

## Size-fractionated plutonium isotopes in a coastal environment

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### Abstract

We have examined the distribution of individual Pu isotopes (<sup>239</sup>Pu, <sup>240</sup>Pu, and <sup>241</sup>Pu) in seawater from the Gulf of Maine (GOM). Samples were size-fractionated with a 1 kD cross-flow ultrafiltration (CFF) membrane. Subfractioned samples were radiochemically purified and Pu isotopes were analyzed using a three-stage thermal ionization mass spectrometer (TIMS). To our knowledge, this is the first time that both size class and Pu isotopic data have been obtained for seawater samples. Within measurement uncertainties a single <sup>240</sup>Pu/<sup>239</sup>Pu atom ratio of 0.18 was found for all sample collection depths and sample size fractions. This signifies a current, single Pu source in GOM waters, namely global fallout, and suggests that no measurable isotopic fractionation occurred during CFF processing. The majority of Pu was found in the low molecular weight fraction (<1 kD). Colloidal Pu varied from 8% of the total in surface waters to <1% in the deepest (250 m) seawater sample. Evidence suggests that the vertical distribution of Pu in GOM is primarily controlled by conservative mixing processes. The high Pu fraction found in the low molecular size fraction implies that most of the Pu is in the non-particle-reactive oxidized fraction, and is consistent with the conservative Pu behavior. The activity levels are in agreement with other studies which show a slow decrease in Pu with time due to continued mixing and relatively slow particle removal. © 2000 Elsevier Science B.V.. All rights reserved.

*Keywords:* Plutonium; Isotopes; Colloids; Cross-flow ultrafiltration; Gulf of Maine

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## 1. Introduction

Plutonium had been spread world-wide through above-ground nuclear weapons testing during the 1950s and early 1960s (Perkins and Thomas, 1980; Harley, 1980; Sholkovitz, 1983) and through various accidental releases and reprocessing of nuclear materials (Johnson, 1984; Kim, 1986; Guéguéniat, Germain & Métivier, 1996). The release of artificial radionuclides in general is of environmental concern, but these radionuclides have also become a useful tool for tracing geochemical processes in marine research (Broecker & Peng, 1982; Kershaw & Woodhead, 1991). Consequently, considerable effort has been devoted to the study of radionuclides in the marine environment. However, as Hamilton (1998) recently stated, “In paying attention to the specific needs of radiological protection and the protection of man and the environment from ionizing radiation, insufficient attention has been paid to the identification of prime processes which control the distributions of radionuclides”. Moreover, most of the results for Pu in the environment are based upon the measurement of combined activities of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  by alpha spectrometry. Since alpha spectrometry is not able to distinguish the decay energies of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , these results can rarely identify local Pu sources (such as close-in fallout or reprocessing waste streams) and must assume an identical geochemical behavior of Pu from its various sources. Source information for Pu is best achieved using high-sensitivity mass spectrometry techniques (e.g. TIMS or the less sensitive inductively coupled plasma mass spectrometry).

It has become increasingly evident that Pu transport in the marine environment depends dramatically on its sources (global fallout vs. close-in fallout, Buesseler and Sholkovitz, 1987; Buesseler, 1997) and its speciation (Baxter, Fowler & Povinec, 1995). While oxidation states of Pu in seawater have been measured (e.g., Nelson and Lovett, 1978, 1981; Orlandini, Penrose & Nelson, 1986; Choppin and Kobashi, 1990; Mitchell et al., 1991, 1995), its size fractionation and partitioning are less commonly studied. The lack of size partitioning data is primarily associated with its extremely low concentration (subfemtogram, or  $<10^{-15}$  g/l) in seawater and even lower concentration in the fractionated samples. Thus highly sensitive analytical techniques are required. Size-fractionation utilizing CFF techniques, which allows for processing of multi-liter sample volumes, was only recently introduced to the marine sciences, in the early 1990s (Benner, 1991; Buesseler et al., 1996; Guo & Santschi 1997; Dai et al., 1998). CFF is the only practical technique able to process large-volume samples and, as shown in this paper, low blanks and reasonable mass balances for Pu can be achieved through careful application of this tool. The combination of TIMS and CFF provides us therefore with a unique approach for studying Pu sources and host (e.g., particles, colloids) size distribution in the marine environment.

Aarkrog (1988) summarized existing Pu studies in the ocean and concluded that Pu is highly associated with particles/sediments. Thus, Pu is expected to be rapidly removed from the water column, particularly in highly particle-laden coastal waters. We report in this paper a novel data set from the GOM showing that a dominant fraction of Pu passes through our 1 kD CFF membrane. We suggest that even in

coastal waters, Pu is relatively soluble and appears to have a longer residence time in the water column than earlier studies would have predicted.

## 2. Materials and methods

### 2.1. Study area

The Gulf of Maine is a semi-enclosed coastal sea on the Northwest Atlantic shelf. Water circulation within the GOM is complex. Within Wilkinson Basin, surface waters generally flow in a cyclonic pattern and Atlantic slope waters enter the GOM through the Northeast channel (Brooks, 1992). This slope water affects the distribution of Pu in the Gulf.

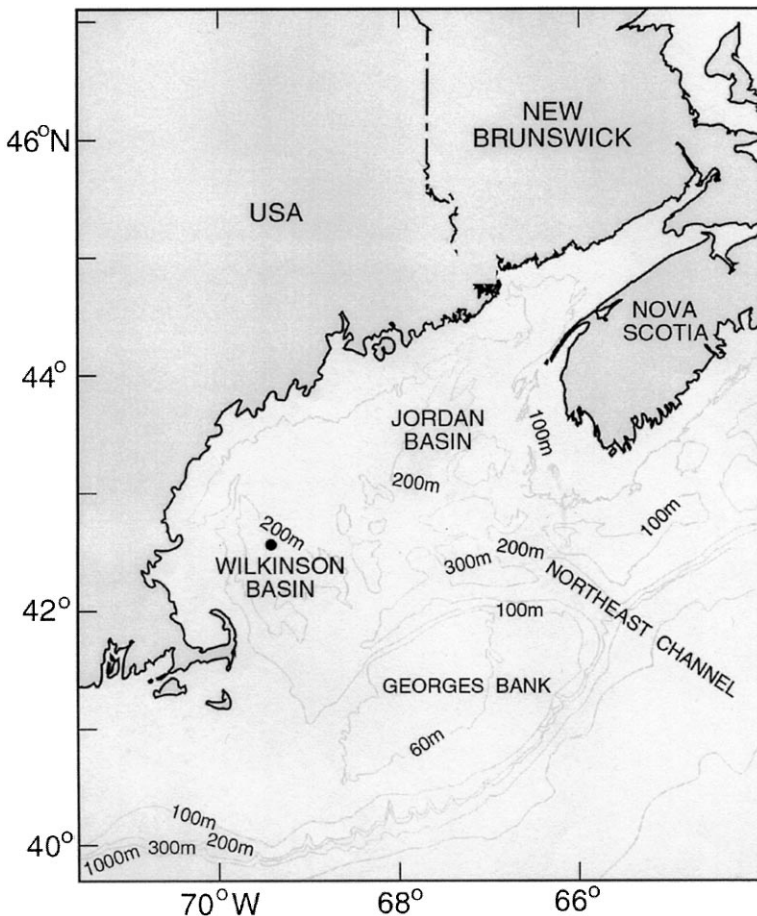


Fig. 1. Map showing the location of the Gulf of Maine and the sampling station at the Wilkinson Basin.

## 2.2. Sampling

Seawater samples were collected in the GOM from Wilkinson Basin at a station located at 42°29.1N and 69°43.7W (Fig. 1) aboard the R/V *Cape Hatteras* in July, 1997. The total water depth of the sampling station is 272 m. Samples were collected from 30 Niskin bottles and pumped directly via Teflon tubing through acid-cleaned polycarbonate Nuclepore filters (142 mm diameter; 1.0 µm pore size) and subsequently through the CFF system. Unfiltered samples were also collected and particulate Pu concentrations were calculated by difference between the unfiltered and filtered samples.

We shall use the following terms in the text. “Permeate” is the fraction passing through a CFF membrane while “retentate” is the fraction retained by the membrane. We define the colloidal fraction as the material which passes through a 1.0 µm prefilter and is retained by our 1 kD CFF membranes. Particulate is the fraction retained by a 1 µm Nuclepore prefilter. The total dissolved fraction is that which passes through this prefilter.

## 2.3. CFF processing

Detailed CFF processing procedures are described in Dai et al. (1998). Briefly, our CFF system is composed of a Flojet polypropylene diaphragm pump, plumbing (mostly of Teflon) and Millipore Prep/Scale™-TFF PLAC regenerated cellulose CFF membranes. We used 3 CFF membranes (nominal molecular weight cutoff = 1 kD) in parallel (surface area 18 ft<sup>2</sup>) to increase the ultrafiltration rate to about 150 ml/min. The prefiltered seawater (through 1 µm Nuclepore filters) was continuously fed into a 4 l fluorinated polyethylene bottle. The membrane pressure was maintained at ~14–16 psi during CFF operation.

Before and after a typical sample run, the CFF system was cleaned by flushing with > 20 L nano-pure water (referred to as Q-water hereafter) followed by 0.01 N NaOH and 0.01 N HCl solutions made from the same Q-water. The base or acid solution was recirculated for at least one hour followed by rinsing with Q water until pH~7. These cleaning steps were followed by preconditioning with prefiltered seawater (4–6 l). The cleaning was conducted just prior to each sample run.

“Integrated” refers to samples of permeate and retentate collected from the CFF system for Pu isotopes at the end of sampling.

## 2.4. Colloidal concentration

The colloidal Pu concentration is calculated based on the Pu concentrations measured in the integrated permeate and retentate samples, and the concentration factor cf.

$$[\text{Pu}_{\text{colloidal}}] = ([\text{Pu}_{\text{retentate}}] - [\text{Pu}_{\text{permeate}}]) / \text{cf}, \quad (1)$$

$$\text{cf} = (\text{retentate volume} + \text{permeate volume}) / \text{retentate volume} \quad (2)$$

The mass balance, or recovery (R%) can be calculated by comparing the sum of the colloidal and permeate Pu concentrations with the concentration of Pu in the initial source solution (prefiltrate).

### 2.5. Analysis

Size-fractionated samples were collected in acid-cleaned 4 l fluorinated polyethylene bottles and acidified with ultrapure HNO<sub>3</sub> to pH~2 followed by addition of standardized <sup>244</sup>Pu tracers and FeCl<sub>3</sub> (~1 mg Fe/1 l sample). Nominal aliquot sizes taken for Pu analyses were about 4 kg except for the retentate fraction, in which case 1.5 kg aliquots were used. Samples were allowed to equilibrate for >48 h while being slowly stirred at ~40°C in order to remove CO<sub>2</sub> in the sample. Carbonates which form soluble complex compounds with Pu must be absent prior to the co-precipitation. Pu was then co-precipitated with iron hydroxide by adjusting the pH to 8–9 with ultrapure NH<sub>4</sub>OH (Seastar). Samples were allowed to stand overnight and the precipitates were filtered onto acid-cleaned Duropore filters (47 mm diameter; 0.45 μm pore size, Millipore). After digestion, samples were radiochemically purified by running sequentially through two anion exchange columns (AG1-X4, 100-200 mesh, Bio-Rad Lab., Richmond, CA). The first is a 4 ml bed-volume anion exchange column, and the second is a 100 μl micro-volume column. Pu was eluted with 1.2 M HCl onto a Teflon pad. Next, samples were even more stringently purified by employing, instead of a column, a single 800 μm diameter resin bead. The maximum volume of analyte used in this operation, which is carried out under a microscope, is 20 μl. Finally, Pu was incorporated in a single, nominally 150 μm diameter resin bead from 1 μl of 7.5 M HNO<sub>3</sub>. The bead was transferred into the trough of a rhenium filament formed into a V-shape as a mass spectrometry ion source. During all procedures, only ultrapure acids (Seastar or Ultrex) were used.

The mass spectrometer is a three-stage instrument with a pulse-counting ion detection system (Lagergren and Stoffels, 1970). The instrument is equipped with a sliding-shaft vacuum lock that enables precise positioning of the mass spectrometer source. Masses were scanned by sweeping the magnetic field. The bead was pyrolyzed, the filament carburized, and the mass spectrometry measurements conducted using standard Pacific Northwest National Laboratory (PNNL) operating procedures. The high sensitivity associated with TIMS analysis enables detection of extremely low atom concentrations of elements of interest. To insure the absence of measurable (> 10<sup>4</sup> atoms) contamination, process blanks were liberally interspersed with samples.

## 3. Results and discussion

### 3.1. Process blank and CFF mass balance

In the light of our previous experience with the application of CFF to thorium studies (Dai et al., 1998), we carefully evaluated CFF performance. The two crucial

Table 1  
 CFF system blank of Pu isotopes ( $\mu\text{Bq/kg}$ )

Sample	$^{239}\text{Pu}$	$^{240}\text{Pu}$	$^{241}\text{Pu}$
Permeate blank	<0.02	<0.02	<0.007
Retentate blank <sup>a</sup>	<0.02	<0.008	<0.008

<sup>a</sup> Retentate blank refers to Q-water being concentrated by a factor of 4 with the CFF.

issues related to CFF's applicability are system blanks and mass balance issues (Buesseler et al., 1996; Dai et al., 1998). After careful cleaning, we achieved Pu blanks that were at or below TIMS detection limits, i.e. 0.02  $\mu\text{Bq/kg}$ . The blanks were not significant with respect to Pu isotope levels subsequently measured in samples (see Table 1).

CFF mass balance provides a first-order check on sorptive losses. The recoveries of Pu in this study were generally  $100 \pm 10\%$  (Table 2), indicating that on balance no significant losses or contamination occurred during the CFF processing of seawater samples. For the 37 m sample, the CFF mass balance was only  $86 \pm 3\%$  for  $^{239}\text{Pu}$ . The concentration factor (cf) for this sample was the highest among the samples processed (12.7 vs.  $\leq 10$ ). We have noted previously that losses of high molecular weight material onto the CFF membranes may occur preferentially at higher CFF concentration factors (Dai et al., 1998).

### 3.2. Pu isotopic ratios

Listed in Table 3 are the Pu isotopic ratios in the different size fractions. The atom ratios of  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{241}\text{Pu}/^{239}\text{Pu}$  were similar in all fractions. We do not expect there to be any fractionation related to CFF processing and these uniform data confirm this expectation. When plotted it is easy to see that the measured  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios are indistinguishable from those observed for global fallout in the Northern Hemisphere ( $0.18 \pm 0.014$ , Kelley, Bond & Beasley, 1999), indicating that Pu in the GOM originated primarily from global fallout (Fig. 2). This is similar to most other water-column Pu data, except in the vicinity of close-in fallout sources, such as the Marshall Islands (Buesseler, 1997) and Mururoa Atoll (Chiappini, Millies-Lacroix, Le Petit & Poiturier, 1998), where anomalous  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios have been found. There were only 4 colloidal Pu samples with sufficient signal to quantify  $^{240}\text{Pu}/^{239}\text{Pu}$ , and two of these (37 and 65 m) are slightly lower than the global fallout average; but within the errors these data overlap with the soil data (Fig. 2). Using the simple two end-member mixing model of Krey et al. (1976), a  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of 0.170 requires  $\sim 2\%$  of Nevada Pu being contributed (Nevada  $^{240}\text{Pu}/^{239}\text{Pu} = 0.035$ , Krey et al., 1976). This study shows that most of  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in the GOM water column is  $> 0.170$ , hence there is no evidence that there remains sufficient Nevada Pu in the water column to lower the bulk water-column  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio while low-ratio Pu has been detected in the sediments off the NE US coast from Nevada fallout (Buesseler and Sholkovitz, 1987).

Table 2  
<sup>239</sup>Pu concentrations in different size fractions of Gulf of Maine samples<sup>a</sup>

Depth m	Unfiltered μBq/kg ± 1σ error	Total dissolved μBq/kg ± 1σ error	Permeate μBq/kg ± 1σ error	Colloidal μBq/kg ± 1σ error	% of unfiltered μBq/kg ± 1σ error	% of total dissolved fraction ± 1σ error	Particulate μBq/kg ± 1σ error	% of unfiltered fraction ± 1σ error	CFF recovery % ± 1σ error							
1	3.98	0.05	3.72	0.17	0.01	4.17	0.25	4.34	0.26	0.16	0.07	4.0	1.7	101.5	1.8	
15 <sup>b</sup>	4.21	0.05	2.81	0.06	<b>2.46</b>	<b>0.32</b>	0.35	0.03	8.25	0.79	12.35	1.21	1.40	0.08	33.2	1.9
37	4.76	0.30	4.46	0.12	3.54	0.08	0.28	0.02	5.87	0.50	6.27	0.40	0.30	0.32	<14	—
65	5.58	0.08	5.33	0.08	4.47	0.08	0.41	0.02	7.36	0.40	7.71	0.42	0.25	0.11	4.5	2.0
200	8.15	0.08	7.40	0.06	17.48	0.06	0.24	0.01	2.92	0.16	3.22	0.18	0.75	0.10	9.2	1.3
250	9.07	0.12	8.01	0.11	7.61	0.14	0.00	0.02	<0.5	—	<0.5	—	1.06	0.16	11.6	1.8

<sup>a</sup> Size fractions: total dissolved, <1 μm; permeate, <1 kD; colloidal, 1 kD–1 μm; particulate, >1 μm. A <sup>239</sup>Pu half-life of 24119 ± 27 y was used to convert the measured atom concentrations to the activity units (Bq/kg water) presented here.

<sup>b</sup> The permeate fraction of the 15 m sample was lost during preparation for measurement. The concentration value for this fraction is shown in bold type and was calculated in accordance with Eq. (1) (see text) from the <sup>239</sup>Pu concentration in the retentate fraction, the measured concentration factor, and an assumed value for the CFF recovery of 100 ± 10%, which is also shown in bold type.

Table 3  
Pu isotopic ratios in different size fractions of Gulf of Maine samples<sup>a</sup>

Depth m	Unfiltered atom ratio	$\pm 1\sigma$ error	Total dissolved atom ratio	$\pm 1\sigma$ error	Permeate atom ratio	$\pm 1\sigma$ error	Colloidal atom ratio	$\pm 1\sigma$ error	Particulate atom ratio	$\pm 1\sigma$ error
<b><sup>240</sup>Pu/<sup>239</sup>Pu</b>										
1	0.1892	0.0027	0.1873	0.0030	0.1830	0.0031	0.186	0.023	0.1748	0.0046
15 <sup>b</sup>	0.1833	0.0026	0.1801	0.0054	<b>0.177</b>	<b>0.034</b>	0.204	0.028	0.1794	0.0029
37	0.194	0.010	0.1760	0.0070	0.1831	0.0062	0.157	0.023	0.1809	0.0045
65	0.1808	0.0028	0.1769	0.0032	0.1823	0.0028	0.169	0.017	0.26	0.17
200	0.1837	0.0017	0.1844	0.0015	0.1831	0.0014	0.179	0.019	0.176	0.042
250	0.1803	0.0024	0.1790	0.0025	0.1826	0.0035	—	—	0.190	0.050
<b><sup>241</sup>Pu/<sup>239</sup>Pu<sup>c</sup></b>										
10.0026	0.0005	0.0025	0.0005	0.0025	0.0006	N/A	N/A	0.0025	0.0012	
15	0.0027	0.0005	0.0025	0.0008	N/A	N/A	N/A	N/A	0.0030	0.0008
37	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
65	0.0026	0.0009	0.0028	0.0007	0.0030	0.0005	N/A	N/A	N/A	N/A
200	0.0025	0.0002	0.0026	0.0003	0.0028	0.0003	N/A	N/A	N/A	N/A
250	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	N/A	N/A	N/A	N/A

<sup>a</sup>Size fractions: Total dissolved, <1 μm; permeate, <1 kD; colloidal, 1 kD–1 μm; particulate, > 1 μm.

<sup>b</sup>The permeate fraction of the 15 m sample was lost during preparation for measurement. The <sup>240</sup>Pu/<sup>239</sup>Pu atom ratio value for this fraction is shown in bold type and was calculated in accordance with Eq. (1) (see text) from the <sup>239</sup>Pu and <sup>240</sup>Pu concentrations in the retentate fraction, the measured concentration factor, and an assumed value for the CFF recovery of 100 ± 10%.

<sup>c</sup><sup>241</sup>Pu was decay corrected to January 1, 1998.



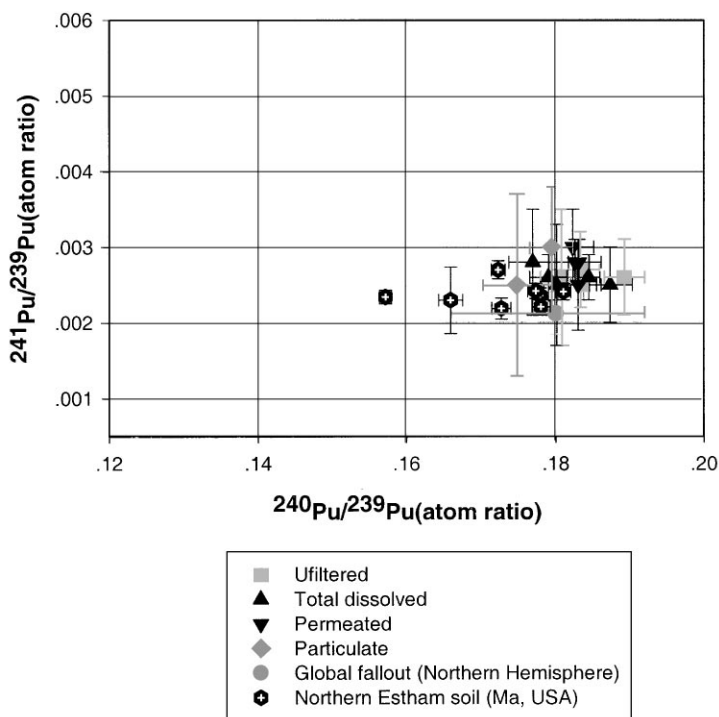


Fig. 2. Plot of  $^{240}\text{Pu}/^{239}\text{Pu}$  against  $^{241}\text{Pu}/^{239}\text{Pu}$  atom ratio in fractionated GOM seawater samples. Also shown are the global fallout average ratios ( $^{240}\text{Pu}/^{239}\text{Pu} = 0.18 \pm 0.01$ ,  $^{241}\text{Pu}/^{239}\text{Pu} = 2.13 \times 10^{-3} \pm 0.28 \times 10^{-3}$ , compiled by Kelley et al., 1999) and ratios in Northern Estham soil samples (data from Kelley).

The  $^{241}\text{Pu}/^{239}\text{Pu}$  ratio is analytically quite challenging to measure on these small sample sizes ( $10^4$ – $10^6$  atoms), and is rarely reported for Pu. In the fractions where we could quantify  $^{241}\text{Pu}/^{239}\text{Pu}$ , the mean ratio does not appear to be significantly different from the Northern Hemisphere fallout ratio defined by Kelley et al. (1999) (Fig. 2; decay-corrected to January 1, 1998;  $t_{1/2}$   $^{241}\text{Pu} = 14.33$  y). Thus from both the  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{241}\text{Pu}/^{239}\text{Pu}$  ratios, we conclude that the GOM Pu is derived from global fallout sources.

### 3.3. Pu concentrations

Pu concentration results of this work are compared in Table 4 with results from previous research. Here, concentrations are presented in terms of  $^{239,240}\text{Pu}$  alpha activities. To express our mass spectrometrically determined results as activities, we used half-life values for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  of  $24,119 \pm 27$  and  $6564 \pm 11$  yr, respectively. The  $^{239,240}\text{Pu}$  concentration in GOM surface waters has decreased over

Table 4  
Concentration of  $^{239,240}\text{Pu}$  in the Gulf of Maine and comparable North Atlantic regions<sup>a</sup>

	Sampling date	$^{239,240}\text{Pu}$ mBq/kg	$\pm 1\sigma$ error	Reference
Gulf of Maine				
1 m	1997	6.752	0.090	This study
15 m	1997	7.045	0.093	This study
37 m	1997	8.18	0.55	This study
65 m	1997	9.28	0.14	This study
200 m	1997	13.65	0.17	This study
250 m	1997	15.07	0.22	This study
Surface	1975	30.27	N/A	Cochran and Livingston (1987)
260 m	1975	50.45	N/A	Cochran and Livingston (1987)
Narragansett Bay (surface)	1976	31.95	0.34	Santschi et al. (1980)
Sargasso Sea (surface)	1984	23.2	1.5	Buesseler and Sholkovitz (1987)
Sargasso Sea (surface)	1984	21.7	1.5	Buesseler and Sholkovitz (1987)
Sargasso Sea (10 m)	1972	60.5	1.3	Livingston et al. (1985)
Sargasso Sea (4859 m)	1972	0.84	0.34	Livingston et al. (1985)
SEEP STA-D (454 m)	1984	20.85	0.12	Buesseler and Sholkovitz (1987)
SEEP STA-D (1700 m)	1984	16.7	1.5	Buesseler and Sholkovitz (1987)
Atlantic surface(40–50°)	1992–1993	6.9–11.5		Bourlat et al. (1996)

<sup>a</sup> All results presented here represent unfiltered sample collections. To express the mass spectrometrically determined results of this study in terms of alpha activities, we used half-life values for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  of  $24,119 \pm 27$  y and  $6,564 \pm 11$  y, respectively.

the last two decades by a factor of 4, from  $30 \mu\text{Bq/kg}$  in 1975 (GOM surface waters reported in Cochran and Livingston, 1987) to  $6.7 \mu\text{Bq/kg}$  (mean from this study).  $^{239,240}\text{Pu}$  concentrations in 1976 surface-water collections in the Narragansett Bay just south of the GOM (Santschi, Li, Bell, Trier & Kawtaluk, 1980) are also similar to the Cochran and Livingston results, suggesting that the earlier higher activities were representative of the region.

This decrease with time reflects the continuing decline of fallout input after the end of above-ground nuclear tests in 1980, and the corresponding subsequent decrease of stratospheric Pu input (Rosner, Hotzl & Winkler, 1997). In addition, there is continued removal of Pu from surface waters due to mixing and particulate scavenging processes. Long-term observations on Pu in air show a decrease of Pu deposition by a factor  $>10$  between 1978 and 1991 at Munich-Neuherberg, Germany (Rosner, Hotzl & Winkler, 1997). It is reasonable to assume that the change in fallout deposition would be similar in the GOM region, and hence the decline of Pu in surface seawater is slower than the decline in fallout input.

A decline in Pu concentration in surface waters is also seen elsewhere. According to Hirose, Sugimura and Aoyama (1992), Pu had decreased to about one-fifth of the 1979 value by 1987 in Northern Pacific surface waters. Holm, Sugimura & Aoyama (1991) noted a 4–5-fold decline in surface Pu concentrations from 1972 (GEOSECS) to 1988 (Swedish expedition) in Atlantic surface waters between  $73^\circ\text{N}$  and  $72^\circ\text{S}$ . Papucci et al. (1996) reported a 4-fold decrease in surface Pu in the Western Mediterranean from the early 1970s to the early 1990s. We note that much of the

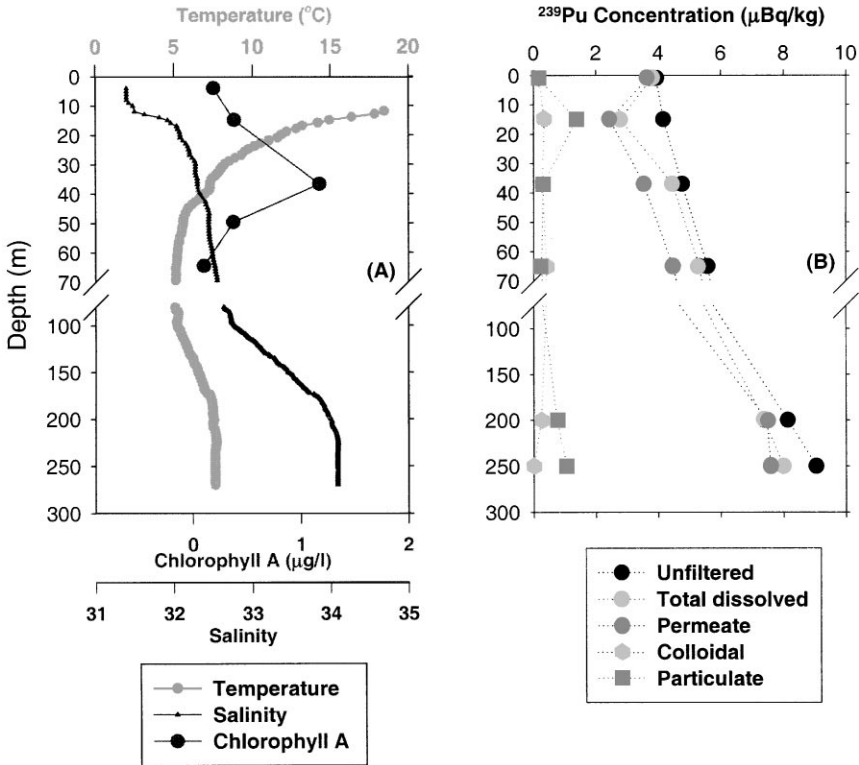


Fig. 3. Profiles of <sup>239</sup>Pu fractions and temperature, salinity in the Gulf of Maine seawater. In plots B, total dissolved, <1 µm; permeate, <1 kD; colloidal, 1 kD–1 µm; particulate, >1 µm. See the text for details. Note that all Pu concentrations are in the unit of Bg/kg water.

decline in Pu can be attributed to physical mixing in the Mediterranean. Papucci et al. (1996) reported a decrease in the conservative fallout radionuclide <sup>137</sup>Cs by a factor of 1.7 (decay corrected) between 1970 and 1982, at the same time that the Pu decrease was only slightly higher, or a factor of 2.2. It is clear that site-specific variations in the rates of mixing and sedimentation will alter the relative decrease of surface-water Pu and <sup>137</sup>Cs with time. Surface GOM Pu concentrations continue to decrease, similar to other regions, but much of the decrease appears to be due to physical mixing rather than local scavenging and sedimentation processes.

### 3.4. Pu vertical distribution

Fig. 3 shows the vertical distributions of size-fractionated Pu (<sup>239</sup>Pu data only, since <sup>240</sup>Pu/<sup>239</sup>Pu ratios are constant, see Table 3) along with temperature and salinity. We observed a linear increase in total Pu concentration (unfiltered samples) with depth by a factor of 2 (see Fig. 3B). The total dissolved and permeate Pu

concentrations similarly increase with depth, except at 15 m where these concentrations abruptly fall before rising again. At this 15 m depth, we note a clearly related maximum in the particulate Pu concentration. Cochran and Livingston (1987) reported a similar vertical profile in terms of  $^{239,240}\text{Pu}$  concentration at this same location. They attributed this pattern to the increase in the concentration of suspended particles (and associated  $^{239,240}\text{Pu}$ ) near the bottom. While our data show a  $^{239,240}\text{Pu}$  concentration increase in the particulate fraction near the bottom, it is too slight to account for the large difference between surface- and bottom-water total Pu levels.

Open ocean Pu concentration profiles are characterized by a depletion in surface waters, an increase with depth in the upper 100–400 m, and a decrease below forming a subsurface maximum (see for example GEOSECS data by Livingston et al., 1985). Many locations also exhibit an increase near the bottom, particularly in the vicinity of the Pacific test sites (Livingston et al., 1985). Shallower sites do not always show these features.

The increase in Pu concentration with depth in the GOM is similar to that found for Pu at shallower stations in the Mediterranean Sea (Papucci et al., 1996), and is characteristic of elements whose distributions are controlled by surface removal and deep regeneration in the ocean. We argue however, that simple conservative mixing between low Pu concentrations in near-shore waters and higher concentrations in off-shore waters would produce a Pu concentration profile similar to the one found here. Indeed, warmer and saline Atlantic slope water was clearly seen at the bottom of the studied region (see Fig. 3A). This Atlantic slope water characterized by higher Pu concentration flows into the GOM through the Northeast Channel (Brooks, 1992). We will further address this mixing phenomenon below.

### 3.5. Pu size fractionation and partitioning

The majority of Pu was found in the low molecular weight fraction (<1 kD) as shown in Table 2. Colloidal Pu varied from 8% of the total in surface waters to <1% in the deepest (250 m) seawater sample. Note that colloidal organic carbon (COC) represents ~20% of the DOC at this depth (Dai & Benitez-Nelson, 2000). Since total Pu is increasing with depth, and near-bottom, colloidal Pu is decreasing, this implies a different Pu partitioning affinity near the bottom. This low Pu affinity to COC in bottom waters may be related to the characteristics of the deep-water COC macromolecules (usually older) and/or the speciation of Pu. Pu is found in both reduced and oxidized forms in the oceans but with a dominant fraction in the oxidized form (Nelson, Carey & Bowen, 1984; Orlandini et al., 1986; Choppin and Kobashi, 1990; Mitchell et al., 1991). The oxidized Pu species are considerably less surface-reactive, hence an increase in oxidized Pu near bottom should correspond to a decrease in particulate and colloidal forms of Pu. An increase in the percentage of oxidized Pu near bottom was reported by Nelson et al. (1984) for the North Pacific Ocean. They suggested that chemical reactions near the sediment–water interface, possibly involving  $\text{MnO}_2$  as an active catalyst, would promote the oxidation of Pu.

Particulate Pu concentration is similar to that of colloidal Pu, except at 15 m, and in the deepest samples. At 15 m, particulate Pu represents 33% of the Pu in an unfiltered collection (Table 2; Fig. 3). The high particulate Pu concentration at 15 m does not directly correlate with chlorophyll or particulate organic carbon data, which peak at 37 m; however, this sample is at the base of a shallow pycnocline (Fig. 3A). It is noteworthy that our samples were taken in July right after the spring bloom in the GOM, which might be an alternative reason that both surface colloidal and particulate Pu concentrations were low in the GOM.

Particulate Pu concentration decreases overall with depth until the bottom-water interface, where an increase in particulate Pu concentration to > 10% of that of the unfiltered sample is observed (Fig. 3B). The increase near bottom is likely to be related to sediment resuspension. A nepheloid layer at the sediment–water interface caused by sediment resuspension is frequently reported at Wilkinson Basin (Pike, 1998 and references therein). However, as mentioned above, the resuspension of particles is not enough to account for the increase in Pu accumulated at the bottom.

There is no evidence in the study area that Pu forms complexes with organic matter or that Pu is enriched in a high-DOM environment as suggested by Nelson, Penrose, Karttunen and Mehlhaff (1985). Instead, dissolved Pu has a negative correlation with DOC in this study (Fig. 4A). Dissolved and permeate Pu have a positive correlation with salinity (Fig. 4B), with a slight reduction at 15 m where the particulate Pu maximum occurs. Generally, GOM surface waters are thus characterized by low Pu concentrations, low salinities, and relatively high DOC levels. Conservative mixing between these surface waters, and deeper high salinity, low DOC waters can generate the observed Pu concentration increase with depth with the exception of 15 m, where this increase reverses briefly and Pu seems to be more effectively scavenged by particles than at other depths. In the New York Bight, Santschi et al. (1980) also found that nearshore, low-salinity waters were lower in Pu concentration than offshore, higher-salinity samples. Thus, there is an overall pattern of higher Pu removal in particle-rich coastal regimes than in offshore regions, as expected with any particle reactive element. But the relatively constant mixing lines shown for DOC level and salinity versus Pu concentration (Fig. 4) suggest that the removal is slow and that mixing processes govern the vertical distribution of Pu in such regimes more so than particle scavenging considerations.

Buesseler, Livingston and Sholkovitz (1985) estimated that the measured Pu inventories in the sediments of the GOM constituted only 45% of the fallout expected at these latitudes. In the open ocean, even lower Pu inventories are found in marine sediments (Aarkrog, 1988), which might suggest that net residence times of Pu with respect to particle removal are larger than originally estimated.

The actual factors that control the Pu oxidation state distribution in the ocean are not known. Generally speaking, Pu in the coastal seas is believed to exist in an oxidized form. For example, Mitchell et al. (1995) reviewed a large data set on Pu oxidation states in the Irish Sea and concluded that some 87% of the Pu is in the oxidized, pentavalent form, Pu(V). Baxter et al. (1995) reached a similar conclusion. This dominant oxidized Pu form has less of an affinity for either colloids (macromolecules) or particles than the reduced ter- and tetravalent Pu forms. Our

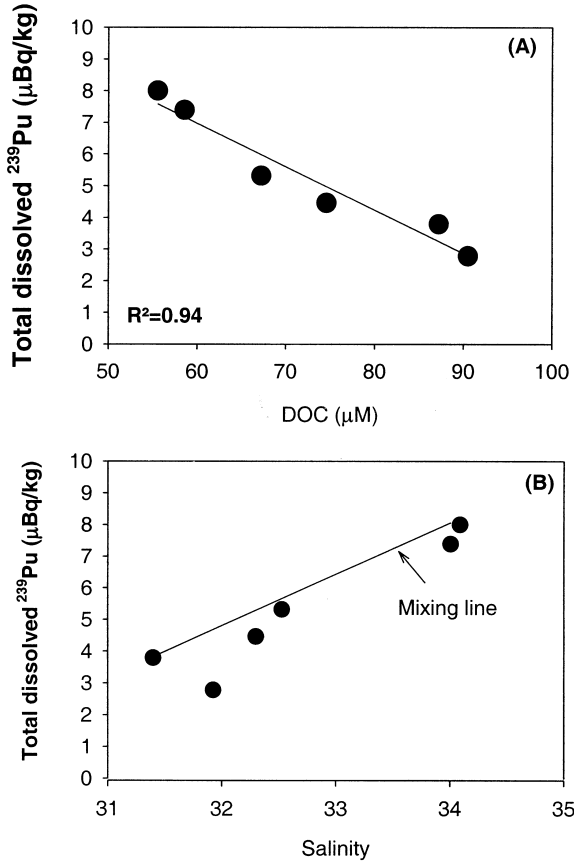


Fig. 4.  $^{239}\text{Pu}$  concentration plots against dissolved organic C (DOC), and salinity: (A)  $^{239}\text{Pu}$ -DOC; (B)  $^{239}\text{Pu}$ -salinity. Plots show mixing as a dominant process controlling the Pu distribution.

observation of low percentages of both colloidal and particulate Pu, and the conservative mixing lines for Pu and salinity found in our results may thus be attributed to the dominance of the less particle reactive oxidized forms of Pu.

#### 4. Summary

This investigation has shown for the first time that a combination of CFF and TIMS can be used for separating dissolved and colloidal forms of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in seawater. After careful cleaning CFF blanks are negligible and the CFF mass balance for Pu isotopes is acceptable in most cases. The results suggest that colloidal Pu is only a minor fraction of the total, as most of the Pu in the studied area occurs in the low molecular weight fraction ( $<1$  kD). The high Pu fraction found in this low molecular size fraction implies that most of the Pu is conservative, probably due

to its redox speciation being in the oxidized fraction. The source of Pu in the GOM is clearly global fallout, as seen in the  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{241}\text{Pu}/^{240}\text{Pu}$  isotopic ratios, and the activity levels are consistent with other studies which show a slow Pu decrease with time due to continued mixing and particle removal. The increase of Pu with depth is typical of highly scavenged elements in the oceans and the particulate maximum at 15 m suggests enhanced particulate removal at the base of the mixed layer. However, the constant mixing lines between high DOC, low salinity and low Pu surface waters and elevated deep Pu with lower DOC and higher salinity suggests that particle removal rates are slow and that the local vertical distribution of Pu is dominated by physical mixing processes on these time scales.

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