Ultra-trace plutonium determination in small volume seawater by sector field inductively coupled plasma mass spectrometry with application to Fukushima seawater samples

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ABSTRACT

Long-term monitoring of Pu isotopes in seawater is required for assessing Pu contamination in the marine environment from the Fukushima Dai-ichi Nuclear Power Plant accident. In this study, we established an accurate and precise analytical method based on anion-exchange chromatography and SF-ICP-MS. This method was able to determine Pu isotopes in seawater samples with small volumes (20–60 L). The U decontamination factor was $3 \times 10^7 - 1 \times 10^8$, which provided sufficient removal of interfering U from the seawater samples. The estimated limits of detection for ^{239}Pu and ^{240}Pu were 0.11 fg mL^{-1} and 0.08 fg mL^{-1}, respectively, which corresponded to 0.01 mBq m^{-3} for ^{239}Pu and 0.03 mBq m^{-3} for ^{240}Pu when a 20 L volume of seawater was measured. We achieved good precision (2.9%) and accuracy (0.8%) for measurement of the ^{240}Pu/^{239}Pu atom ratio in the standard Pu solution with a ^{239}Pu concentration of 11 fg mL^{-1} and ^{240}Pu concentration of 2.7 fg mL^{-1}. Seawater reference materials were used for the method validation and both the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios agreed well with the expected values. Surface and bottom seawater samples collected off Fukushima in the western North Pacific since March 2011 were analyzed. Our results suggested that there was no significant variation of the Pu distribution in seawater in the investigated areas compared to the distribution before the accident.

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1. Introduction

Plutonium isotopes (^{239}Pu, $t_{1/2}$ = 24,100 y; ^{240}Pu, $t_{1/2}$ = 6561 y) have been released into the marine environment as a result of global fallout from the atmospheric nuclear weapons testing, reprocessing of nuclear fuels, accidents of military nuclear facilities and accidents in nuclear plants [1]. Studying the concentration of plutonium isotopes in marine environment is important because Pu presents a potential threat to human health due to its radiotoxicity and its chemical toxicity. In addition, Pu isotopes play important roles as tracers for understanding ocean processes, such as sediment mixing and particle scavenging in the water column, and the atom ratio of ^{240}Pu/^{239}Pu, which varies from different sources,

serves as a key fingerprint for Pu source identification [2,3]. From these viewpoints, determination of Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater is highly necessary to understand fully the behavior and fate of Pu in marine environment. Although the total amount of Pu input to the ocean is large (8.6 PBq $^{239+240}$Pu by the year 2000 [4]), the concentration of Pu in seawater is extremely low. The $^{239+240}$Pu concentrations in the surface waters of the world ocean decreased exponentially over recent decades [5,6]. For instance, the $^{239+240}$Pu concentrations in the surface seawater of the North Pacific ranged from 8.1 to 35 mBq m^{-3} in the early 1970s, while in 2000, values were estimated to be 0.3–2.7 mBq m^{-3} [7]. This decrease of more than ten-fold has made it more difficult to make Pu measurements in seawater nowadays.

Conventionally, alpha spectrometry has usually been used for Pu measurement in seawater. With alpha spectrometry, large volumes of seawater (~200 L) and long counting times (days to several weeks) are normally needed. Moreover, alpha spectrometry cannot

distinguish ^{239}Pu and ^{240}Pu due to their close alpha radiation energies (5.16 Mev and 5.17 MeV for ^{239}Pu and ^{240}Pu, respectively); thus the ^{240}Pu/^{230}Pu atom ratio fingerprint cannot be given. Recently, the application of inductively coupled plasma mass spectrometry (ICP-MS) to the measurement of $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu atom ratio in various environmental samples at trace and ultra-trace levels has been widely studied [8–10]. The advantages of ICP-MS for the determination of Pu isotopes include easy sample preparation, short measurement time, and high sensitivity, precision and accuracy [11–13].

When ICP-MS is used for Pu determination, polyatomic interferences, especially from uranium hydrides, need to be carefully checked. The average ^{238}U concentration in seawater in the oceans is ca. 3 μg L^{-1}, nine to ten orders of magnitude higher than that of Pu [1,14]. Thus the severest interferences for the determination of Pu in seawater by ICP-MS come from the tailing effect of the ^{238}U$^+$ peak and the uranium hydrides (^{238}UH$^+$ and ^{238}UH$_2$$^+$), which cannot be resolved from ^{239}Pu$^+$ and ^{240}Pu$^+$ even with the HR mode ($m/\Delta m = 10,000$). Although efforts have been made to reduce the intensity ratio of ^{238}UH$^+$/^{238}U$^+$ detected by sector field ICP-MS (SF-ICP-MS) to become as low as 1–3×10^{-5} when proper sample introduction systems are used [14–17], complicated chemical procedures for the separation of Pu in seawater are still strongly needed prior to the ICP-MS analysis. If we assume a 20 L volume of seawater is used for the determination of Pu and the final sample is prepared in a 1 mL solution, a U decontamination factor greater than 1×10^7 is needed to reduce the ^{238}U concentration in the final sample solution to become less than 5 pg mL^{-1}, which is required to make the effect of ^{238}U negligible. In order to eliminate the troublesome interferences from seawater samples, efforts such as co-precipitation, anion-exchange chromatography, extraction chromatography and the combination of these methods have been taken in recent years [18–21].

The Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident caused the release of large amounts of radionuclides into the ocean [22,23]. The radioactive contamination status in the marine environment is of great concern. Intensive investigations of radioactivity in the marine environment focusing on fission radionuclides, such as ^{134}Cs, ^{137}Cs, ^{131}I and ^{90}Sr, have been carried out since the FDNPP accident [24–26]; however, corresponding studies about the actinides, especially Pu isotopes in seawater are limited. Normally, only 20–60 L seawater is collected for environment monitoring at a marine station due to the difficulty of seawater sampling and transportation. Thus in order to assess the possible Pu contamination in seawater from the FDNPP accident, an accurate and precise analytical method is highly desired for the measurement of Pu isotopes in small-volume seawater samples.

As Pu is an important element involved in the GEOTRACES program, six laboratories participated in its inter-calibration exercise on Pu determination in seawater samples [27]. The reported values showed measurement of $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater at current concentration levels with a sample volume of 20 L remains a challenge. In this work, an analytical method based on anion-exchange chromatography using Dowex 1X8 resin and SF-ICP-MS for the determination of plutonium isotopes at the ultra-trace level in seawater was established. The aim of this study was to establish and validate the required analytical method for Pu measurement in small-volume (20–60 L) seawater as part of the on-going project for long-term and continuous assessment of the oceanic Pu contamination from the FDNPP accident. The analytical merits of this method, including U decontamination, analytical precision and accuracy were discussed. Seawater reference materials were measured for validation of the method. Finally, this method was applied to determine $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater collected off the FDNPP site in the western North
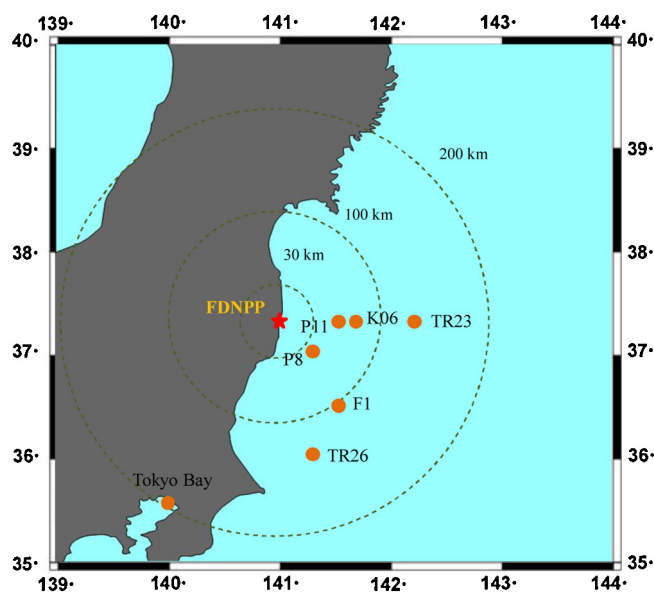

Fig. 1. Map showing seawater collection stations from the western North Pacific and Tokyo Bay since the FDNPP accident.

Pacific since March 2011 to identify the possible Pu contamination from the accident in the marine environment.

2. Materials and methods

2.1. Reagents and seawater samples

A Millipore Milli-Q-Plus water purification system was used for the preparation of high-purity water (18 MΩ cm^{-1}). All commercial chemicals used were of analytical grade except for source preparation prior to ICP-MS measurement, in which ultrapure grade 68% HNO$_3$ (Tama Chemicals, Japan) was used. Fe-carrier (20 mg mL^{-1} Fe in 1 M HNO$_3$) was prepared from iron (III) chloride hexahydrate. The anion exchange resins used in this study were Dowex 1X8 (100–200 mesh, Wako Chemical, Ltd., Japan), AG 1X8 (100–200 mesh, Bio-rad Laboratories, Inc., USA and Eichrom Technologies, LLC., USA) and AG MP-1 M (100–200 mesh, Bio-rad Laboratories, Inc., USA). ^{242}Pu (CRM 130, plutonium spike assay and isotopic standard, New Brunswick Laboratory, USA), as a yield tracer, was used to spike the seawater samples.

Two certified seawater reference materials IAEA-381 and IAEA-443 were obtained from International Atomic Energy Agency (IAEA, Vienna, Austria). Surface seawater samples (20 L for each sample) were collected from Tokyo Bay in April 2013 for the method optimization. Surface and bottom seawater samples (20–60 L for each sample) were gotten 30 km off the FDNPP site in the western North Pacific during the cruises of MR 11-05, KH 11-07 and KT-13-1 from July 2011 to January 2013 from the following stations: K06 (37°20′ N 141°40′ E), F1 (36°29′ N 141°30′ E), P8 (37°00′ N 141°17′ E), P11 (37°20′ N 141°28′ E), TR23 (37°20′ N 142°10′ E) and TR26 (36°00′ N 141°20′ E). These locations for the seawater collection are shown in Fig. 1.

2.2. Uranium extraction from anion-exchange resins

In order to choose the proper anion-exchange resin for the separation of Pu in seawater samples, we compared the extracted U by 8 M HNO$_3$ from the four different kinds of resins. About 2.0 g resin was weighed out into a 15 mL centrifuge tube and 5 mL 8 M HNO$_3$ was added for the extraction of U from the resin. The centrifuge tubes were put on a shake stage and shook for 2 h. The slurry was
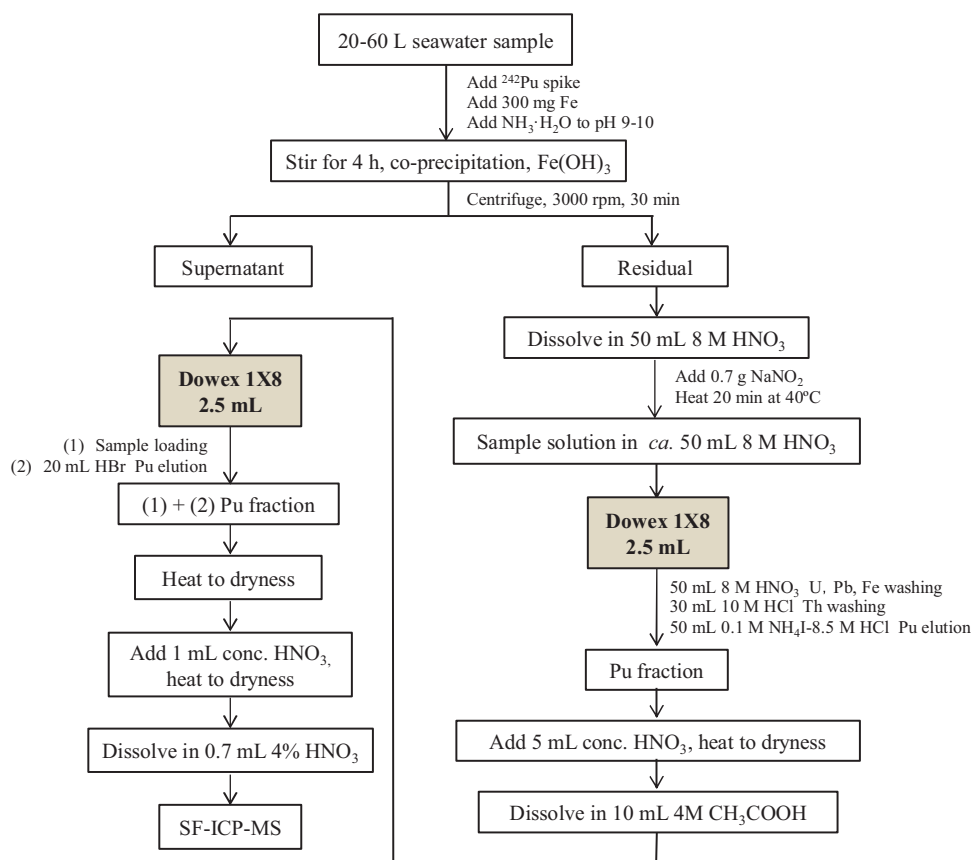
Fig. 2. Flow chart of the analytical procedure for the determination of Pu isotopes in seawater by anion-exchange chromatography and SF-ICP-MS.

then filtered through an Advantec filter (0.45 μm). The obtained pure solution was heated to dryness and dissolved in 1 mL 4% HNO_3, in preparation for the SF-ICP-MS analysis. For each type of resin, three replicates were prepared and measured.

2.3. Seawater sample preparation

Prior to the analysis by SF-ICP-MS, Pu in seawater needs to be separated from interfering elements. In this study, we used $Fe(OH)_3$ co-precipitation for the initial Pu concentration step, followed by the anion-exchange method for the separation and further purification of Pu. The overall seawater sample preparation procedure is illustrated in Fig. 2.

2.3.1. Fe(OH)₃ co-precipitation

Seawater was first acidified to pH 1.5–2 with concentrated HCl and then filtered through an Advantec PTFE Capsule Filter (0.22 μm) (Toyo Roshi Kaisha, Ltd., Japan) into a HDPE bucket (20 L) (Teraoka Company, Japan). About 0.6 pg ^{242}Pu was added as a yield monitor. The seawater sample and ^{242}Pu spike were equilibrated for 24 h. After adding 15 mL Fe solution (20 mg mL^{-1} Fe in 1 M HNO_3) to the sample, the pH was adjusted to 9–10 by the addition of concentrated NH_4OH. Pu and other actinides were co-precipitated with iron hydroxide. This procedure was the first-step U elimination and less than 10% of U in seawater would be co-precipitated at the pH of 9–10 [28]. The formed $Fe(OH)_3$ precipitates were stirred for at least 4 h using a K-1RN stirrer (ASONE Company, Japan) and then allowed to settle overnight. The sample supernatant was carefully siphoned away. The obtained Fe precipitate slurry was collected in a 250 mL centrifuge tube and the small volumes (20–30 mL) of pure water used to rinse out the sample bucket (2–3 times) were also added to the tube. The slurry was then

centrifuged at 3000 rpm for 30 min. After pouring off the overlying solution, the Fe precipitates were dissolved in 50 mL 8 M HNO_3 and transferred to a 150 mL glass beaker.

2.3.2. Separation and purification

As shown in Fig. 2, a two-stage anion-exchange chromatography method using Dowex 1X8 was employed for the separation and further purification of Pu. The Dowex 1X8 resin was pretreated with 1.2% NaOH and 6 M HCl and then kept in pure water before use. After co-precipitation and dissolution in 50 mL 8 M HNO_3, 0.7 g $NaNO_2$ was added to the sample solution and this was heated at 40 °C for 20 min to convert Pu to the tetravalent state. The Dowex 1X8 resin was packed in a PTFE column (2.5 mL, 6.5–8.5 × 58 mm, i.d.). After preconditioning the column with 20 mL 8 M HNO_3–0.2 M $NaNO_2$, the seawater sample was loaded onto it. Then 50 mL 8 M HNO_3 was used to wash out U, Pb and Fe, and 30 mL 10 M HCl was used to wash out Th. After that, 50 mL 0.1 M NH_4I–8.5 M HCl was loaded for Pu elution. The eluent was collected in a 100 mL Teflon beaker. After adding 5 mL conc. HNO_3, the sample was evaporated to dryness on a hotplate (160 °C) to destroy any residual organic material and remove iodine. Then the sample was dissolved in 10 mL 4 M CH_3COOH, in preparation for loading onto the second resin column (2.5 mL, 6.5–8.5 × 58 mm, i.d.).

The second Dowex 1X8 resin column was preconditioned with 30 mL 4% NaOH, followed by 30 mL H_2O and 30 mL 4 M CH_3COOH. Then the sample solution was loaded. U and tetravalent Pu were absorbed on the column while Pu in other valence states passed through it and was collected in a 50 mL Teflon beaker. The tetravalent Pu on the column was eluted with 20 mL conc. HBr and the eluent was collected in the same 50 mL Teflon beaker. After evaporating the obtained sample solution to near dryness on a hotplate, 1 mL conc. HNO_3 was added and heating was continued to remove

Table 1
Operation parameters for SF-ICP-MS and APEX-Q system.

SF-ICP-MS	
RF Power	1370 W
Nebulizer	Conical concentric
Sample cone	Nickel
Skimmer cone	X-cone
Cool gas	16 L min^{-1}
Auxiliary gas	0.92 L min^{-1}
Sample gas	0.97–1.00 L min^{-1} (optimized daily)
Extraction	−2000 V
Torch X-position	1.7 mm
Torch Y-position	2.1 mm
Torch Z-position	−3.4 mm
Mass resolution	Low ($m/\Delta m = 300$)
Acquisition mode	E-scan (peak jumping)
Monitored isotopes	$^{238}U^+$, $^{239}Pu^+$, $^{240}Pu^+$, $^{242}Pu^+$
No. of scans (runs × passes)	15 × 3
Mass window	10%
Sample per peaks	100
Sample time	$^{238}U^+$ (10 ms), $^{239}Pu^+$ (70 ms), $^{240}Pu^+$ (100 ms), $^{242}Pu^+$ (30 ms)
Integration type	Average
Total time of analysis	130 s
APEX-Q system	
Sample uptake	0.2 mL min^{-1}
Spray chamber temperature	140 °C
Condenser temperature	2 °C
Sweep gas	3 L min^{-1}
Additional gas	0.11 L min^{-1}
N$_2$ gas	~10 mL min^{-1}

Table 2
Amount of ^{238}U extracted by 8 M HNO$_3$ using different types of resins.

Resin type	Manufacture	U (ng g^{-1})[a]
Dowex 1X8, 100–200 mesh	Wako Chemical, Ltd.	0.011 ± 0.001
AG 1X8, 100–200 mesh	Bio-Rad Laboratories, Inc.	0.034 ± 0.013
AG 1X8, 100–200 mesh	Eichrom Technologies, LCC.	0.124 ± 0.027
AG MP-1M, 100–200 mesh	Bio-Rad Laboratories, Inc.	0.097 ± 0.021

[a] Results are given as average of three replicates ± standard deviation.

any trace of HBr. When near dryness, the final residual was dissolved in 0.7 mL 4% HNO$_3$, prepared for the SF-ICP-MS analysis.

2.4. SF-ICP-MS measurements

Measurements of Pu isotopes were carried out with a SF-ICP-MS (Finigan Element 2, Germany). An APEX-Q high efficiency sample introduction system (Elemental Scientific Inc, USA) combined with a membrane desolvation unit (ACM) and equipped with a conical concentric nebulizer was used for sample introduction.

The measurements were performed in a low resolution mode ($m/\Delta m = 300$) to maximize the instrument sensitivity. We used the self-aspirating mode to reduce the risk of contamination by the peristaltic pump tubing and the sample flow rate was 150 μL min^{-1}. The isotopes of interest (^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu) were analyzed in the peak hopping mode and the peak tops of the masses were measured at 10% of their respective peak width. The typical operational setup and parameters of this analytical system for the Pu analysis are summarized in Table 1. Each time before measuring the samples, a 0.1 ng mL^{-1} U standard solution (Merck standard) was used for the optimization of the SF-ICP-MS system. The mixed Pu isotope standard solution NBS-947 ($^{240}Pu/^{239}Pu = 0.242$, National Bureau of Standards, USA) was used for mass bias correction.

3. Results and discussion

3.1. Anion-exchange resin selection

For the separation of Pu isotopes, the most widely used anion-exchange resin types are Dowex 1X8, AG 1X8 and AG MP-1M [17,29,30]. As the elimination of U from the seawater sample is one of the main purposes for Pu separation, the U concentration in the anion-exchange resins should be checked. Here, we compared these anion-exchange resins: Dowex 1X8 (100–200 mesh), AG 1X8 (100–200 mesh) and AG MP-1M (100–200 mesh). The analytical results of ^{238}U extracted from each type of resin are shown in Table 2. We can see that Dowex 1X8 (100–200 mesh) resin has

the lowest ^{238}U concentration (0.011 ± 0.001 ng g^{-1}) for extraction by 8 M HNO$_3$. Thus we chose it for the separation of Pu in seawater sample in this study.

3.2. Separation of Pu and U by anion-exchange chromatography

In this study, Dowex 1X8 resin was used for the separation of Pu from the seawater sample matrixes. Although the one stage anion-exchange column has been demonstrated to provide sufficient separation of Pu from interfering elements such as Pb and Hg in various environment samples, a certain amounts of U still remains in the final sample solution [29,31]. For example, Muramatsu et al. [29] used the one stage Dowex 1X8 resin column for the separation of Pu in sediment and soil samples and found that U in the final sample solution ranged from 40 to 200 pg mL^{-1} and the U decontamination factor was of the order of 10^4 to 10^5. As mentioned in the introduction section, in order to ignore the U hydride interferences, U decontamination factor larger than 1×10^7 is needed for the accurate determination of Pu isotopes in seawater. Thus for the further elimination of U from the seawater sample, we used a second Dowex 1X8 resin column to purify Pu prior to the SF-ICP-MS analysis.

In previous studies using Dowex 1X8 resin for Pu separation [32–34], after loading the Pu sample solution (in 4 M CH$_3$COOH) onto the Dowex 1X8 resin column, another 10–20 mL 4 M CH$_3$COOH was used for the elution of Pu in the column. As U in 4 M CH$_3$COOH was absorbed on the Dowex 1X8 resin column, this procedure could ensure the further separation of Pu and U. However, after Pu was eluted with 0.1 M NH$_4$I–8.5 M HCl from the first Dowex 1X8 resin column, 5 mL conc. HNO$_3$ was added to the sample solution and evaporated to near dryness to eliminate the residual I$^-$ and destroy any organic matter. The concentrated HNO$_3$ also oxidized part of the trivalent Pu to the tetravalent state. The tetravalent Pu was absorbed on the second Dowex 1X8 resin column and could not be eluted by 4 M CH$_3$COOH, thus leading to low Pu chemical recovery. In order to sufficiently elute Pu from the second Dowex 1X8 resin column, we used conc. HBr instead of 4 M CH$_3$COOH for Pu elution after sample loading. Two seawater samples (Tokyo Bay seawater, 20 L for each) were analyzed to investigate the sorption and elution behavior of Pu and U on the second Dowex 1X8 resin column. Effluent and eluent were collected at 5 mL intervals and were prepared for analysis. The Pu yield and concentration of ^{238}U in the effluent and eluent of the second Dowex 1X8 resin column after sample loading are shown in Fig. 3.

We can see that most of the Pu was in the effluent of sample loading and the eluent of 20 mL HBr. The concentration of ^{238}U in either the effluent of sample loading or the eluent of HBr was quite low (0.13–0.21 pg mL^{-1}), indicating there was sufficient separation of Pu and U in seawater by the two-stage anion-exchange chromatography employed in this study.

3.3. SF-ICP-MS sensitivity and detection limit

High sensitivity and low detection limit are needed for the analysis of Pu in small-volume seawater due to the low concentration of Pu. We used an APEX-Q sample introduction system to
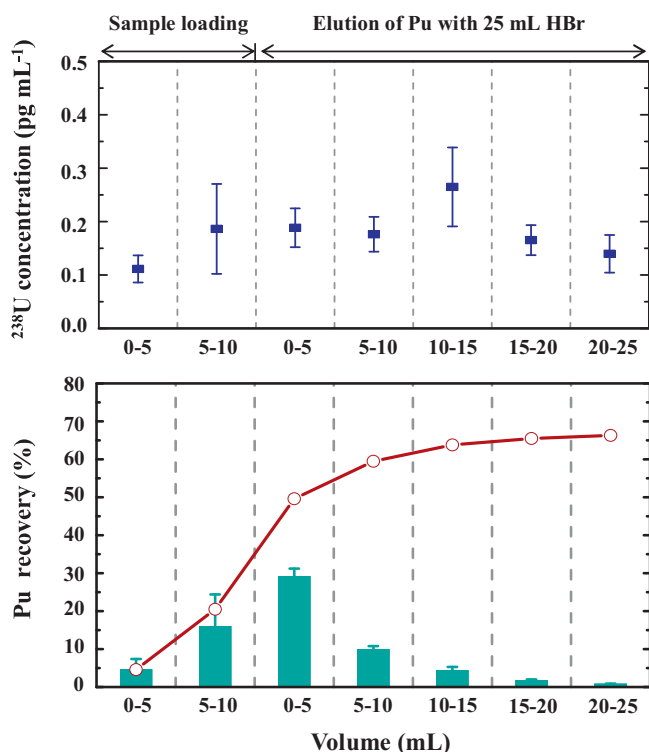
Sample loading | Elution of Pu with 25 mL HBr

Fig. 3. Pu chemical recoveries and ^{238}U concentrations in the effluent and eluent of the second Dowex 1X8 resin column. The cyan column represents the individual Pu chemical recovery. The brown line represents the accumulated Pu chemical recovery. The error bars represent the standard deviation of two replicates.

Fig. 4. Comparison of flow rate standardized sensitivity (per 100 μL min^{-1}) for ^{238}U in SF-ICP-MS with the APEX-Q system using different nebulizers. Nebulizers: 1, PFA-100 nebulizer (12 M cps ppb^{-1}, 100 μL min^{-1}); 2, ST-nebulizer (15 M cps ppb^{-1}, 400 μL min^{-1}); 3, conical nebulizer (20 M cps ppb^{-1}, 150 μL min^{-1}); 4, Micromist nebulizer (15 M cps ppb^{-1}, 200 μL min^{-1}); 5, HPCN nebulizer (22 M cps ppb^{-1}, 300 μL min^{-1}).

improve the sensitivity of SF-ICP-MS. This system can be equipped with various nebulizers operating over a wide range of sample uptake rates from 20 μL min^{-1} to over 1 mL min^{-1} and the nebulizers can be either self-aspirated or pumped [17]. The normally used nebulizers coupled with SF-ICP-MS for the analysis of long-lived radionuclides in our laboratory include the PFA-100 nebulizer (100 μL min^{-1}), the ST-nebulizer (400 μL min^{-1}), the micromist nebulizer (200 μL min^{-1}) and the conical nebulizer (150 μL min^{-1}). Recently, a high performance concentric nebulizer (HPCN), which has a triple tube concentric structure and consists of a concentric type nebulizer body and a fused silica glass capillary, was developed [35]. The HPCN has been confirmed to have fine aerosol generation and good capacity for low liquid flow rate. Here, we tested the capacity of the HPCN coupled with the APEX-Q system and SF-ICP-MS for the analysis of Pu and made a comparison with the other mentioned nebulizers to find the most suitable nebulizer for the analysis of Pu in seawater. For each type of nebulizer, 0.1 ng mL^{-1} ^{238}U solution was used and the operational setup and parameters were optimized to achieve the highest sensitivity with the acceptable UH$^+$/U$^+$ and UO$^+$/U$^+$ ratios.

Fig. 4 shows the comparison of the flow rate standardized sensitivities for ^{238}U in SF-ICPMS with the different nebulizers coupled with the APEX-Q as the sample introduction system. The highest absolute sensitivity (22 M cps ppb^{-1}) of ^{238}U was achieved by the HPCN. However, to achieve this high sensitivity, the sample uptake rate of the HPCN rose to 300 μL min^{-1}, thus there was no significant improvement on the absolute detection limit for the HPCN compared with the conical nebulizer as more sample solution was needed with the same analysis time. Moreover, the HPCN worked with the peristaltic pump, and the memory effect caused by the contamination of the peristaltic pump tubing during the analysis made it time-consuming (>5 min) to reduce the interference signals to the blank level. Thus we chose the conical nebulizer,
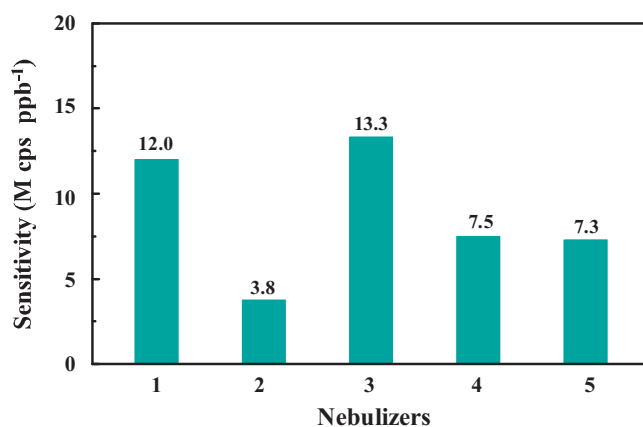
which has the highest flow rate standardized ^{238}U sensitivity of 13.3 M cps ppb^{-1} with a sample uptake rate of 150 μL min^{-1}, for Pu analysis.

We measured 20 L pure water following the same chemical procedure for Pu determination in seawater to determine operational blank count rates for 239 and 240 masses. The limit of detection (LOD) was estimated based on the IUPAC recommendations [36]. The LOD for ^{239}Pu and ^{240}Pu were 0.11 fg mL^{-1} and 0.08 fg mL^{-1}, respectively, corresponding to 0.01 mBq m^{-3} for ^{239}Pu and 0.03 mBq m^{-3} for ^{240}Pu when a 20 L volume of seawater was measured.

3.4. Accuracy and precision for ^{240}Pu/^{239}Pu atom ratio measurement

To study the accuracy and precision of the ^{240}Pu/^{239}Pu atom ratio measured by our analytical system, a certified Pu isotope standard solution (NBS-947) with the certified ^{240}Pu/^{239}Pu atom ratio of 0.242 was used. The NBS-947 solution was diluted to two different concentrations (^{239}Pu concentration of 110 fg mL^{-1} and ^{240}Pu concentration of 26.7 fg mL^{-1}; ^{239}Pu concentration of 11 fg mL^{-1} and ^{240}Pu concentration of 2.7 fg mL^{-1}). Analysis was done ten times for both solutions with different concentrations. The analytical results are illustrated in Fig. 5. For the analysis of the NBS-947 solution at ^{239}Pu concentration of 110 fg mL^{-1}, the measured ^{240}Pu/^{239}Pu atom ratio was 0.241 ± 0.008 ($k = 2$) and the precision (RSD) and accuracy were 1.7% and −0.4%, respectively. When the ^{239}Pu concentration was reduced to 11 fg mL^{-1}, the measured ^{240}Pu/^{239}Pu atom ratio was 0.244 ± 0.014 ($k = 2$) and the precision and accuracy were 2.9% and 0.8%, respectively. All the measured ^{240}Pu/^{239}Pu atom ratios were in the 95% confidence level, suggesting a reliable determination method with good precision for Pu analysis. Lindahl et al. [21] used MC-ICP-MS for the determination of Pu isotopes in marine samples, and they achieved a precision of 2.6% ($n = 10$) for the measurement solution with ^{239}Pu concentration of ~193 fg mL^{-1} and a precision of 1.3% ($n = 10$) for the measurement solution with ^{239}Pu concentration of ~84 fg mL^{-1}. Our results obtained with SF-ICP-MS were comparable to their reported values.

3.5. Validation of the developed analytical method

Two seawater reference materials IAEA-381 and IAEA-443 were used for the validation of our analytical method. The $^{239+240}$Pu
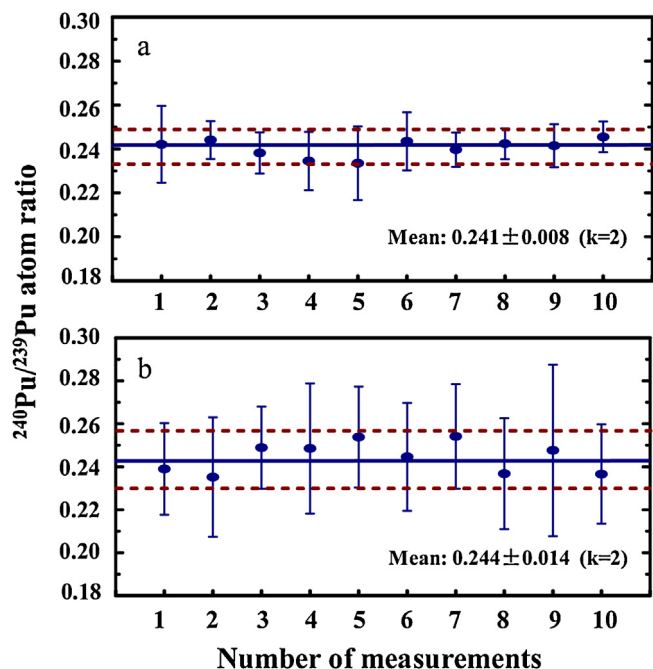
Fig. 5. Precision of ^{240}Pu/^{239}Pu atom ratio measurements obtained for Pu standard solution NBS-947. The error bars represent the standard deviation of the repeated 15 measurements during each analysis. The horizontal solid line represents the certified ^{240}Pu/^{239}Pu atom ratio (0.242). The dashed lines represent the expanded uncertainties ($k = 2$) for all analyses. (a) NBS-947 solution with ^{239}Pu concentration of 110 fg mL^{-1} and ^{240}Pu concentration of 26.7 fg mL^{-1}. (b) NBS-947 solution with ^{239}Pu concentration of 11 fg mL^{-1} and ^{240}Pu concentration of 2.7 fg mL^{-1}.

activities in the two seawater reference materials were relatively high (13.7 ± 1.2 mBq L^{-1} for IAEA-381 and 14.6 ± 0.4 mBq L^{-1} for IAEA-443). In order to test the validity of our analytical method for the determination of Pu isotopes in seawater with an ultra-trace low level of Pu concentrations, small amounts of seawater reference materials were added to pure water and 20 L seawater from Tokyo Bay for analysis of $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios. Comparisons of the measured $^{239+240}$Pu activities with the expected values and the measured ^{240}Pu/^{239}Pu atom ratios with the reference values are shown in Table 3. The $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios for the seawater samples collected from the Tokyo Bay together with ^{238}U concentrations in the final sample solutions and the Pu chemical recoveries are also presented.

The measured $^{239+240}$Pu activities of the seawater reference materials agreed well with the expected values. For the two seawater samples (S1, S2 in Table 3) that mixed 20 L seawater from the Tokyo Bay with 50 mL IAEA-381, the measured $^{239+240}$Pu activities were still in the range of the added activity ranges. As the $^{239+240}$Pu activities for the Tokyo Bay seawater ranged from 1.09 to 1.92 mBq m^{-3}, 20 L seawater from the Tokyo Bay introduced only 0.02 to 0.04 mBq $^{239+240}$Pu to the measured activities. There was no significant variation for the ^{240}Pu/^{239}Pu atom ratios between the two reference materials and the seawater from Tokyo Bay. All the measured ^{240}Pu/^{239}Pu atom ratios of the reference materials were consist with the reference values.

The main interference for the analysis of Pu isotopes in seawater by ICP-MS comes from ^{238}U. Kim et al. [37] applied a two-stage online extraction chromatographic method using TEVA-Spec and Sr-Spec for the separation and purification of Pu from seawater prior to ICP-MS analysis and they found that the ^{238}U concentrations in the final sample solutions were approximately 13 pg mL^{-1} when less than 10 L seawater was used. Lindahl et al. [21] employed an anion-exchange and extraction chromatography combined method (AG 1X8 + UTEVA + TRU) for the determination of Pu in seawater and reported that the ^{238}U concentrations in the final sample solutions were 1.3–4.1 pg mL^{-1}. For all the reference and seawater samples from Tokyo Bay measured in our study, ^{238}U concentrations in the final sample solutions ranged from 0.88 to 4.16 pg mL^{-1}. Our results were lower than that reported by Kim et al. [37] and comparable with the results reported by Lindahl et al. [21] with a three stage chromatographic separation. When a 60 L seawater was analyzed by our method, the ^{238}U concentration in the final sample solution was still below 5 pg mL^{-1}. The U decontamination factor was calculated to be 3×10^7–1×10^8. Typical mass spectra of a 20 L seawater determined by our method and an operational blank are presented in Fig. 6. The ^{238}U signal intensities for the seawater sample detected by SF-ICP-MS were about 20,000 cps, similar to that of the operational blank. As the ^{238}UH$^+$/^{238}U$^+$ ratio for our SF-ICP-MS system was less than 2×10^{-5}, the contribution of ^{238}UH$^+$ to the ^{239}Pu$^+$ of interest was below 0.5 cps. Considering that the intensity of ^{239}Pu in the seawater sample exceeded 120 cps, our method made the determination of Pu isotopes in seawater free of U interference.

The Pu chemical recoveries of our method ranged from 58% to 82% with an average of 67 ± 8%. This chemical recovery was comparable with the values reported by other researchers for the analysis of Pu isotopes in seawater samples [20,37,38].

Table 3
Results of seawater reference materials measured by our method for comparison with the reference values.

Sample	^{238}U in final sample solution (pg mL^{-1})[a]	Added $^{239+240}$Pu activity (mBq)[b]	Measured $^{239+240}$Pu activity (mBq)[a]	Certified ^{240}Pu/^{239}Pu atom ratio	Measured ^{240}Pu/^{239}Pu atom ratio[a]	Pu chemical recovery (%)
S1	1.25 ± 0.11	0.67–0.70	0.69 ± 0.04	0.22 ± 0.03	0.235 ± 0.015	57.9 ± 2.0
S2	1.24 ± 0.12	0.67–0.70	0.71 ± 0.03	0.22 ± 0.03	0.224 ± 0.013	59.8 ± 1.9
S3	3.40 ± 0.09	0.73–0.77	0.74 ± 0.02	0.229 ± 0.006	0.229 ± 0.013	70.4 ± 1.4
S4	1.90 ± 0.02	0.73–0.77	0.76 ± 0.05	0.229 ± 0.006	0.244 ± 0.032	61.9 ± 1.7
S5	0.88 ± 0.03	1.46–1.54	1.40 ± 0.03	0.229 ± 0.006	0.232 ± 0.013	72.1 ± 1.5

Tokyo Bay seawater

Sample	^{238}U in final sample solution (pg mL^{-1})[a]	$^{239+240}$Pu activity (mBq m^{-3})[a]	^{240}Pu/^{239}Pu atom ratio[a]	Pu chemical recovery (%)
S6	3.78 ± 0.20	1.40 ± 0.13	0.235 ± 0.040	82.3 ± 0.9
S7	4.16 ± 0.17	1.09 ± 0.17	0.215 ± 0.033	72.9 ± 1.8
S8	3.28 ± 0.10	1.55 ± 0.20	0.234 ± 0.031	64.2 ± 2.4
S9	4.16 ± 0.09	1.92 ± 0.21	0.237 ± 0.029	65.3 ± 2.0

[a] Uncertainties are expressed as the expanded standard uncertainty with a coverage factor of 2.
[b] Data with 95% confidence interval; Sample S1, 50 mL IAEA-381 + 20 L Tokyo Bay seawater; Sample S2, 50 mL IAEA-381 + 20 L Tokyo Bay seawater; Sample S3, 50 mL IAEA-443 + 20 L pure water; Sample S4, 50 mL IAEA-443 + 20 L pure water; Sample S5, 100 mL IAEA-443 + 20 L pure water; Samples S6-S9: 20 L Tokyo Bay seawater.

Table 4
$^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater samples collected in the western North Pacific since the FDNPP accident.

Sample	Depth (m)[a]	Sample volume (L)	^{238}U in final solution (pg mL^{-1})[b]	$^{239+240}$Pu activity (mBq m^{-3})[b]	^{240}Pu/^{239}Pu atom ratio[b]
K06	0	20	2.08 ± 0.03	5.59 ± 0.39	0.251 ± 0.034
F1	Bottom-10	20	1.89 ± 0.09	1.44 ± 0.19	0.284 ± 0.057
P8	Bottom-10	20	1.47 ± 0.04	1.80 ± 0.25	0.230 ± 0.040
P11	Bottom-10	20	1.61 ± 0.03	0.43 ± 0.07	–
TR 23	0	55	2.28 ± 0.03	2.15 ± 0.12	0.227 ± 0.024
TR 23	75	60	1.18 ± 0.05	0.60 ± 0.13	–
TR 23	Bottom-10	50	1.62 ± 0.04	1.96 ± 0.31	0.276 ± 0.025
TR 26	0	60	1.40 ± 0.06	2.15 ± 0.11	0.237 ± 0.026
TR 26	Bottom-10	55	1.42 ± 0.06	3.45 ± 0.31	0.231 ± 0.021

[a] Bottom-10 indicates seawater collected at the depth from the sea floor to 10 m above the sea floor.
[b] Uncertainties are expressed as the expanded standard uncertainty with a coverage factor of 2.

3.6. Determination of Pu isotopes in seawater off Fukushima

The FDNPP accident caused the release of large amounts of radionuclides into the ocean and the release continued even one year after the accident [39]. As marine products are a major component in the Japanese diet, seafood safety is of great concern. The impact of the FDNPP accident on the Pu contamination in marine environment needs to be investigated. Kim et al. [40] determined Pu isotopes in surface and vertically collected seawater samples from the seas adjacent to Korea one to three months after the FDNPP accident, and they found that there was no significant variation for Pu distribution in seawater before and after the FDNPP accident. More recently, Sakaguchi et al. [41] analyzed Pu isotopes in two seawater samples collected in the Pacific Ocean 50 km off the FDNPP site by AMS and they found that their results were comparable to results reported for the Northwest Pacific Ocean before the FDNPP accident. Here, the established analytical method was used to determine the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in surface and bottom seawater samples obtained 30 km off the FDNPP site in the western North Pacific after the FDNPP accident. The analytical results are shown in Table 4.

For all the seawater samples in this study, the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios ranged from 0.43 to 5.59 mBq m^{-3} and from 0.227 to 0.284, respectively. Before the FDNPP accident, Pu isotopes in seawater collected off the near coast of Japan from 2008 to 2010 had been monitored for the assessment of the radiological impact of the routine operated nuclear facilities on marine environment [42]. The $^{239+240}$Pu activities of the surface seawater and the bottom seawater were below 8.3 mBq m^{-3} and 22 mBq m^{-3} respectively, and the ^{240}Pu/^{239}Pu atom ratios ranged from 0.173 to 0.322. The ^{240}Pu/^{239}Pu atom ratios in the seawater of the western North Pacific were higher than the global fallout ratio (0.18) due to the influence of the Pacific Proving Ground nuclear weapon tests site, which was characterized by a high ^{240}Pu/^{239}Pu atom ratio (0.30–0.36) [8,43,44]. The MEXT reported values [42] could be considered as the background data for Pu isotopes in seawater in the near coast of Japan before the FDNPP accident. We can see that our results were typically in the background data range, suggesting no remarkable Pu contamination from the accident in the marine environment 30 km off the FDNPP site was identified. This conclusion was consistent with findings we have made in our previous studies based on the investigation of Pu isotopes in marine sediments in the western North Pacific after the FDNPP accident [33,45,46].

4. Conclusions

In this study, an accurate and precise analytical method was developed based on anion-exchange chromatography and SF-ICP-MS for the determination of Pu isotopes in seawater samples. A high U decontamination factor of $3 \times 10^7 – 1 \times 10^8$ was achieved, which made the analysis of Pu isotopes in seawater free of U interference. The LODs for ^{239}Pu and ^{240}Pu were 0.11 fg mL^{-1} and 0.08 fg mL^{-1}, respectively, which corresponded to 0.01 mBq m^{-3} for ^{239}Pu and 0.03 mBq m^{-3} for ^{240}Pu when 20 L seawater was measured. Our method was capable of determining Pu isotopes in small-volume (20–60 L) seawater samples with low $^{239+240}$Pu activity levels (<1 mBq m^{-3}). This method was used to determine $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater samples collected 30 km off the FDNPP site in the western North Pacific since the FDNPP accident. No significant variation of Pu distribution in seawater from the investigated areas was observed in comparison with the distribution before the accident.

Fig. 6. Typical mass spectra. (a) The operational blank; (b) a 20 L seawater sample analyzed by our method.

References

[1] K. Hirose, J. Nucl. Radiochem. Sci. 10 (2009) R7.
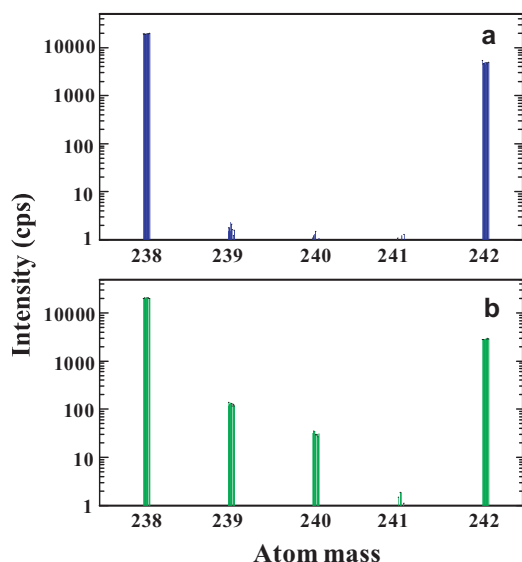[2] P. Lindahl, S.H. Lee, P. Worsfold, M.K. Roach, Mar. Environ. Res. 69 (2010) 73.

[3] M. Ketterer, J. Zheng, M. Yamada, in: M. Baskaran (Ed.), Handbook of Environmental Isotope Geochemistry, Springer, Berlin, 2011, p. 359.

[4] A. Aarkrog, Deep-Sea Res. II 50 (2005) 2597.

[5] P.P. Povinec, A. Aarkrog, K.O. Buesseler, R. Delfanti, K. Hirose, G.H. Hong, T. Ito, H.D. Livingston, H. Nies, V.E. Noshkin, S. Shima, O. Togawa, J. Environ. Radioact. 81 (2005) 63.

[6] K. Hirose, M. Aoyama, T. Miyao, Y. Igarashi, J. Radioanal. Nucl. Chem. 248 (2001) 771.

[7] K. Hirose, M. Aoyama, Deep-Sea Res. II 50 (2003) 2675.

[8] Y. Muramatsu, T. Hamilton, S. Uchida, K. Tagami, S. Yoshida, W. Robison, Sci. Total Environ. 278 (2001) 151.

[9] M.E. Ketterer, K.M. Hafer, J.W. Mietelski, J. Environ. Radioact. 73 (2004) 183.

[10] J. Qiao, X. Hou, P. Roos, M. Miro, Anal. Chem. 81 (2009) 8185.

[11] C.S. Kim, C.K. Kim, P. Martin, U. Sansone, J. Anal. At. Spectrom. 22 (2007) 827.

[12] J. Zheng, K. Tagami, S. Homma-Takeda, W. Bu, J. Anal. At. Spectrom. 28 (2013) 1676.

[13] X. Hou, P. Roos, Anal. Chim. Acta 608 (2008) 105.

[14] J.H. Chen, R.L. Edwards, G.J. Wasserburg, Earth Planet. Sci. Lett. 80 (1986) 241.

[15] C.S. Kim, C.K. Kim, J.I. Lee, K.J. Lee, J. Anal. At. Spectrom. 15 (2000) 247.

[16] J.S. Becker, J. Anal. At. Spectrom. 17 (2002) 1172.

[17] J. Zheng, M. Yamada, Talanta 69 (2006) 1246.

[18] K. Norisuye, K. Okamura, Y. Sohrin, H. Hasegawa, T. Nakanishi, J. Radioanal. Nucl. Chem. 267 (2006) 183.

[19] A.E. Eroglu, C.W. McLeod, K.S. Leonard, D. McCubbin, Spectrochim. Acta B 53 (1998) 1211.

[20] J. Zheng, M. Yamada, Appl. Radiat. Isot. 70 (2012) 1944.

[21] P. Lindahl, M. Keith-Roach, P. Worsfold, M.S. Choi, H.S. Shi, S.H. Lee, Anal. Chim. Acta 671 (2010) 61.

[22] K.O. Buesseler, M. Aoyama, M. Fukasawa, Environ. Sci. Technol. 45 (2011) 9931.

[23] N. Yoshida, J. Kanda, Science 336 (2012) 1115.

[24] M. Aoyama, M. Tsumune, Y. Hamajima, J. Radioanal. Nucl. Chem. 296 (2013) 535.

[25] S. Oikawa, H. Takata, T. Watabe, J. Misonoo, M. Kusakabe, Biogeoscience 10 (2013) 5031.

[26] P.P. Povinec, K. Hirose, M. Aoyama, Environ. Sci. Technol. 46 (2013) 10356.

[27] T.C. Kenna, P. Masque, J.L. Mas, P. Camara-Mor, E. Chamizo, J. Scholten, M. Eriksson, J. Sanchez-Cabeza, J. Gastaud, I. Levy, J. Hermann, P. Lindahl, G. Hong, S. Nielsen, Limnol. Oceanogr.: Methods 10 (2012) 590.

[28] Y. Sohrin, K. Isshiki (Eds.), Co-precipitation, in Chemistry of Sea and Lake. Part II. Analytical Chemistry of Trace Elements in Hydrosphere, Kyoto University Press, Kyoto, Japan, 2005, p. 397 (in Japanese).

[29] Y. Muramatsu, S. Uchida, K. Tagami, S. Yoshida, T. Fujikawa, J. Anal. At. Spectrom. 14 (1999) 859.

[30] J. Qiao, X. Hou, P. Roos, M. Miro, Anal. Chem. 83 (2011) 374.

[31] U. Nygren, I. Rodushkin, C. Nilsson, D.C. Baxter, J. Anal. At. Spectrom. 18 (2003) 1426.

[32] MEXT, Rapid analysis of Pu in environmental samples, http://www.kankyo-hoshano.go.jp/series/main_pdf_series_28.html

[33] J. Zheng, T. Aono, S. Uchida, J. Zhang, M.C. Honda, Geochem. J. 46 (2012) 361.

[34] M. Yamamoto, S. Oikawa, A. Sakaguchi, J. Tomita, M. Hoshi, K.N. Apsalikov, Health Phys. 95 (2008) 291.

[35] K. Inagaki, S.I. Fujii, A. Takatsu, K. Chiba, J. Anal. At. Spectrom. 26 (2011) 623.

[36] J. Mocak, A.M. Bond, S. Mitchell, G. Scollary, Pure Appl. Chem. 69 (1997) 297.

[37] C.S. Kim, C.K. Kim, K.J. Lee, Anal. Chem. 74 (2002) 3824.

[38] J.S. Becker, M. Zoriy, L. Halicz, N. Teplyakov, C. Muller, I. Segal, C. Pickhardt, I.T. Platzner, J. Anal. At. Spectrom. 19 (2004) 1257.

[39] J. Kanda, Biogeoscience 10 (2013) 6107.

[40] C.K. Kim, J.I. Byun, J.S. Chae, H.Y. Choi, S.W. Choi, D.J. Kim, Y.J. Kim, D.M. Lee, W.J. Park, S.A. Yim, J.Y. Yun, J. Environ. Radioact. 111 (2012) 70.

[41] A. Sakaguchi, A. Kadokura, P. Steier, K. Tanaka, Y. Takahashi, H. Chiga, A. Matsushima, S. Nakashima, Y. Onda, Geochem. J. 46 (2012) 355.

[42] MEXT, Environmental Radiation Database, http://www.kankyo-hoshano.go.jp/08/ers_lib/ers_abs53.pdf

[43] K.O. Buesseler, J. Environ. Radioact. 36 (1997) 69.

[44] M. Yamada, J. Zheng, Z.L. Wang, J. Environ. Radioact. 98 (2007) 274.

[45] W.T. Bu, J. Zheng, T. Aono, K. Tagami, S. Uchida, J. Zhang, M.C. Honda, Q.J. Guo, M. Yamada, Biogeoscience 10 (2013) 2497.

[46] W. Bu, J. Zheng, Q. Guo, T. Aono, H. Tazoe, K. Tagami, S. Uchida, M. Yamada, Environ. Sci. Technol. 48 (2014).