Plutonium concentration and isotopic ratio in soil samples from central-eastern Japan collected around the 1970s

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Obtaining Pu background data in the environment is essential for contamination source identification and assessment of environmental impact of Pu released from the Fukushima Daiichi nuclear power plant (FDNPP) accident. However, no baseline information on Pu isotopes in Fukushima Prefecture has been reported. Here we analyzed 80 surface soil samples collected from the central-eastern Japan during 1969–1977 for $^{239,240}$Pu activity concentration and $^{240}$Pu/$^{239}$Pu atom ratio to establish the baseline before the FDNPP accident. We found that $^{239,240}$Pu activity concentrations ranged from 0.004 –1.46 mBq g$^{-1}$, and $^{240}$Pu/$^{239}$Pu atom ratios varied narrowly from 0.148 to 0.229 with a mean of 0.186 ± 0.015. We also reconstructed the surface deposition density of $^{241}$Pu using the $^{241}$Pu/$^{239}$Pu atom ratio in the Japanese fallout reference material. The obtained results indicated that, for the FDNPP-accident released $^{241}$Pu, a similar radiation impact can be estimated as was seen for the global fallout deposited $^{241}$Pu in the last decades.

The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in 2011 resulted in trace release of the reactor core Pu into the atmosphere after intentional venting operation and reactor hydrogen explosions$^{1–7}$. Atmospheric Pu was subsequently deposited on the ground by the wet and dry deposition processes$^8$. To estimate the environmental impact of the FDNPP source Pu, background data on Pu distributions in the environment before the FDNPP accident are critical.

Due to the difficulty of Pu analysis, baseline information on Pu activity in Japanese soils is very limited. Yamamoto et al.$^9$ examined the concentrations of $^{239,240}$Pu for 30 rice-field surface soil samples collected from 15 locations in Japan mostly in 1963 and 1976, and for 15 soil samples periodically collected from 2 locations during 1957–1980. Their study found the integrated deposits of Pu isotopes on the Japan Sea coast of Honshu were 2.5 to 3 times higher than those on the Pacific coast, and the concentrations of $^{239,240}$Pu in rice-field soils ranged from 0.078 to 1.43 mBq g$^{-1}$. A similar $^{239,240}$Pu concentration range of 0.07–0.7 mBq g$^{-1}$ was observed in agricultural upland fields soils in Rokkasho, Aomori Prefecture$^{10}$. In addition, $^{239}$Pu concentration in surface layer (0–5 cm) soil samples collected in 1995 in Kyushu was reported to range from 0.50–0.65 mBq g$^{-1}$.$^{11}$ A more recent study conducted by Muramatsu et al.$^{12}$ analyzed $^{239,240}$Pu concentrations in 20 soil samples collected from agricultural fields (vegetable/wheat fields and rice paddy fields) and forests in several places in Japan. They found the range of the $^{239,240}$Pu concentrations to be 0.15–4.31 mBq g$^{-1}$; the highest concentration of 4.31 mBq g$^{-1}$ was found in a surface soil (0–2 cm) sample collected from a forest in Aomori Prefecture. In addition to the Pu activity, the Pu isotopic ratio is an important fingerprint for contamination source identification. The $^{240}$Pu/$^{239}$Pu atom ratio is of special interest; for nuclear tests this ratio changes with the weapon type and yield, while for nuclear reactors it changes with the reactor type and nuclear fuel burn up. Therefore, the $^{240}$Pu/$^{239}$Pu atom ratio can provide valuable information on the nature of the Pu emitting source$^{13,14}$. In previous investigations to obtain the background data for Pu in Japanese soil, the $^{240}$Pu/$^{239}$Pu atom ratio was found to be in the range of 0.14–0.24, which revealed that the major source of Pu in the environment was global fallout from the atmospheric nuclear explosions conducted in the last century$^{8–15}$.

However, to our knowledge, no baseline information on Pu activity distribution and atom ratio in Fukushima Prefecture are available for times prior to the 2011 nuclear accident. From 1967 to 1994, the National Institute of Radiological Sciences (NIRS) collected surface soils mainly from school grounds in Japan to establish a surface soil database for understanding the natural radiation level. Therefore, in this work, we used the NIRS archived soil samples collected in during 1969 to 1977 from Fukushima and its adjacent Prefectures in central-eastern Japan (Fig. 1) to establish background data on the $^{239,240}$Pu activity concentrations and $^{240}$Pu/$^{239}$Pu atom ratio. In addition, since a high $^{241}$Pu/$^{239,240}$Pu activity ratio (higher than 100), was observed in the FDNPP-source Pu',
we also reconstructed $^{241}$Pu activities in the analyzed soil samples based on the $^{240}$Pu/$^{239}$Pu atom ratio in the Japanese fallout reference material. The obtained background data are important to estimate the radiation dose due to the deposition of global fallout Pu and the FDNPP-source Pu.

Results
The results of activity concentrations of $^{239+240}$Pu and the atom ratios of $^{240}$Pu/$^{239}$Pu in all soil samples are summarized in Table S1 in the Supplementary Material, and the mean values of activities of $^{239+240}$Pu and the atom ratios of $^{240}$Pu/$^{239}$Pu in each Prefecture are presented in Table 1. The $^{239+240}$Pu activities in school ground soils are quite low, ranging from 0.004 to 0.412 mBq g$^{-1}$. In the two samples collected from residential area in Okuma and Futaba, Fukushima Prefecture, $^{239+240}$Pu activities were 0.294 and 0.695 mBq g$^{-1}$, respectively. The highest $^{239+240}$Pu activity of 1.46 mBq g$^{-1}$ in this study was found in the soil collected from the grounds of one Park in Sendai, Miyagi Prefecture. Fig. 2a shows the frequency distribution of

![Figure 1](http://www.nature.com/scientificreports)  
Figure 1 | Map showing the soil sampling locations in central-eastern Japan. This map was prepared with Arc GIS 10.0 software.

| Table 1 | Mean values of Pu activity concentrations and atom ratios in soils of each Prefecture and Tokyo |
|-----------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Prefecture      | Sample size | $^{239+240}$Pu activity concentration (Bq kg$^{-1}$) | $^{240}$Pu/$^{239}$Pu atom ratio | $^{241}$Pu activity concentration (Bq kg$^{-1}$)$^a$ |
| Fukushima       | 22          | 0.127 ± 0.157                                      | 0.183 ± 0.011                                      | 1.88 ± 2.31                                   |
| Ibaraki         | 5           | 0.134 ± 0.075                                      | 0.182 ± 0.009                                      | 1.98 ± 1.15                                   |
| Miyagi          | 13          | 0.207 ± 0.387                                      | 0.192 ± 0.011                                      | 3.03 ± 5.65                                   |
| Iwate           | 9           | 0.154 ± 0.131                                      | 0.190 ± 0.015                                      | 2.26 ± 1.93                                   |
| Tochigi         | 5           | 0.038 ± 0.032                                      | 0.185 ± 0.011                                      | 0.56 ± 0.47                                   |
| Gunma           | 4           | 0.055 ± 0.045                                      | 0.166 ± 0.018                                      | 0.86 ± 0.71                                   |
| Saitama         | 6           | 0.054 ± 0.045                                      | 0.180 ± 0.025                                      | 0.82 ± 0.69                                   |
| Chiba           | 10          | 0.048 ± 0.039                                      | 0.189 ± 0.009                                      | 0.70 ± 0.56                                   |
| Tokyo           | 6           | 0.047 ± 0.082                                      | 0.194 ± 0.037                                      | 0.69 ± 1.20                                   |

$^a$Activity of $^{241}$Pu decay corrected to January 1, 1964.
$^{239+240}$Pu activities in soil samples (school grounds, residential areas and park grounds). Among the 80 soil samples analyzed, 48.8% were lower than 0.05 mBq g$^{-1}$, and 77.5% were lower than 0.15 mBq g$^{-1}$.

The $^{240}$Pu/$^{239}$Pu atom ratios of all samples are plotted against $^{239}$Pu/$^{240}$Pu activity concentrations in Fig. 3. It can be seen that the $^{240}$Pu/$^{239}$Pu atom ratios ranged from 0.148 to 0.229 in the investigated school grounds soil. For the two samples from the residential areas and the one sample from the park grounds, the $^{240}$Pu/$^{239}$Pu atom ratios ranged from 0.182 to 0.188. The frequency distribution of $^{240}$Pu/$^{239}$Pu atom ratios in all samples is plotted in Fig. 2b. A typical Gaussian distribution was obtained. Among the 80 soil samples, 30 samples had $^{240}$Pu/$^{239}$Pu atom ratios ranging from 0.18–0.19, and 58 samples had $^{240}$Pu/$^{239}$Pu atom ratios of 0.17–0.20. The mean $^{240}$Pu/$^{239}$Pu atom ratio was 0.186 ± 0.015, which is similar to that of global fallout (0.180 ± 0.007)\textsuperscript{13}, indicating that global fallout Pu deposition was the major source, although a small contribution of the Chinese Nuclear Tests at Lop Nor has been observed in fallout samples collected in the 1970s in Japan\textsuperscript{16}.

**Discussion**

Eighty soil samples in this study were collected from central-eastern Japan in the period from 1969 to 1977. From 1945 to 1980, 543 atmospheric nuclear tests were conducted worldwide, and during 1964–1980, 22 atmospheric nuclear weapons tests were conducted by China at Lop Nor\textsuperscript{17}. The Nagasaki atomic bomb detonation on August 9, 1945 released Pu into the environment; a study on the geographic distribution of Nagasaki atomic bomb-derived Pu indicated that plutonium from the atomic bomb was deposited in the eastern area from the hypocenter reaching up to 100 km eastwards\textsuperscript{18}. In addition, there was no detectable deposition of Chernobyl accident-sourced Pu in 1986, so Pu in the soil samples of the present

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**Figure 2** Frequency distributions of $^{239+240}$Pu activity concentrations (mBq kg$^{-1}$) (a), and $^{240}$Pu/$^{239}$Pu atom ratios (b) in soil samples (school ground, residential areas and park grounds) collected in central-eastern Japan in the 1970s.
Japan in the 1970s. The study was assumed to have come mainly from the global fallout due to the atmospheric nuclear tests. The 239+240Pu activity concentrations in our study were in the range of 0.004–1.46 mBq g⁻¹, which were comparable with previous studies on the activity levels of Pu in soils in Japan before the FDNPP accident (0.07–4.31 mBq g⁻¹) as shown in Table 2. Xu et al.¹⁹ demonstrated that the combined effects of many environmental factors were responsible for the variation of Pu concentrations in the surface soils. We compared the activity concentrations of 239+240Pu with organic contents in the investigated surface soil samples; however, no significant correlation between Pu activities and organic matter contents was found. Therefore, more detailed information should be obtained in the future to reveal the variation of concentrations in the surface soils.

As shown in Table 1, higher 239+240Pu activity concentrations can be seen in the four prefectures of Iwate, Ibaraki, Miyagi, and Fukushima, with mean values of 0.154 ± 0.131, 0.134 ± 0.075, 0.103 ± 0.101, and 0.091 ± 0.085 mBq g⁻¹, respectively. While for Tokyo and the four prefectures, Tochigi, Gunma, Saitama and Chiba, significantly lower mean values varying narrowly from 0.038–0.055 mBq g⁻¹ were observed. The similar variation trend was seen in the surface deposition density (0–5 cm) of 239+240Pu as shown in Fig. 4. The surface deposition density of 239+240Pu ranged from 0.3 Bq m⁻² to 27 Bq m⁻² for the school ground soils samples. Relatively higher 239+240Pu surface inventories of 19–45 Bq m⁻² were found for two residential surface soil samples, and of 95 Bq m⁻² for surface soil sample of park grounds. Recently, a large scale investigation on the surface deposition of Pu in soils collected at 100 sites in September 2013 northwestern of the FDNPP was reported²⁰. It was found that the surface deposition density (Bq m⁻²) ranged from 0.35 to 40; these values are comparable to those we detected in the soils collected in the 1970s, indicating that the FDNPP accident did not cause significant increase of Pu deposition in central-eastern Japan.

However, alteration of the 240Pu/239Pu atom ratio in various environmental samples was significant after the FDNPP accident. Fig. 5 compares the atom ratios of 240Pu/239Pu in different environmental samples contaminated by the FDNPP accident and the background data of 240Pu/239Pu atom ratios in environmental samples collected before the FDNPP accident. Regarding the background 240Pu/239Pu atom ratio in the Japanese environment, in this investigation, we found that the fingerprint of Pu (240Pu/239Pu atom ratios) in soil from central-eastern Japan varied narrowly from 0.148 to 0.229 (with a mean of 0.186 ± 0.015) as mentioned above. Kelley et al.¹³ reported 240Pu/239Pu atom ratios in two surface soil samples from Tokyo and Sapporo (in northern Japan) were 0.1755 ± 0.0012 and 0.1765 ± 0.0011, which fall into the interval in our study. During the period after the Chernobyl accident in 1986 and before the Fukushima accident in 2011, 240Pu/239Pu atom ratios in Japanese soils were in the range of 0.14–0.24¹⁰–¹². We can conclude, therefore, that the release of Pu from the Chernobyl accident resulted in almost no change in the Pu contamination in Japanese soil. After the FDNPP accident, obviously high atom ratios of 240Pu/239Pu were found in several environmental samples. Zheng et al.¹ and Yamamoto et al.²¹ noted that atom ratios of 240Pu/239Pu in litter samples and black substances (road dust) collected in northwest of the FDNPP site varied very narrowly from 0.323 to 0.335, and from 0.285 to 0.365, respectively. Zheng et al. also measured the atom ratio of 240Pu/239Pu in one surface soil sample (0–2 cm) collected 20 km south of the FDNPP site and obtained the value of 0.303 ± 0.030. Schneider et al.² reported a high 240Pu/239Pu atom ratio in one vegetation sample (0.381 ± 0.046). Recently, Shinonaga et al.¹ demonstrated that the FDNPP accident-released Pu was transported 120 km after the FDNPP accident by measuring the Pu atom ratio in aerosol samples (they obtained atom ratios of 240Pu/239Pu of 0.333–0.426). Nishihara et al.²¹ have estimated the possible atom ratios of 240Pu/239Pu that existed in March 2011 in the FDNPP reactor cores (0.320–0.336) and spent fuel pools (0.394–0.468) using the ORIGEN2 code and the fuel burn-up data from the Tokyo Electric Power Company. These comparisons have clearly indicated the wide distribution of the FDNPP accident-released Pu in the environment.

Among the Pu isotopes released from severe reactor accident, like the Fukushima nuclear accident, 241Pu is important for radiation dose estimation. It is a beta-emitter with a half-life of 14.4 years. With its decay, the ingrowth of 239Pu (alpha and gamma-emitter, T₁/₂ = 432.7 years) will present a new radiation risk. The release of 241Pu with a high 240Pu/239Pu activity ratio (> 100) from the FDNPP accident was first reported by Zheng et al.¹ by the analysis of litter samples in Fukushima Prefecture. Recently, Ikeuchi²⁰ reported a comprehensive investigation on the deposition of the FDNPP accident-released Pu isotopes in surface soils in Fukushima Prefecture, and confirmed the wide distribution of FDNPP-sourced 240Pu. To better understand the radiation impact of the FDNPP-sourced 241Pu in the environmental, the background data on the deposition level of 241Pu, especially in the period of peak of global fallout is critical.

Due to the low activities of 241Pu in the school ground soils after five decades of decay, 241Pu was below the detection limit of the analytical method (1 mBq/g), and thus not detected in this study. In order to establish background data of the 241Pu activity in the analyzed soil samples, we used the 241Pu/239Pu atom ratio of 0.00261 ± 0.00026 (241Pu decay reference to January 1, 2000) in fallout reference material reported by Zhang et al.¹⁹. This reference
Table 2 | Pu activity concentrations and atom ratios in soils collected before and after the FDNPP accident

| Sample | Site                                      | Collection date   | \(^{239-240}\text{Pu} \text{ activity} \ (\text{Bq kg}^{-1}\text{-dry}) | \(^{240/239}\text{Pu} \text{ atom ratio} \) | \(^{241}\text{Pu} \text{ activity} \ (\text{Bq kg}^{-1}\text{-dry}) | \(^{241/239}\text{Pu} \text{ atom ratio} \) | Ref. |
|--------|------------------------------------------|-------------------|-------------------------------------------------|----------------------------------|----------------------------------|----------------------------------|-----|
| **After FDNPP accident** |                                |                   |                                                 |                                  |                                  |                                  |     |
| Contaminated soil (0–2 cm) | South 20 km from FDNPP | 4/20/2011         | 0.059 ± 0.004                                  | 0.303 ± 0.030                    | 4.52 ± 0.56a                     | 0.103 ± 0.013a                   | 1   |
| Non-contaminated soil     | Chiba, Mito, Japan           | 5/20/2011–8/9/2011| 0.016–1.400                                    | 0.144–0.209                      | ND                               | ND                               | 1   |
| Top soil                  | Minamisoma, Japan            | 10/31/2011        | 0.205 ± 0.039                                  |                                  | ND                               | ND                               | 3   |
| Road dust                 | Fukushima, Japan             | 2012              | 0.145–1.14                                     |                                  |                                  |                                  | 4   |
| Road dust                 | Fukushima, Japan             | 2012–2013         | 0.013–3.92                                     | 0.286–0.365                     |                                  |                                  | 5   |
| Soil                      | Fukushima, Japan             | 3/27/2011–5/25/2011| 0.001–0.353                                    |                                  |                                  |                                  | 8   |
| Soil (0–10 cm)            | Fukushima, Japan             | 10/6/2011–6/30/2013| <1.71                                           |                                  |                                  |                                  | 5   |
| **Before FDNPP accident** |                                |                   |                                                 |                                  |                                  |                                  |     |
| Soil                      | Tokyo, Japan                 | 1970/1971         | 0.1755 ± 0.0012                                |                                  | 0.00171 ± 0.00010c               | 13                                             |
| Soil                      | Sapporo, Japan               | 1970/1971         | 0.1765 ± 0.0011                                |                                  | 0.00183 ± 0.00011c               | 13                                             |
| Rice-field surface soilsb | Japan                       | 1957–1980         | 0.078–1.43                                     |                                  |                                  |                                  | 9   |
| Soil                      | Central-eastern Japan        | 1969–1977         | 0.004–1.46                                     | 0.186 ± 0.015                    |                                  |                                  | 10  |
| Upland fields soils (0–100 cm) | Rokkasho, Japan            | 2001              | 0.07–0.7                                       | 0.18 ± 0.04                      |                                  |                                  | 11  |
| Campus surface soil       | Kyushu, Japan                | 1995              | 0.50–0.65                                      | 0.19 ± 0.05                      |                                  |                                  | 12  |
| Agricultural fields and forests soil | Japan | 1963–1979 | 0.15–4.31                                      | 0.155–0.194                     | 0.192 ± 0.0044                   | 0.00287 ± 0.00056c                | 16  |
| Atmospheric fallout in Japan | 30°–71°N                   | 1963–1979         | 0.180 ± 0.007                                  |                                  | 0.00194 ± 0.00014d               | 13                                             |
| Global fallout            | 0–30°N                      |                   | 0.178 ± 0.010                                  |                                  | 0.00188 ± 0.00039c               | 13                                             |

\(^{a}\)Decay of \(^{241}\text{Pu}\) corrected to March 15, 2011.

\(^{b}\)Soil samples from surface to a depth of 12–20 cm.

\(^{c}\)Decay of \(^{241}\text{Pu}\) corrected to January 1, 2000.
fallout material was prepared from fallout deposition samples collected monthly at 14 stations throughout Japan in 1963–1979. Since the fallout reference material and the soils samples we investigated in this study were sampled in the period after large scale atmospheric nuclear weapons tests and before the widespread operation of nuclear power plants in Japan, we consider that they have the same source of Pu isotopes, i.e. mainly from the global fallout with a small contribution from the Chinese nuclear tests, therefore, we can use the $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratio detected in the fallout reference material to reconstruct the $^{240}\text{Pu}$ activities in the soil samples we analyzed. To understand the highest background level of $^{241}\text{Pu}$ activity in the soil samples, decay of $^{241}\text{Pu}$ was corrected to January 1, 1964, the year of peak deposition of global fallout Pu. As shown in Fig. 6, the reconstructed $^{241}\text{Pu}$ activities were highly correlated with the $^{239}\text{Pu}/^{240}\text{Pu}$ activity, thus the $^{241}\text{Pu}/^{239}\text{Pu}/^{240}\text{Pu}$ activity ratio of 14.8 was obtained. Since the half-lives of $^{239}\text{Pu}$ and $^{240}\text{Pu}$ are very long ($2.41 \times 10^4$ y and $6.56 \times 10^3$ y, respectively), in the timescale of several decades, the $^{239}\text{Pu}/^{240}\text{Pu}$ activity can be considered unchanged, the $^{241}\text{Pu}/^{239}\text{Pu}/^{240}\text{Pu}$ activity ratio of 14.8 obtained in this study can be used to estimate $^{241}\text{Pu}$ background in soils collected in other areas in Japan, once $^{239}\text{Pu}/^{240}\text{Pu}$ activity is measured. The estimated $^{241}\text{Pu}/^{239}\text{Pu}/^{240}\text{Pu}$ activity ratio in the present study is slightly higher than that of global fallout (ca. 12.1) obtained from lake sediments.

The estimated $^{241}\text{Pu}$ activities are summarized in Table S1. It was found that the $^{241}\text{Pu}$ activities ranged from 0.06 to 6.07 mBq g$^{-1}$ in 77
school grounds soil samples. Higher $^{241}\text{Pu}$ activities were found in the soil samples collected from residential areas and the park grounds, ranging from 4.28 MBq g$^{-1}$ to 21.25 MBq g$^{-1}$. It was noted that the distribution patterns of measured $^{239,240}\text{Pu}$ activities and the estimated $^{241}\text{Pu}$ activities were quite similar. For the $^{241}\text{Pu}$ activities, among the investigated soil samples, 89.6% were less than 0.3 MBq g$^{-1}$. The northern prefectures of Ibaraki, Fukushima, Miyagi and Iwate presented relatively higher $^{241}\text{Pu}$ activities than those in the four southern prefectures (Tochigi, Gunma, Saitama, and Chiba) and Tokyo.

Fig. 7 showed the re-constructed surface deposition density of $^{241}\text{Pu}$ (Bq m$^{-2}$) in central-eastern Japan in the period of the peak global fallout in 1964. The surface deposition density of $^{241}\text{Pu}$ ranged from 3.9 to 394 Bq m$^{-2}$. Similar to the distribution of $^{239,240}\text{Pu}$, higher deposition was seen in the four northern prefectures. The recent study reported by Ikeuchi indicated that the FDNPP-sourced $^{241}\text{Pu}$ was detected in 41 sites among the 100 sites investigated in Fukushima Prefecture. The surface deposition density (0–5 cm) of $^{241}\text{Pu}$ varied from 12 to 240 Bq m$^{-2}$; this is in the same levels as the $^{241}\text{Pu}$ deposition in 1964. Therefore, we consider that although the release and deposition of $^{241}\text{Pu}$ with extremely high $^{241}\text{Pu}/^{239}\text{Pu}$ activity ratios ($0.96–129.6$) was widely detected in the environment after the FDNPP accident, a similar radiation impact can be estimated as that of the global fallout deposited $^{241}\text{Pu}$ during the last five decades.

Methods
Reagents and materials. High-purity water (18 MΩ·cm$^{-1}$) was prepared with a Millipore Milli-Q-Plus water purification system. All chemicals (HCl, HNO$_3$, NaNO$_2$, NH$_4$I, H$_2$O$_2$, HBr) were of analytical grade, except for the final solution prepared for the ICP-MS measurement, in which ultrapure grade 68% HNO$_3$ (Tama Chemicals, Japan) was used. The two anion-exchange resins, AG 1X8 (100–200 mesh, Cl-form) and AG MP-1M (100–200 mesh, Cl-form) was used. The two anion-exchange resins, AG 1X8 (100–200 mesh, Cl-form) and AG MP-1M (100–200 mesh, Cl-form) were obtained from Bio-Rad, which were packed in a Muromac mini-column (M type, 6.5 mm$^3$) for Pu separation and purification.

$^{241}\text{Pu}$ (CRM 130, plutonium spike assay and isotopic standard, New Brunswick Laboratory, USA) was used to spike the soil samples as a yield tracer. The mixed Pu isotopes standard solution (NBS-947) with certified $^{240}\text{Pu}/^{241}\text{Pu}$ atom ratio of 0.242 was employed for mass bias correction. Two soil standard reference materials (IAEA-soil-6 and IAEA-375) were used to validate our analytical method.

Analytical procedure. The full experimental procedure was described elsewhere. In the brief, the soil samples were dried at 105°C for 24 h, and pulverized to about 80 mesh. About 1–3 g of a dried soil sample was weighed out. After ashing at 450°C for 5 h to destroy the organic matter, ca. 1 pg $^{242}\text{Pu}$ was added for each sample as a yield monitor. HNO$_3$ (20–40 mL conc.) leaching at 180°C for at least 4 h was done in a tightened lidded Teflon vessel (120 mL, Savillex Corporation, Minnesota, USA) to avoid the loss of acid and improve the acid leaching efficiency. After cooling, the supernatant was filtered through an Advance filter into a beaker (100 mL), and the Teflon vessel and filter paper were washed with 10–20 mL concentrated HNO$_3$. High-purity water was added to adjust the sample solution to the concentration of 8 M HNO$_3$. Then, NaNO$_2$ was added to a concentration of 0.2 M and heated at 40°C for 30 min to adjust Pu to the tetravalent state prior to loading onto the first AG 1X8 resin column.

The AG 1X8 resin column (2.5 mL) was pre-conditioned with 20 mL 8 M HNO$_3$. After sample loading, 50 mL 8 M HNO$_3$ was used to wash U, Pb and Fe from the column. Then 30 mL 10 M HCl was used for washing Th and converting the resin back into the chloride form. Finally, Pu was eluted with 40 mL 0.1 M NH$_4$I-8.5 M HCl collected in a 100 mL Teflon beaker and evaporated to near dryness. Aquas regia (1 mL) was added and then the solution was heated to dryness again. This procedure was repeated twice to destroy the organic matter and remove the residual iodine. Subsequently, 2 mL concentrated HCl was added and the mixture was evaporated to dryness. After adding ca. 4 mL freshly prepared HCl-H$_2$O$_2$ solution (10 mL conc. HCl with 0.01 M 30% H$_2$O$_2$) and heating at 40°C for about 30 min, the sample solution was ready for loading onto the second AG MP-1M resin column.

The AG MP-1M resin column (2.5 mL) was pre-conditioned with 8 mL HCl-H$_2$O$_2$ solution. After sample loading, 20 mL 8 M HNO$_3$ was used for washing U. Then, 8 mL 10 M HCl was added to wash the residual HNO$_3$ in the column and for further Th washing. Pu was eluted from the column with 16 mL HBr into a 30 mL Teflon beaker. After evaporating to near dryness, 1 mL concentrated HNO$_3$ was added to the Teflon beaker and heated to remove any trace of HBr. When nearly dry, the final residual was dissolved in 0.8 M 4% HNO$_3$ in preparation for the SF-ICP-MS analysis.

Instrumentation. A high efficiency sample introduction system (APEX-Q) equipped with a conical concentric nebulizer was combined with SF-ICP-MS (Thermo Fisher Scientific, Element 2, Bremen, Germany) for Pu isotopic analysis. This system consisted of a heated cyclonic spray chamber, a Peltier cooled condenser and an ACM Nafion fluoropolymer membrane desolvation module. A small flow of nitrogen was used to increase transport efficiency and signal stability. The low resolution mode was used to utilize the maximal instrument sensitivity. All the measurements were made in the self-aspiration mode with an uptake rate of ~0.2 mL min$^{-1}$ to reduce the risk of contamination from the peristaltic pump tubing. The SF-ICP-MS was optimized on a daily basis using 0.1 ng mL$^{-1}$ U standard solution to provide optimum intensities and peak shapes.

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Author contributions
J.Z., K.T. and S.U. designed the study. G.S.Y. conducted the Pu analysis. G.S.Y. and J.Z. wrote the manuscript. K.T. and S.U. discussed the results and commented on the manuscript.

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