ Bq m}^{-3}$  in Enewetak in 1994,<sup>111-113</sup> and more than  $0.1 \text{ Bq m}^{-3}$  in Mururoa in 1991<sup>114-116</sup>) were observed, although no information is available on the effects on the outflow of local  $^{239,240}\text{Pu}$  contaminated waters to the open ocean. The  $^{239,240}\text{Pu}$  concentrations for

the Mururoa lagoon waters decreased, with an apparent HRT of nine years.

#### 4. Concluding remarks

Knowledge provided by plutonium studies in the ocean during the past four decades is summarized as follows.

1.  $\alpha$ -spectrometry is still the major technique for determining plutonium in seawater, although mass spectrometric techniques such as ICP-MS are predicted to be a powerful tool.

2. The present geographical distribution of surface  $^{239,240}\text{Pu}$  is governed by oceanographic processes rather than input processes. The  $^{239,240}\text{Pu}$  concentration in surface waters revealed temporal variations, decreasing exponentially in mid-latitudes and the subtropical regions of the Pacific. However, decrease rates depended on the sea areas, whereas no decrease tendency of the equatorial Pacific surface  $^{239,240}\text{Pu}$  has been detected since 1985.

3. The vertical profiles of  $^{239,240}\text{Pu}$  in the water columns of the Pacific exhibited a typical pattern with a surface minimum, mid-depth maximum, and gradual decrease with increasing depth. The temporal variation of the  $^{239,240}\text{Pu}$  vertical profiles depended on the sea areas. In the mid-latitude region of the North Pacific, the  $^{239,240}\text{Pu}$  maximum layer deepened with time, and the corresponding  $^{239,240}\text{Pu}$  concentrations decreased; however, no change of the  $^{239,240}\text{Pu}$  vertical profiles was observed in the subtropical and equatorial North Pacific.

4. The  $^{239,240}\text{Pu}$  concentrations in deep waters (>2000 m depth) of the Pacific had a spatial structure that seemed to reflect input patterns of global fallout and close-in fallout. This finding suggests that temporal variation of deep  $^{239,240}\text{Pu}$  may be a tool for determining deep-water circulation because of its smaller biogeochemical contribution, although little temporal variability of deep  $^{239,240}\text{Pu}$  may occur on a time scale of several decades.

5. The plutonium isotope signature, which is useful for identifying sources, suggests that a large amount of  $^{239,240}\text{Pu}$  was injected into the subtropical western North Pacific as close-in fallout of the Pacific Proving Ground nuclear testing in the early 1950s, and spread due to advection and diffusion in the North Pacific over the subsequent five decades.

6. A large latitudinal gradient of current  $^{239,240}\text{Pu}$  inventories was observed in the Pacific, with a high inventory in the western North Pacific and a low inventory in the South Pacific. Individual  $^{239,240}\text{Pu}$  inventories from global fallout and close-in fallout were estimated using plutonium isotope ratios; the close-in fallout  $^{239,240}\text{Pu}$  still accounted for 37 to 61% of the  $^{239,240}\text{Pu}$  water column inventory in the subtropical North Pacific.

7. Chemical speciation studies revealed that the major dissolved plutonium species was inorganic complexes of Pu(V), whereas particulate plutonium was an organic complex of Pu(IV) with ligands in particulate matter.

The development of analytical tools has resulted in increasing information about distributions and behavior of plutonium in the ocean. However, less data exists on  $^{239,240}\text{Pu}$  concentrations in the ocean than on  $^{137}\text{Cs}$ .<sup>14</sup> Plutonium is a unique transient tracer of biogeochemical processes in the marine environment. In order to gain a better understanding of the biogeochemical behavior of  $^{239,240}\text{Pu}$  in the ocean, we need much more  $^{239,240}\text{Pu}$  concentration data in seawater, especially in deep waters. Thus, further development of analytical techniques, including improvement of measurement system sensitivity to reduce sample volumes of less than 10L and simplification of separation and purification processes, is required.

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