



Comparisons of soil pretreatment methods for SF-ICP-MS determination of ultra-trace level plutonium in water soluble and exchangeable fractions

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Abstract

In this study, we developed a method to evaluate the potentially bioavailable fraction of Pu in agricultural soils by determining their water soluble and exchangeable fractions. Three commonly used pretreatment methods were compared for their ability and performances to process the extracted solutions. Results showed that these three methods were able to obtain consistent Pu concentration results; however, based on the experimental performance factors, we considered that wet-ashing followed by Fe(OH)₃ co-precipitation was the best pretreatment method, with which high ²⁴²Pu recoveries for the overall process were realized for the water soluble fraction (69.8%) and the exchangeable fraction (70.6%).

Keywords Pu · Bioavailability · Fe(OH)₃ co-precipitation · Wet-ashing · Total digestion

Introduction

Plutonium (Pu) in the environment is mainly originated from global fallout due to the atmospheric nuclear tests conducted in the middle of the 20th century. Since the detonation of the first Pu device at the “Trinity Site” in the USA in 1945, in total, approximately 6.52 PBq of ²³⁹Pu and 5.35 PBq of ²⁴⁰Pu have been released into the atmosphere from nuclear tests worldwide [1]. Apart from this

global source, other sources such as nuclear accidents and nuclear fuel reprocessing facilities have also released certain amounts of Pu to the environment while their influences have tended to be on local or regional scales [2, 3]. The main isotopes of Pu are ²³⁹Pu and ²⁴⁰Pu, and the IAEA labels them as the most radiotoxic “Group 1” radionuclides [4]. Because of their long radiological half-lives (24100 y and 6563 y for ²³⁹Pu and ²⁴⁰Pu, respectively) as well as their significantly long biological half-lives in organisms [5], ²³⁹Pu and ²⁴⁰Pu would pose a long term radiological impact to the human body once ingested through the food chain by forming sources of local irradiation after enrichment in the bone tissue and liver [5, 6]. The globalization of food trade also presents immense world-wide challenges once contamination of local agricultural products arises. Indeed, the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in 2011 has reinforced public concerns about food safety and highlighted the need to study the transfer of radioisotopes from soil to crops. Furthermore, comprehensive understanding of the bioavailability and migration of Pu in the biosphere is also a requirement for the assessment and management of high level radioactive waste disposal. Thus, it is very necessary to investigate the bioavailability of Pu in agricultural soils since it governs the transfer of Pu from soil to crops and strongly relates to food safety.

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The bioavailability of a radionuclide is roughly determined by its physicochemical forms in soil. However, it is difficult to determine the physicochemical forms of a radionuclide in soil in non-contaminated level areas because in the environment, concentrations of radionuclides such as from global fallout and naturally occurring radionuclides are usually very low and also it is difficult to separate forms singly. Thus, instead of determining single forms, researchers usually choose the way to classify the radionuclide forms using various extractants, namely the operationally-defined “fractions” [7, 8]. Among these fractions, water soluble and ion exchangeable fractions are generally considered accessible for plant uptake through roots and thus can be employed to estimate bioavailability of radionuclides [7–10]. The water soluble fraction represents radionuclides that are the most mobile while the exchangeable fraction includes radionuclide forms bound to ion exchange sites on the soil particle surfaces that can be released by ion exchange process [11]. Information on the speciation or fraction of radionuclides in the environment is valuable in predictive models for environmental studies and has been included in studies such as the bioavailability and migration/partitioning of Pu etc. in the environment [12, 13].

Menzies et al. [14] compared the effectiveness of different types of reagents i.e. acid (e.g. HCl), complexing reagent (e.g. DTPA, EDTA) and neutral salt solution (e.g. CaCl₂, MgCl₂, NH₄OAc) for evaluation of metal bioavailability by statistical analysis of a large dataset from the literature; they concluded that the soil fraction extracted with a neutral salt solution appeared to provide the most useful indicator of metal bioavailability in soil.

Although enormous works have been reported focusing on the choice of extractants for evaluation of Pu speciation and application of those results in the environmental studies [12, 13, 15]. Attempts to make a systematical comparison of the commonly adopted pretreatment methods for water soluble/exchangeable extractions before further chemical separation are scarce. In such studies, even the Pu recoveries were not usually mentioned since those values were not an important point. In the absence of a comparison on experimental performance factors such as chemical recoveries and time/labor costs, sometimes researchers decide arbitrarily on which pretreatment method to adopt from among those in the literature. In fact, various kinds of pretreatments with extracted solutions, differing in rigorousness, have been employed by researchers for processing water soluble/exchangeable Pu extracted from soil or sediment samples. For example, Guillén et al. [16] and Baeza et al. [17] dried the soil extractant with CH₃COONH₄ (hereafter NH₄OAc) as exchangeable fractions, followed by calcination and HF–HNO₃–HCl microwave digestion to remove silica before

the subsequent ion exchange chromatography separation of Pu; they also used Fe(OH)₃ co-precipitation between HF/HNO₃ digestion and chromatography separation in an earlier work [18]. By comparison, Bunzl et al. [19, 20] chose to evaporate the NH₄OAc extracted solution to nearly dryness and then used HNO₃–H₂O₂ digestion to remove organic matter prior to chemical separation. The same wet-ashing procedure was also carried out by Ovsianikova et al. [21] to process the H₂O extracted and NH₄OAc extracted solutions followed by Fe(OH)₃ co-precipitation. Other than these two types of pretreatment which aim at destroying organic matter and/or silica in the extracted solution, researchers have concentrated Pu in extracted solutions by simple evaporation [22] or direct Fe(OH)₃ co-precipitation [23] before further anion exchange chromatographic separation.

For soil or sediment samples, their water soluble/exchangeable fractions contain many complex matrices, especially when large sample sizes (e.g. 100 g) are required for the analysis of ultra-trace levels of Pu. Although it is difficult to distinctively elucidate these matrices as well as their effects on further chemical procedures, their possible effects should not be ignored. During the extraction step, organic matter (e.g. labile soil organic matter) could be partly extracted with which Pu presents high affinity [24]. On the one hand, the presence of organic matter in the solution might influence the efficiency of Fe(OH)₃ co-precipitation and the later anion exchange chromatography; high recovery is often critical for ultra-trace level Pu analysis. On the other hand, it is also imperative that any Pu complexed with organic matter be liberated into the solution from the perspective of accurate quantification of Pu. Therefore, Pu amounts in extractants to determine bioavailable fractions in soil (by water or reagents such as NH₄OAc) might have been underestimated in previous studies if they were indeed affected by the pretreatment methods. Due to the lack of a universal procedure and reference material to validate the effectiveness for Pu extraction and separation, it is difficult to compare Pu bioavailabilities in soil samples as obtained by different methods. In addition, if a large amount of silica is present in the loading solution, silica gel is likely to precipitate later in the ion exchange column and even cause column clogging and thus deteriorate experimental performance factors [25]. Therefore, a comparison of different pretreatment methods for the extracted solutions from the same soil sample is required to bridge the gap of the knowledge about the possible influences of pretreatment methods on both the experimental performance factors and consistency of Pu concentration results of the overall process. This information would be instructive for researchers to choose the proper pretreatment method to deal with the

extracted solutions in some speciation-related studies of Pu.

The aim of this study was to compare three pretreatment methods with different levels of rigorousness in view of their experimental performance factors as well as consistency of results. The three pretreatment methods were compared in detail by incorporating them separately with the same subsequent separation procedure. Then, we recommended one as the best pretreatment method for the determination of ultra-trace levels of Pu in water soluble and exchangeable fractions in agricultural soils. We employed H₂O and NH₄OAc to extract water soluble and exchangeable fractions of Pu, respectively, the sum of which was considered as potentially bioavailable to plants.

Experimental

Sample collection

Soils used in this work were collected in 2007 in Japan, and included two types of agricultural soils, i.e. upland field soil (coded as EF-SD) and paddy soil (coded as EP-SD). Each soil sample was air-dried and sieved through a 2 mm mesh sieve to remove gravel and plant roots, followed by homogenized mixing. We had previously analyzed the total ²³⁹⁺²⁴⁰Pu concentration as well as ²⁴⁰Pu/²³⁹Pu atom ratio of in the soil samples, and those results indicated that Pu in them was sourced from global fallout [26].

Reagents and apparatuses

Analytical grade pure reagents NH₄OAc, HNO₃ (68%), HCl (35–37%), HBr (47%–49%), NH₄I, H₂O₂ (30–36%), NaNO₂, HF (38%), HClO₄ (70%), FeCl₃·6H₂O and NH₃ solution (20%) used during the extraction and separation were purchased from Kanto Chemicals (Tokyo, Japan). Ultra-pure HNO₃ obtained from Tama Chemicals (Tokyo, Japan) was used for the final sample preparation. Pure water (18.2 MΩ cm) was produced by a Milli-Q water system. The ion exchange resins AG 1 × 8 (100–200 mesh, Cl form) and AG MP-1 M (100–200 mesh, Cl form) were obtained from Bio-Rad (Hercules, CA, USA). ²⁴²Pu (CRM 130, New Brunswick Laboratory, NJ, USA) was used as a yield tracer. The vacuum filtration system was purchased from Agilent Technologies (CA, USA). An ICP-MS multi-element standard solution containing 1 μg L⁻¹ depleted U was purchased from Thermo Fisher Scientific (Bremen, Germany). The Rhodium (Rh) ICP-MS standard solution was bought from Merck KGaA (Darmstadt, Germany). Whatman GF/F filter paper (0.7 μm) was used during the vacuum filtration. An electromagnetic stirrer was purchased from AS ONE Corp. (Osaka, Japan). The

type of centrifuge machine was the H-40α which was obtained from KOKUSAN Co., Ltd. (Tokyo, Japan).

A sector-field ICP-MS (Element XR, Thermo Fisher Scientific, Bremen, Germany) combined with a high efficiency sample introduction system (APEX-Q, Elemental Scientific Inc., Omaha, NE, USA) was employed for Pu measurements. The low resolution mode was utilized to obtain the maximum instrument sensitivity. All measurements were conducted under self-aspiration mode to reduce the risk of contamination from the peristaltic pump tubing. The instrument was optimized with the 50-times diluted multi-element ICP-MS standard solution (containing 0.02 ng mL⁻¹ U) to provide optimum performance. Detailed operation parameters were presented elsewhere [27]. Typically, a sensitivity of 35 M cps/ppb for ²³⁸U was obtained in this study. Due to the extremely low content of ²⁴⁰Pu in the extracted fractions, we only measured ²³⁹Pu here.

Extraction of Pu from agricultural soil samples

To determine the potentially bioavailable Pu in agricultural soil samples, we employed H₂O and 1 M NH₄OAc as extractants considering water soluble and NH₄⁺ exchangeable fractions. For each sample, a 100 g amount of soil was used for analysis because we estimated that the extractable Pu amounts would be at ultra-trace levels. One liter of pure water was added to the soil sample in a 2 L glass beaker to make a suspension, followed by continuous stirring for 1 h with the electromagnetic stirrer. This solution was left to stand overnight in order to get sufficient soil and solution contact and also remove large soil particles before the supernatant was transferred to centrifuge tubes. The residue was washed with 50 mL pure water and the washing solution was combined for centrifugation. After centrifugation at 3000 rpm for 15 min, sample solution was vacuum filtered and then acidified by adding 1 mL of 1 M HNO₃ to the filtration container before transferring to glass beakers; this solution was collected as the water soluble fraction sample. Then the residue after the H₂O extraction and the solid on the filter paper were combined together for the next extraction step, and 1 L 1 M NH₄OAc solution was added to the combined residue to extract ion exchangeable Pu. The following separation steps were the same as those for the water soluble fraction mentioned above. Then 0.57 pg ²⁴²Pu was separately added to the two obtained extracted solutions (nominal water soluble fraction and exchangeable fraction) as a yield tracer.

Pretreatment of extracted solutions with three methods

To test the performance and consistency of the pretreatment methods with different levels of rigorousness that have been commonly employed [16–23], we used two upland soil samples and two rice paddy soil samples for comparison. Each soil sample was divided into three subsamples (100 g each). After performing the extraction process as described in the Section of Extraction of Pu from agricultural soil samples, extracted solutions of the three subsamples were prepared separately by the three pretreatment methods as described below.

Method A, direct Fe(OH)₃ co-precipitation

40 mg Fe³⁺ in the form of FeCl₃ solution was added to the extracted solutions of the water soluble and exchangeable fractions and electromagnetically stirred for 10 min. Then NH₃ solution was slowly pipetted into each solution to reach pH 9–10 at which Pu was co-precipitated with Fe(OH)₃; meanwhile, most of the U present would have remained in the supernatant at that pH [28]. The solution containing the precipitate was further separated by centrifugation (3000 rpm, 15 min). After discarding the supernatant and dissolving the precipitate with 3 mL conc. HNO₃ followed by 30 mL 8 M HNO₃, NaNO₂ was added to the sample solution for valence adjustment of Pu to Pu (IV). Pu was then purified using anion exchange chromatography as described in the later Section of anion exchange chromatographic separation.

Method B, wet-ashing + Fe(OH)₃ co-precipitation

First, extracted solutions of the water soluble and exchangeable fractions were separately evaporated to dryness at 200 °C. Then, 40 mL conc. HNO₃ was used to dissolve the two dark colored residues, followed by carefully adding proper amount (30–60 mL) of 30% H₂O₂ until the sample solution became colorless. The sample solution was heated to dryness and the finally obtained residue was dissolved in 10 mL 0.1 M HNO₃ before 1 L pure water was added. This final solution was then subjected to the Fe(OH)₃ co-precipitation as described in Method A.

Method C, total digestion + Fe(OH)₃ co-precipitation

The extracted solution of the water soluble fraction was heated to reduce the volume to ca. 10 mL and this solution was transferred from the glass beaker to a PTFE vessel since HF was used in the subsequent steps. The glass beaker was rinsed with conc. HNO₃ and the rinsing

solution was combined with the sample solution in the PTFE vessel and evaporated to dryness. Then, obtained residue was dissolved in 12 mL conc. HNO₃ followed by heating to near dryness. After that, 4 mL HF was added to destroy silicates. As soon as the sample was heated to become paste-like, 2 mL HClO₄ was added to remove undissolved fluorides and any remaining organic matter by heating to nearly dryness, resulting in white-paste residue. Next, 10 mL conc. HNO₃ was added to expel remaining chloride by heating to dryness. The obtained residue was dissolved in 10 mL 0.1 M HNO₃ and transferred to a glass beaker followed by the addition of 1 L pure water. This final solution was then subjected to the Fe(OH)₃ co-precipitation as described in Method A. The experimental steps were a little different for the NH₄OAc extracted exchangeable fraction compared with the water soluble fraction. Because ammonium might be present throughout the entire digestion procedure, in order to avoid the risk of forming the extremely unstable and dangerous ammonium perchlorate, HClO₄ was not used after evaporating the HF solution. Instead, we carried out HNO₃–H₂O₂ wet digestion with the sample to remove organic matter right after the sample solution was heated to dryness in the glass beaker. Then the sample was reconstituted with 10 mL HNO₃ and transferred to the PTFE vessel. Next, HNO₃–HF–HNO₃ was successively used just the same as that for the water soluble fraction. The sample solution was finally transferred back to the glass beaker and this final solution was then subjected to the Fe(OH)₃ co-precipitation as described in Method A.

Anion exchange chromatographic separation

For the further purification of Pu, a two-stage anion exchange chromatography method was used based on its good capability for removing complex matrixes. A detailed description of this procedure was presented elsewhere [29]. In brief, Pu was first separated from interference elements (U, Th, Pb, etc.) on the AG 1 × 8 resin column with the rinse by 50 mL 8 M HNO₃ and 30 mL 10 M HCl. After elution of Pu using 8.5 M HCl–0.1 M NH₄I followed by heating to dryness, 1 mL aqua regia was added to the sample and the solution was heated to dryness (this step was repeated twice). Then the sample was dissolved in 4 mL HCl–H₂O₂ with heating for 30 min before loading onto the second AG MP-1 M resin column. The AG MP-1 M resin was employed mainly for further removal of interfering U. After rinsing the resin with 20 mL 8 M HNO₃ and 8 mL 10 M HCl, Pu was eluted with 16 mL conc. HBr and the solution was evaporated to dryness. Then 1 mL ultrapure HNO₃ was added to the solution and this was evaporated to dryness. Finally, the sample was taken up in 0.8 mL 4% ultra-pure HNO₃ with

0.02 ng mL⁻¹ Rh as internal standard in preparation for the ICP-MS measurement. The overall process incorporating pretreatment Method B is presented in Fig. 1.

Results and discussion

Experimental performance factors with three pretreatment methods

Three pretreatment methods with different levels of rigorosity were employed to determine the potentially bioavailable concentration of Pu in agricultural soils which is presumably the sum of the water soluble and exchangeable fractions. The experimental performance factors such as time/labor costs, simplicity of operation, and the chemical recoveries of ²⁴²Pu tracer varied distinctively. The recoveries of the overall process, including each of the three pretreatment methods, are presented in Table 1.

Among the pretreatment methods, Method A which was rather mild and straightforward is time-saving since no extra time was needed before the Fe(OH)₃ co-precipitation step, resulting in the minimal time cost. However, the straightforward Fe(OH)₃ co-precipitation by Method A occasionally resulted in clogging of the AG 1 × 8 resin column in the subsequent sample loading process and that led to low recovery of Pu; this was mostly likely to be a result of the precipitation of silica gel in the resin column [25]. For chemical recovery of ²⁴²Pu tracer, Method A had the lowest Pu recovery for three water soluble fraction samples and one exchangeable fraction samples among

these methods. On average whole chemical recoveries for Method A were 62.1 and 50.0% for water soluble and exchangeable fractions. Interestingly, the recoveries of Method A seemed to be negatively affected by the organic matter content of the soil samples. Higher recoveries were obtained for soils with low organic matter content; EP-SD-44 (6.2%) and EP-SD-47 (4.4%) had much lower organic matter content than EF-SD-60 (11.5%) and EF-SD-76 (15.8%), and the recoveries of EP-SD-44 and EP-SD-47 were obviously higher than the latter two for both water soluble and exchangeable fractions. Apart from organic matter, Pu chemical recovery might also be influenced by another factor such as ionic strength, which was the biggest difference between water soluble and exchangeable fraction solutions. When the Fe(OH)₃ precipitation was carried out directly with these two solutions, the recoveries of the water soluble fraction were all higher than the NH₄OAc fraction for all four soil samples. Presumably, the higher ionic strength in the NH₄OAc extraction posed more competition against Pu ions in its association with Fe(OH)₃ precipitate compared with the case of H₂O extraction. Staunton et al. [30] observed that the increase of solution ionic strength could reduce the affinity for Cs on minerals, with a decreasing value of the solid-solution distribution coefficient K_d. A similar influence by ionic strength on ²³⁹Pu adsorption was also reported by Lu et al. [31] who found that the increase of ionic strength caused a decrease of ²³⁹Pu adsorption by montmorillonite and silica colloids.

When Method B was applied (in which extractions of samples underwent wet-ashing to destroy organic matter), enhanced Pu recoveries were observed for both water

Fig. 1 Flow chart of the overall process incorporating pretreatment Method B for determination of potentially bioavailable Pu in soil samples

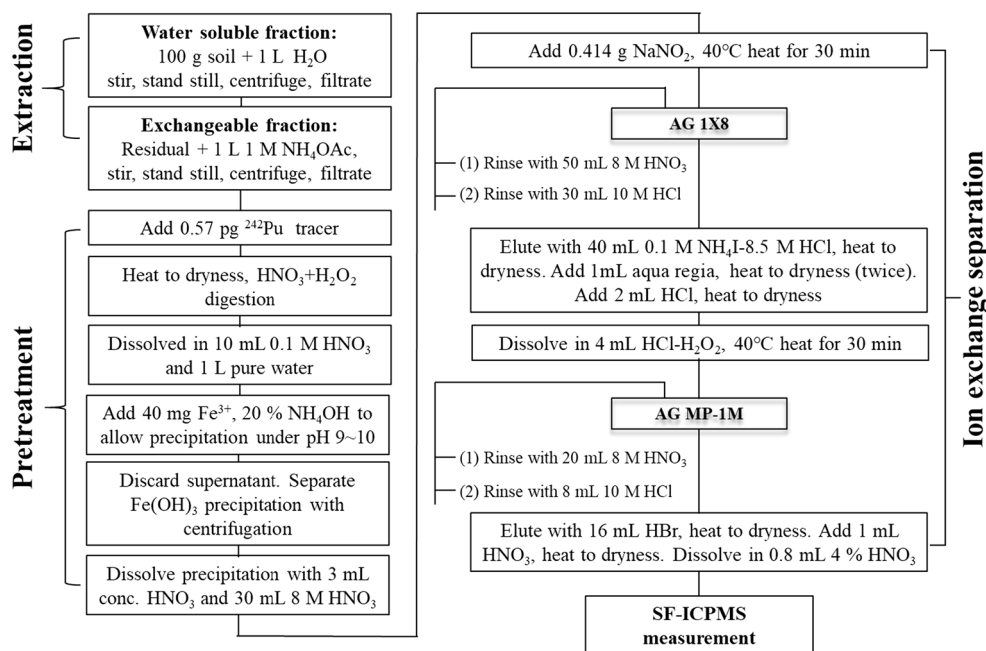


Table 1 Whole procedure ^{242}Pu recoveries for water soluble and exchangeable fractions employing three different pretreatment methods

Sample ID	Organic matter ^a (%)	Water soluble fraction			Exchangeable fraction		
		Method A (%)	Method B (%)	Method C (%)	Method A (%)	Method B (%)	Method C (%)
EF-SD-60	11.5	50.2	57.4	53.9	48.1	78.9	24.2
EF-SD-76	15.8	51.8	61.9	67.8	41.3	82.0	58.2
EP-SD-44	6.2	67.5	81.2	81.5	52.4	66.1	51.0
EP-SD-47	4.4	79.1	78.5	68.1	58.3	55.4	70.3
Average		62.1 ± 13.7	69.8 ± 11.9	67.8 ± 11.3	50.0 ± 7.2	70.6 ± 12.2	50.9 ± 19.5

^aOrganic matter contents (%) were calculated by the weight loss of soils during ignition at 450 °C

soluble and exchangeable fraction samples except EP-SD-47 (low organic matter content soil). Interestingly, the enhancements were more significant for both water soluble and exchangeable fractions of EF-SD-60 and EF-SD-76 which had higher organic matter content than the other two soils. These findings indicated there were interfering effects by organic matter on the chemical recovery. One possible explanation is that the organic matters in the solution could complex Pu with their functional groups and Pu was partially remained in the supernatant of $\text{Fe}(\text{OH})_3$ co-precipitation, thus caused the decrease of Pu recovery. Similar negative influence of organic matter on the co-precipitation behavior of Pu with $\text{Fe}(\text{OH})_3$ has also been reported by Qiao et al. [32]. Removal of organic matter before co-precipitation and further separation served the purpose of enhancing Pu recovery. On average, high recoveries of 69.8 and 70.6% were reached by Method B for water soluble and exchangeable samples. Bu et al. [29] had employed the same ion exchange chromatography procedure as was used in this study for Pu analysis in soil and sediment samples, Pu recoveries in their studies ranged from 45 to 76% for small (< 2.5 g) soil/sediment samples with an average recovery of 64%. Recoveries of the overall process in our work with pretreatment Method B and ion exchange chromatography were slightly higher than those of Bu et al. [29], indicating relatively lower loss of Pu although huge amount (100 g) of soil were used for extraction and separation.

Pretreatment Method C was regarded as the most aggressive and rigorous since organic matter and silica were presumably removed, both of which were thought to worsen Pu recovery as mentioned above. However, Method C was the most tedious and time-consuming method. Moreover, after reducing the NH_4OAc extracted solution to a small volume with evaporating, the solution was prone to solidification once the heating was stopped. If $\text{HNO}_3\text{-H}_2\text{O}_2$ was employed to digest the residue, similar phenomenon occurred when the digested solution was nearly dried up and heating was stopped. The solidification of solution

caused a problem for the later transfer step of the sample from the glass beaker to the PTFE vessel so that much attention should be paid. From our experience, we would recommend transfer of the sample solution before it cooled and use of extra HNO_3 to dissolve the solid that remained on the beaker wall to reduce the loss of Pu and thus increase recovery. For these reasons, Method C did not always show the best recovery compared to other two methods, and it was worse than Method B for most for the extracted sample solutions. Moreover, large variance of Pu recoveries was observed as summarized in Table 1, especially for NH_4OAc extraction in which sample solidification kept occurring. Average Pu recoveries were 67.8 and 50.9% for water soluble and exchangeable fractions with Method C.

From these results, analysis of Pu with these three pretreatment methods gave consistent ^{242}Pu recoveries in the same soil samples for the water soluble fraction, but large differences were found for the exchangeable fraction. Method A was the simplest and most straightforward, but the ^{242}Pu recoveries were usually low probably due to the presence of organic matter in the extraction before the $\text{Fe}(\text{OH})_3$ co-precipitation, especially for high organic matter content samples. Besides, clogging of the AG 1 × 8 resin column was occasionally encountered as a consequence of silica gel precipitation. Method B significantly enhanced the recovery through the decomposition of organic matter, and presented the highest Pu recovery among the three pretreatment methods. Method C sometimes had better Pu recovery than Method A by removing both organic matter and silica to the fullest extent. However, the average recovery of Pu for the NH_4OAc extracted solution was still not comparable to that of Method B due to the tedious sample transfer process and the problem of sample solidification. Besides, the uses of hazardous HF and HClO_4 are highly regulated and bring extra burdens to laboratory management. For these reasons, Method B was the recommended pretreatment method for determining potentially bioavailable Pu in agricultural soils because of

its relatively simple procedure and the outstanding Pu recovery. Our recommended overall process for determination of potentially bioavailable Pu in soil samples is presented in Fig. 1.

Concentrations of Pu determined by three pretreatment methods

^{239}Pu concentrations determined by the three pretreatment methods with different levels of rigorousness are summarized in Table 2. Based on the previously determined total ^{239}Pu concentration of these soils and the average potentially bioavailable ^{239}Pu concentration resulting from the three methods, we calculated the percentages of potentially bioavailable fractions in these soils as shown in the table.

With regard to the consistency of ^{239}Pu concentration results, in general the results obtained via Methods A, B and C for the same soil sample corresponded well to each other. This illustrated that decomposition of organic matter or removal of silica in the extraction before $\text{Fe}(\text{OH})_3$ coprecipitation had no significant influence on the final Pu concentration results if Pu yield tracer could be added right after obtaining the extracted solutions before pretreatment.

The water soluble ^{239}Pu concentration in the four soil samples ranged from 0.02 ± 0.01 to 0.44 ± 0.05 mBq kg^{-1} , while the exchangeable ^{239}Pu concentration was systematically lower, varying from 0.02 ± 0.01 to 0.06 ± 0.01 mBq kg^{-1} . The percentages of water soluble and exchangeable fractions in these soil samples are depicted in Fig. 2. These results illustrated that the present analytical method employing different pretreatment methods successfully determined low level potentially bioavailable Pu in agricultural soils sourced from global fallout. The concentration of exchangeable fractions of Pu

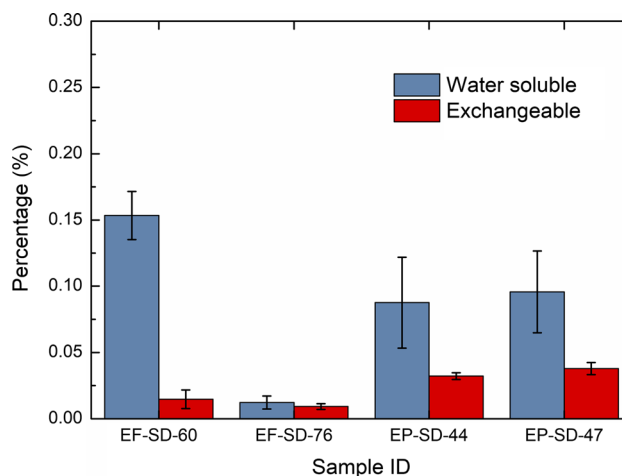


Fig. 2 Percentages of water soluble fractions and exchangeable fractions of Pu in four Japanese agricultural soil samples

in these samples had less variation than the concentration of water soluble fractions. Compared with total ^{239}Pu in soil, the potentially bioavailable concentration of ^{239}Pu summed as the water soluble and exchangeable fraction concentrations was very low. Upland field soil EF-SD-76 had the lowest potentially bioavailable Pu fraction, only 0.02% of the total Pu in soil. The highest value was observed for EF-SD-60, but it was only 0.17% of the total Pu in soil. Such information will be useful for the study of Pu bioavailability and its transfer in the biosphere; meanwhile, it also fostered the need for future systematic investigations to assess potential radiological risks of Pu through the soil-crop pathway after nuclear emergencies occur.

Table 2 ^{239}Pu concentration in different fractions determined by the three pretreatment methods^a

Concentration	Method	EF-SD-60	EF-SD-76	EP-SD-44	EP-SD-47
Water soluble mBq kg^{-1}	A	0.44 ± 0.05	0.02 ± 0.01	0.15 ± 0.02	0.13 ± 0.02
	B	0.42 ± 0.04	0.03 ± 0.01	0.15 ± 0.02	0.16 ± 0.02
	C	0.35 ± 0.04	0.04 ± 0.01	0.07 ± 0.01	0.08 ± 0.01
Exchangeable mBq kg^{-1}	A	0.03 ± 0.01	0.02 ± 0.01	0.04 ± 0.01	0.04 ± 0.01
	B	0.03 ± 0.01	0.02 ± 0.01	0.04 ± 0.01	0.05 ± 0.02
	C	0.06 ± 0.01	0.03 ± 0.01	0.05 ± 0.01	0.06 ± 0.01
Potentially bioavailable mBq kg^{-1}	A	0.47 ± 0.05	0.04 ± 0.01	0.20 ± 0.02	0.17 ± 0.02
	B	0.45 ± 0.04	0.05 ± 0.01	0.20 ± 0.02	0.21 ± 0.03
	C	0.41 ± 0.04	0.07 ± 0.01	0.12 ± 0.02	0.14 ± 0.02
^{239}Pu in soil ^c mBq kg^{-1}		270 ± 20	230 ± 10	140 ± 10	130 ± 10
Potentially bioavailable fraction ^b %		0.17	0.02	0.12	0.13

^aResults are given with 1σ

^bThe ratio of the average potentially bioavailable ^{239}Pu concentration from the three methods to the total ^{239}Pu concentration in bulk soil samples

^cThe ^{239}Pu concentration in soil was cited from Ref. [26]

Limit of detection (LOD)

The limit of detection (LOD) for the overall process incorporating pretreatment Method B was calculated based on three times the standard deviation of operational blanks as recommended by the IUPAC [33]. The LOD of ^{239}Pu for the overall process was $0.009 \text{ mBq kg}^{-1}$ based on a sample size of 100 g and a mean recovery of 66% for the operational blank ($n = 6$). This corresponded to an absolute detection limit of $0.9 \text{ }\mu\text{Bq}$ for ^{239}Pu . Compared with other studies on determination of Pu in soil samples using ICP-MS, the absolute detection limit of the overall process was lower than the $34 \text{ }\mu\text{Bq}$ reported by Varga et al. [34] and the $1.95 \text{ }\mu\text{Bq}$ reported by Truscott et al. [35]. Recently Wang et al. [36] employed the SF-ICP-MS and APEX-Q system for rapid determination of Pu in soil and sediment samples. The absolute detection limit of ^{239}Pu was equivalent to $0.56 \text{ }\mu\text{Bq}$ in their study and our absolute detection limit was comparable to that. The relatively low LOD of our overall process incorporating pretreatment Method B guarantees its efficient application in the study of Pu bioavailability in agricultural soils.

Conclusions

In this study, we developed a method for the determination of low level water soluble and exchangeable Pu in the agricultural soils which were assumed to be potentially bioavailable for plant uptake. We compared three pretreatment methods for soil samples and found from the results that wet-ashing with $\text{HNO}_3\text{-H}_2\text{O}_2$ to decompose organic matter followed by $\text{Fe}(\text{OH})_3$ coprecipitation was the best based on its good experimental performance factors, especially the high recoveries of Pu. The overall process we recommended includes extraction of soil sample with $\text{H}_2\text{O}/\text{NH}_4\text{OAc}$, wet-ashing with $\text{HNO}_3\text{-H}_2\text{O}_2$, $\text{Fe}(\text{OH})_3$ co-precipitation, ion exchange chromatography and SF-ICP-MS measurement. High recoveries of this method for the water soluble fraction and exchangeable fraction samples were realized, reaching 69.8 and 70.6%, respectively. The limit of detection of the whole procedure for ^{239}Pu was $0.009 \text{ mBq kg}^{-1}$ based on a sample size of 100 g. We have successfully employed this method to determine potentially bioavailable Pu in Japanese upland and paddy soil samples. However, we also admit that further systematic study is still required to gain a better understanding of the bioavailability of Pu in agricultural soils.

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References

1. United Nations Scientific Committee on the Effects of Atomic Radiation (2000), Sources and Effects of Ionizing Radiation. Report to the General Assembly, with Scientific Annexes, I, United Nations, New York
2. Zheng J, Tagami K, Uchida S (2013) Release of plutonium isotopes into the environment from the Fukushima Daiichi nuclear power plant accident: what is known and what needs to be known. *Environ Sci Technol* 47:9584–9595
3. Thakur P, Khaing H, Salminen-Paatero S (2017) Plutonium in the atmosphere: a global perspective. *J Environ Radioact* 175:39–51
4. International Atomic Energy Agency (1973) Safe Handling of Radionuclides. Safety series, 1, Vienna
5. Clarke RH, Dunster J, Nenot JC, Smith H, Voeltz G (1996) The environmental safety and health implications of plutonium. *J Radiol Prot* 16:91–105
6. Sokolik GA, Ovsiannikova SV, Ivanova TG, Leinova SL (2004) Soil-plant transfer of plutonium and americium in contaminated regions of Belarus after the Chernobyl catastrophe. *Environ Int* 30:939–947
7. Kennedy VH, Sanchez AL, Oughton DH, Rowland AP (1997) Use of single and sequential chemical extractants to assess radionuclide and heavy metal availability from soils for root uptake. *Analyst* 122:89–100
8. Fawaris BH, Johanson KJ (1995) Fractionation of caesium (^{137}Cs) in coniferous forest soil in central Sweden. *Sci Total Environ* 170:221–228
9. Evans EJ, Dekker AJ (1969) Effect of nitrogen on cesium-137 in soils and its uptake by oat plants. *Can J Soil Sci* 49:349–355
10. Oughton DH, Salbu B, Riise G, Lien H, Østby G, Nøren A (1992) Radionuclide mobility and bioavailability in Norwegian and Soviet soils. *Analyst* 117:481–486
11. Gleyzes C, Tellier S, Astruc M (2002) Fractionation studies of trace elements in contaminated soils and sediments. *Trends in Anal Chem* 21:451–467
12. Kenna TC (2009) Using sequential extraction techniques to assess the partitioning of plutonium and neptunium-237 from multiple sources in sediments from the Ob River (Siberia). *J Environ Radioact* 100:547–557
13. Komosa A (2002) Study on geochemical association of plutonium in soil using sequential extraction procedure. *J Radioanal Nucl Chem* 252:121–128
14. Menzies NW, Donn MJ, Kopittke PM (2007) Evaluation of extractants for estimation of the phytoavailable trace metals in soils. *Environ Pollut* 145:121–130
15. Goryachenkova TA, Kazinskaya IE, Clark SB, Novikov AP, Myasoedov BF (2005) Comparison of methods for assessing plutonium speciation in environmental objects. *Radiochemistry* 47:599–604
16. Guillén J, Baeza A, Corbacho JA, Muñoz-Muñoz JG (2015) Migration of ^{137}Cs , ^{90}Sr , and $^{239+240}\text{Pu}$ in Mediterranean forests: influence of bioavailability and association with organic acids in soil. *J Environ Radioact* 144:96–102
17. Baeza A, Guillén J, Mietelski JW, Gaca P (2006) Soil-to-fungi transfer of ^{90}Sr , $^{239+240}\text{Pu}$, and ^{241}Am . *Radiochim Acta* 94:75–80
18. Baeza A, Guillén J, Espinosa A, Aragón A, Gutierrez J (2005) A study of the bioavailability of ^{90}Sr , ^{137}Cs , and $^{239+240}\text{Pu}$ in soils

- at two locations of Spain affected by different radionuclide contamination events. *Radioprotection* 40:61–65
19. Bunzl K, Flessa H, Kracke W, Schimmack W (1995) Association of fallout $^{239+240}\text{Pu}$ and ^{241}Am with various soil components in successive layers of a grassland soil. *Environ Sci Technol* 29:2513–2518
 20. Bunzl K, Kracke W, Schimmack W, Zelles L (1998) Forms of Fallout ^{137}Cs and $^{239+240}\text{Pu}$ in Successive Horizons of a Forest Soil. *J Environ Radioact* 39:55–68
 21. Ovsianikova S, Papenia M, Voinikava K, Brown J, Skipperud L, Sokolik G, Svirschevsky S (2010) Migration ability of plutonium and americium in the soils of Polesie State Radiation-Ecological Reserve. *J Radioanal Nucl Chem* 286:409–415
 22. Cook GT, Baxter MS, Duncan HJ, Toole J, Malcolmson R (1984) Geochemical association of plutonium in the Caithness environment. *Nucl Instruments Methods Phys Res.* 223:517–522
 23. Komosa A, Orzel J, Michalik S (2007) Study on plutonium distribution between sequentially extracted phases of arable soils. IAEA-CN-145/114P
 24. Goryachenkova TA, Kazinskaya IE, Kuzovkina EV, Novikov AP, Myasoedov BF (2009) Association of radionuclides with colloids in soil solutions. *Radiochemistry* 51:201–210
 25. Croudace I, Warwick P, Taylor R, Dee S (1998) Rapid procedure for plutonium and uranium determination in soils using a borate fusion followed by ion-exchange and extraction chromatography. *Anal Chim Acta* 371:217–225
 26. National Institute of Radiological Sciences (2010) Report on Biospheric Assessment for Waste Disposal (in Japanese)
 27. Zheng J (2015) Evaluation of a new sector-field ICP-MS with Jet Interface for ultra-trace determination of Pu isotopes: from femtogram to attogram levels. *J Nucl Radiochem Sci* 15:7–13
 28. Sohrin Y, Isshiki K (2005) Co-precipitation, in *Chemistry of Sea and Lake. Part II. Analytical chemistry of trace elements in hydrosphere* (in Japanese). Kyoto University Press, Kyoto, Japan
 29. Bu WT, Zheng J, Guo QJ, Aono T, Tazoe H, Tagami K, Uchida S, Yamada M (2014) A method of measurement of ^{239}Pu , ^{240}Pu , ^{241}Pu in high U content marine sediments by sector field ICP-MS and its application to Fukushima sediment samples. *Environ Sci Technol* 48:534–541
 30. Staunton S, Roubaud M (1997) Adsorption of ^{137}Cs on montmorillonite and illite: effect of charge compensating cation, ionic strength, concentration of Cs, K and fulvic acid. *Clay Miner* 45:251–260
 31. Lu N, Reimus PW, Parker GR, Conca JL, Triay IR (2003) Sorption kinetics and impact of temperature, ionic strength and colloid concentration on the adsorption of plutonium-239 by inorganic colloids. *Radiochim Acta* 91:713–720
 32. Qiao JX, Hou XL, Roos P, Lachner J, Christl M, Xu YH (2013) Sequential injection approach for simultaneous determination of ultratrace plutonium and neptunium in urine with accelerator mass spectrometry. *Anal Chem* 85:8826–8833
 33. Mocak J, Bond AM, Mitchell S, Scollary GA (1997) Statistical overview of standard (IUPAC and ACS) and new procedures for determining the limits of detection and quantification: application to voltammetric and stripping techniques (Technical Report). *Pure Appl Chem* 69:297–328
 34. Varga Z, Surányi G, Vajda N, Stefánka Z (2007) Rapid sequential determination of americium and plutonium in sediment and soil samples by ICP-SFMS and alpha-spectrometry. *Radiochim Acta* 95:81–87
 35. Truscott J, Jones P, Fairman B, Evans E (2003) Determination of actinide elements at femtogram per gram levels in environmental samples by on-line solid phase extraction and sector-field-inductively coupled plasma-mass spectrometry. *Anal Chim Acta* 433:245–253
 36. Wang ZT, Zheng J, Ni YY, Men W, Tagami K, Uchida S (2017) High-performance method for determination of Pu isotopes in soil and sediment samples by sector field-inductively coupled plasma mass spectrometry. *Anal Chem* 89:2221–2226