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Abstract

The Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident led to important releases of radionuclides into the environment, and trace levels of plutonium (Pu) were detected in northeastern Japan. However, measurement of Pu isotopic atom and activity ratios is required to differentiate between the contributions of global nuclear test fallout and FDNPP emissions. In this study, we used a double-focusing sector field ICP-MS to measure Pu atom and activity ratios in recently deposited sediment along rivers draining the most contaminated part of the inland radioactive plume. Results showed that plutonium isotopes (i.e., ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu) were detected in all samples, although in extremely low concentrations. The ^{241}Pu/^{239}Pu atom ratios measured in sediment deposits (0.0017–0.0884) were significantly higher than the corresponding values attributed to the global fallout (0.00113±0.00008 on average for the Northern Hemisphere between 31°-71°N, Kelley, J.M.; Bond, L.A.; Beasley, T.M., Global distribution of Pu isotopes and ^{237}Np, *Sci. Total. Env.*, 1999, 237/238, 483-500). The results indicated the presence of Pu from FDNPP, in slight excess compared to the Pu background from global fallout that represented up to ca. 60% of Pu in the analyzed samples. These results demonstrate that this radionuclide has been transported relatively long distances (~45 km) from FDNPP and been deposited in rivers representing a potential source of Pu to the ocean. In future, the high ^{241}Pu/^{239}Pu atom ratio of the Fukushima accident sourced-Pu should be measured to quantify the supply of continental-originating material from Fukushima Prefecture to the Pacific Ocean.

Introduction

The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident that affected the northeastern part of Japan in March 2011 has led to the largest release of anthropogenic radionuclides into the environment since the Chernobyl accident in 1986. Both accidents were rated 7, the maximum on the International Nuclear and radiological Event Scale (INES). Nevertheless, the total quantities of radionuclides emitted during the Fukushima accident are estimated to correspond to 10 to 15% of Chernobyl emissions[1]. The emitted radionuclides mainly consisted of volatile substances, i.e.^{133}Xe,

^{132}Te, radioiodine and radiocesium. However, semi-volatile and low-volatile radionuclides (e.g., ^{95}Nb, ^{103}Rb) were also detected in the atmosphere after the accident, indicating the likely occurrence of core melting at FDNPP[2]. A broad meltdown of reactor cores was also suggested by modeling studies relying on radionuclide records available from International Monitoring System (IMS) of the Comprehensive Nuclear Test-Ban-Treaty Organization[3].

Most studies that aimed at identifying the emitted radionuclides and tracking their fate in the environment focused on gamma-emitting substances, particularly ^{134}Cs and ^{137}Cs, because of their high abundance and their relatively long half-lives[4]. These substances mainly represent a risk for external exposure of local populations and biota. The presence of alpha-emitters and particularly of long-lived plutonium isotopes would present an additional risk for internal exposure[5]. Although the literature is conflicting on the potential volatilization of actinides in the physico-chemical conditions that prevailed at FDNPP[6], the presence of plutonium with ^{238}Pu/$^{239+240}$Pu activity ratios significantly higher than the ratio measured from plutonium global fallout (~0.03[7,8]) in the region was demonstrated in six soil samples analyzed under the authority of MEXT[9]. Moreover, two recent studies[10,11] showed that the average of these measured ^{238}Pu/$^{239+240}$Pu activity ratios in surface soils at the source correlated well with the model estimates of the spent-fuel inventory from reactors Units 1 and 3, and thus concluded that plutonium was released into the local environment during the venting of these reactors. Plutonium is generally produced in reactor fuel as a mixture of isotopes, among which a dominance of ^{239}Pu ($T_{1/2}$ = 24 100 years) is generated by neutron capture in ^{238}U and subsequent β-decay. When fuel elements containing ^{239}Pu are left in the reactor, they are exposed to further neutron capture, and isotopes with higher mass, i.e. ^{240}Pu ($T_{1/2}$ = 6560 years), ^{241}Pu ($T_{1/2}$ = 14.325 years), and ^{242}Pu ($T_{1/2} = 3.76 \times 10^5$ years), are produced[14]. Several authors[6,10,12] provide estimations of the Pu isotopic activities present in the nuclear fuel of FDNPP reactors and spent fuel storage pools (SFSPs) at the time of the accident. Based on those estimations, it is possible to reconstruct the isotopic composition of the Pu that was potentially emitted by the three damaged reactors and the SFSPs. Zheng et al.[13] also provide estimation of the released Pu isotopic composition from an analysis of litter and surface soil samples. The Pu isotopic ratios characteristic of the three damaged reactors at the time of the accident documented in those studies are compiled in Table S1.

As plutonium isotopic atom and activity ratios provide a powerful tool to quantify those sources and to discriminate between plutonium originating from various past nuclear atmospheric weapon tests (referred to as 'global fallout') and local fallout characterized by significantly different signatures, it is of obvious interest to measure as many Pu isotopic abundances as possible with the highest achievable precision. To this end, the use of mass spectrometry techniques (TIMS or ICP-MS) can provide a more detailed isotopic picture of the Pu detected in the analyzed samples than standard alpha spectrometry techniques, which are not able to differentiate between ^{239}Pu and ^{240}Pu, nor to measure ^{241}Pu[14]. Furthermore, analytical techniques associated with very low detection limits (like for instance sector-field ICP-MS) should be used, as the presence of $^{239+240}$Pu in very low activity concentrations (typically in the tens of mBq/kg to the Bq/kg range) had been reported in the few available studies conducted in the Fukushima Prefecture by 2013[14,15]. Several Pu isotopic measurements conducted on soil samples collected in the vicinity of Fukushima using mass spectrometry have already been published, and ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{241}Pu/$^{239+240}$Pu ratios higher than the global fallout signature were measured by ICP-MS in one soil and two litter samples collected within the 20 to 30 km zone around FDNPP[15]. Furthermore, a ^{240}Pu/^{239}Pu ratio higher than the global fallout value was found in a river water sample collected in Abukuma River[16]. A recent

study based on measurements of $^{238}Pu/^{239+240}Pu$ activity ratio in soils combined with analysis of $^{240}Pu/^{239}Pu$ atom ratio in a set of nine roadside dust samples (associated with radioactive dose rates higher than 100 μSv h^{-1} measured at contact, and referred to as 'black substances' by the authors) and litter samples demonstrated the presence of Pu of FDNPP-origin in material collected in the vicinity of the power plant (i.e., in Futaba, Namie, Okuma municipalities) as well as in Iitate-Mura and Minamisoma City (i.e., outside of the 20-km exclusion zone, to the northwest of FDNPP)[17]. In contrast to observations made on the continent, Pu originating from Fukushima FDNPP was not detected in the marine environment[19,19].

However, the fate of this plutonium in the environment remains poorly documented. As recent publications demonstrated the spread of Fukushima fallout from the main inland contamination plume including Iitate-Mura and Minamisoma City to the Ocean[20.21], we use cutting-edge analytical techniques to document the presence of Pu and measure the Pu isotopic abundances and concentrations of four plutonium isotopes (^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu) in recently deposited riverbed sediment collected along rivers draining the most contaminated part of the inland radioactive plume. This study will thereby provide crucial clues on the origin and the fate of plutonium in coastal catchments that were the most affected by the initial radioactive fallout, which may possibly represent a perennial source of plutonium to the Pacific Ocean during the next decades.

Methodology

Study area and sampling. Fieldwork was conducted in the accessible parts of the Nitta R., Ota R. and Ukedo Rivers draining the main radioactive pollution plume between November 2011 and May 2013 (Fig. 1). Their catchments, covering respectively 271, 79 and 425 km², are dominated by steep forested slopes in upstream mountainous parts (up to 1000 m elevation), and by paddy fields and built-up areas in valley bottoms and coastal plains[20]. Fine sediment that appeared to have recently deposited (i.e., mud drapes on channel-bed sand) was collected along these three rivers. An additional soil sample was taken in the vicinity of the most contaminated sediment sample to allow for comparison. Samples were dried in an oven at 40°C for 72 h, sieved to 2 mm, ground to a fine powder using an agate mortar and stored at room temperature before analysis. Details on the field sampling campaign and strategy are given in a previous publication[20]. For this study, we selected samples to document the Pu contamination of fine sediment deposits along each of the rivers draining the main radioactive contamination plume.

Gamma spectrometry. Radionuclide activities (^{134}Cs, ^{137}Cs, ^{110m}Ag) in all samples were determined by gamma spectrometry using very low-background HPGe detectors. All gamma radionuclide activities were expressed in Bq per kg of dry weight (Bq kg^{-1}). Counting time of soil and sediment samples varied between 8×10^4 and 200×10^4 s to allow the detection of ^{110m}Ag, which was present in much lower activities in the samples (2–2390 Bq kg^{-1}) compared to ^{134}Cs and ^{137}Cs (500–1,245,000 Bq kg^{-1}). Six samples were selected for further Pu analyses because of their high activities in both $^{134+137}Cs$ and ^{110m}Ag.

Sample preparation and purification procedure for plutonium analysis. ~5 gram-aliquots of each soil sample were transferred in Pyrex beakers and reduced to ash at 550°C for 24 hours in an electric

furnace to decompose organic matter. During heating, beakers were covered with watch glasses to prevent cross contaminations. After cooling to room temperature, limited amounts of ^{244}Pu (~100 fg) were added to the samples as isotopic dilution tracer for plutonium quantitative analysis. The stock solution of ~1 pg·g^{-1} used for spiking was prepared by gravimetric dilutions of the mother solution prepared from NBS 131 Certified Reference Material (New Brunswick Laboratory, Argonne, IL, USA). Then, ashes were leached on hot plates with strong acid media in five successive steps: first leaching with fuming HNO_3 (30 ml), evaporation to dryness, second leaching with fuming HNO_3 (30 ml), evaporation to dryness, third leaching with fuming HNO_3 (30 ml) and H_2O_2 (1 ml), evaporation to dryness, fourth leaching with concentrated HCl (30 ml), evaporation to dryness, fifth leaching with 4M HCl (50 ml), evaporation to dryness. Samples were not fully digested. At each leaching step, solutions were back flow heated (120-150°C) for several hours and then evaporated to dryness. All acids used were of analytical grade. Samples were filtered using single-use 0.45 µm analytical filter units (Thermo Scientific, Rochester, NY, USA). Plutonium in the soil and sediment samples, and especially the plutonium possibly released by the FDNPP, was assumed to be present in the dissolved fractions. Therefore, only the dissolved fractions of the samples were further processed. Dissolved fractions were then evaporated to dryness and recovered with 30 ml of concentrated HNO_3. Adjustment and redox state stabilization of Pu at +IV oxidation state were performed by addition of small amounts of $NaNO_2$ followed by evaporation. Samples were recovered with 30 ml of 8N HNO_3 just before introduction into the conditioned ion-exchange resin columns. It should be noted that three process blanks were prepared in the same conditions as the samples. No Pu isotopes were detected in the process blanks.

A first Pu purification was performed with a 20-ml column filled with Dowex AG1X8 anion-exchange resin (10 ml of 50/100 mesh resin at the bottom and 10 ml of 100/200 mesh resin on the top) rinsed twice and conditioned with 8M HNO_3. Further Pu purification is obtained by using a 2 ml-column filled with Dowex AG1X4 anion-exchange resin (100–200 mesh). Both resins are washed with 8 M HNO_3 (U fraction elution), 10 M HCl (Th fraction elution) and, finally, with NH_4I (1.5%) – 12 M HCl solution prepared just before use to elute Pu fraction. Final solutions were evaporated to dryness and recovered with 3 ml of 2% HNO_3 which is the suitable media for ICP-MS measurement. Global Pu recoveries reached an average of ~45% (between 35% and 57% depending on samples).

Mass spectrometry for Pu atom ratio and concentration measurements. Pu isotopic composition and concentrations were measured with a double-focusing sector field ICP-MS ("Element XR", Thermo-Scientific, Bremen, Germany). The separation of the isotope ion beams is carried out through a double-focusing arrangement, both in angle and energy, by means of an electrostatic sector followed by a magnetic sector. This instrument is equipped with the "jet interface" option, composed of a desolvating module ("Apex", ESI, Omaha, NE, USA), high efficiency cones, and a higher capacity primary pump that decreases vacuum in the interface. This option provides increase in sensitivity by a factor of ten compared to the standard configuration of the instrument (i.e. ~4×10^7 counts s^{-1} per µg L^{-1} versus ~4×10^6 counts s^{-1} per µg L^{-1} for the standard configuration). Instrumental background is typically ~0.3±0.2 count s^{-1} in the actinide mass range.

The performance of the instrument is daily optimized with respect to sensitivity, short term stability (10 minutes) and background. The instrument is operated in electric scanning by varying the accelerating voltage, with the intensity of the magnetic field set to a fixed value. A Teflon micro-

concentric nebulizer ("PFA100", ESI, Omaha, NE, USA) was used for sample introduction into the "Apex" desolvating device.

In order to reach high accuracy for isotopic ratio determinations, instrumental mass bias – due to variations in the transmission efficiencies of ions of different masses in the instrument – had to be carefully corrected[22]. This is done by standard bracketing of samples with diluted solutions of NBS U005 (New Brunswick Laboratory, Argonne, IL, USA) and IRMM-184 (IRMM, Geel, Belgium) isotopic standards. The mass bias per mass unit (ε) is determined according to the linear function: $\varepsilon = \left(R_{certified} / R_{measured} - 1\right) / \Delta m$, where Δm is the mass difference between the isotopes of interest.

During the analyses, great care must be taken to avoid contamination and memory effects. As a rule, the glassware, the sampler and skimmer cones must be regularly and carefully cleaned to ensure the lowest background and the best sensitivity and stability. Moreover, the "Element XR" ICPMS is located in a clean room, class 1000, to avoid contamination when handling of the samples. Rinsing blank periods, intended to suppress any memory effect and to avoid cross-contamination by the sample probe, separated the sample measurements. Raw signals were systematically corrected for mass bias, tracer isotopic impurities, peak tailing and ^{238}U hydrides. In order to obtain the most accurate measurement results, raw signals are corrected for polyatomic interferences (mainly PbO_2, IrO_3, and HgAr) that interfere with Pu isotopes[23,24]. Uncertainty calculations followed recommendations from the Guide to the expression of Uncertainty in Measurement[25]. Relative standard uncertainties ranged from 3% to 5% for the ^{240}Pu/^{239}Pu ratios, from 6% to 17% for the ^{241}Pu/^{239}Pu ratios, and from 12% to 48% for the ^{242}Pu/^{239}Pu ratios

Results and discussion

Measured activities for plutonium isotopes, ^{137}Cs and ^{110m}Ag are compiled in Table 1, while measured atom ratios and mass concentration for plutonium are given in Table 2. All measured plutonium isotopes (^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu) were detected in the entire set of samples, although in low activities. Figures 2, 3 and 4 show respectively ^{241}Pu/^{239}Pu versus ^{240}Pu/^{239}Pu atom ratios, ^{242}Pu/^{239}Pu versus ^{240}Pu/^{239}Pu atom ratios, and ^{241}Pu/^{239}Pu versus ^{242}Pu/^{239}Pu atom ratios. Moreover, Pu measurements conducted on soil samples from 54 locations around the world and reported in the literature[7,14,26] are also plotted on these graphs. These measurements provide a global baseline for identifying inputs of non-global fallout Pu. All ^{241}Pu/^{239}Pu ratios were corrected for radioactive decay to the reference date of 15 March 2011, using a half-life of 14.325 years[27].

^{240}Pu/^{239}Pu atom ratios. Many studies characterised the Pu content in soil samples due to global fallout associated with the nuclear tests. They showed that isotopic signatures in soils are not uniform, and that variations may be observed depending on distance from nuclear test sites, proportion of stratospheric / tropospheric debris, location in the Southern or Northern hemisphere, etc. As shown in the literature[26], even samples collected at the same time and at the same location show significant heterogeneities that may be attributed to different amounts of the tropospheric fallout component (the ^{240}Pu/^{239}Pu signature for tropospheric fallout does usually not exceed half that of stratospheric fallout). In this context, fallout isotopic signatures are better represented by "mixing lines", rather than by averages[26]. This allows for a better depiction of regional variations of stratospheric fallout inventories compared to tropospheric fallout inventories. The lowest and

highest $^{240}Pu/^{239}Pu$ ratios amount respectively to ~0.062 (Eureka, Nevada, USA – an area close to the Nevada Test Site) and ~0.205 (Punta Arenas, Chile)[26]. The average $^{240}Pu/^{239}Pu$ atom ratio for the Northern hemisphere is 0.176±0.007 (standard-uncertainty, 1 SD). Regarding Japan, several authors published values representative of the global fallout in Japanese soils. Kelley et al.[26] reported $^{240}Pu/^{239}Pu$ of respectively 0.1755±0.0024 and 0.1765±0.0022 in two soil samples from Tokyo and Sapporo. Muramatsu et al. (2003) also reported $^{240}Pu/^{239}Pu$ atoms ratios measured in Japanese forest soils and they ranged from 0.155±0.003 (1 SD) to 0.194±0.005 (1 SD) (average value 0.176±0.011, 1 SD) with an extremely low value of 0.037±0.002 for a sample collected at Nagasaki[28], a ratio lower than the lowest ratio of 0.062 measured in a soil sample from Eureka (Nevada, USA). Zhang et al.[29]measured a ratio of 0.1922±0.0044 in a composite reference material prepared from soil samples collected at 14 stations in Japan between 1963-1979. In the sediments of the Western North Pacific and its marginal seas, $^{240}Pu/^{239}Pu$ atom ratios ranging from 0.15 to 0.28 were measured before the FDNPP accident[18,19]. Average Pu ratios in the Northern Hemisphere and Pu ratios measured for Japanese soils due to global fallout are also reported in Table S2. However, since the FDNPP accident, several authors measured $^{240}Pu/^{239}Pu$ atom ratios significantly higher than the global fallout ratios. Values comprised between 0.286 and 0.365 were measured by Yamamoto at al.[17] in radioactive roadside dust samples collected in the same area. It appears from Figures 2 and 3 that for all of the samples but FNL 034B, $^{240}Pu/^{239}Pu$ atom ratios measured in this study (red plan circles) are not significantly different from the published global world baseline for fallout Pu (blue empty circles). Actually, $^{240}Pu/^{239}Pu$ measured in this study in 5 out of the 6 samples collected in the vicinity of Fukushima are comprised between 0.150 (FOL 250) and 0.203 (FOL 255) (Table 2). Sample FOL 250 shows a significantly lower $^{240}Pu/^{239}Pu$ atomic ratio than the average ratio reported in soils of the Northern hemisphere and in Japanese soils analyzed before the accident (see excerpt in Fig. 2).

$^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ atom ratios. Only a few values are available regarding the $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ atom ratios due to global fallout (see Table S2). Average values for the Northern Hemisphere is 0.00113±0.00008 (1 SD) for the $^{241}Pu/^{239}Pu$ atom ratios and 0.00387±0.00071 (1 SD) for the $^{242}Pu/^{239}Pu$ ratios[26]. In contrast, $^{241}Pu/^{239}Pu$ atom ratios measured in the 6 samples analyzed in this study (0.0017 – 0.0884) were systematically higher than the corresponding atom ratios attributed to the global fallout (Fig. 2 and 4). This demonstrates that the $^{241}Pu/^{239}Pu$ atom ratio is a much more sensitive indicator of the presence of Pu from nuclear spent fuels like the ones originating from FDNPP than the $^{240}Pu/^{239}Pu$ ratio. Actually, most of the ^{241}Pu from the global fallout plutonium has disappeared because of its relatively short radioactive period (14.325 years). To a lesser extent, the $^{242}Pu/^{239}Pu$ atom ratio is also a valuable indicator of FDNPP-derived Pu (see Figures 3 and 4). Even though the $^{242}Pu/^{239}Pu$ ratios measured in this study have fairly large uncertainties, most of them (with exception of FNS 140 and FOL 250) are higher than the global fallout signature and corresponding ratios measured in Japanese soils[26].

Origin and fate of the detected Pu. Overall, our results demonstrate that Pu isotopic compositions similar to the ones found in roadside dust samples outside the 20-km exclusion zone in Iitate-Mura and Minamisoma municipalities[17] could also be measured in fresh riverbed sediment deposits. They confirm that Pu originating from FDNPP could be transported relatively long distances from the damaged power plant and is already being supplied to coastal rivers, thereby representing a potential source of Pu to the Ocean (Fig. S1). In the main radioactive contamination plume where the highest radiocesium activities were found, the highest plutonium concentrations were measured, i.e. in samples FNS 140, FOL 250, and FEL 385. However, plutonium in these samples is mainly originating

from global fallout as showed by their isotope ratios close to the global fallout signal in Japanese soils. The relatively low $^{240}Pu/^{239}Pu$ ratio (0.150±0.005, 1 SD) of sample FOL 250 is very interesting, as its ^{239}Pu abundance is clearly higher than the one of the other samples. The sample FOL 250 could therefore contain Pu from another source than one or several of the damaged reactors from FDNPP, which would have higher ^{239}Pu abundance than the reported global fallout measured in Japanese soils[26,28,29]. However, the $^{240}Pu/^{239}Pu$ ratio of this sample remains within the range of ratios reported for global fallout (Table S2).

In the coastal plains where initial cesium fallout was comparatively much lower, total Pu concentrations are also lower, although the Pu atom ratios show a clear FDNPP signature, especially higher ^{241}Pu and ^{242}Pu isotopic concentrations. This result would corroborate the findings previously published based on the spatial pattern of $^{110m}Ag:^{137}Cs$ ratio measured in soils after the Fukushima accident (Fig. S1)[20,30]. However, the outlying atom ratios found in sample FNL034B – which is also the most contaminated in both plutonium and radiocesium – are rather surprising. This sample, collected in Nitta River headwaters, is not located within the main radioactive plume, but in its prolongation to the northwest. As this zone is currently being decontaminated, more analyses should be conducted to better understand the Pu isotopic atom ratio patterns and distribution across this area. Transport of Pu to longer distances in Fukushima than in Chernobyl may be explained by the different accidental conditions that prevailed at both sites. In Chernobyl, the Pu bearing particles were larger because of the graphite fires, which likely explains that they deposited at a shorter distance from the power plant[1].

Respective proportions of FDNPP Pu and of global fallout Pu. It is possible to calculate for each analyzed sample the fraction of Pu which originates from the FDNPP, using isotopic abundances. Values taken into account for isotopic compositions of Pu from FDNPP reactors were respectively taken from previous studies[6,10,12,13] (see Table S1). Abundance for the global fallout was the one measured by Kelley et al.[26] for a soil sample collected in Tokyo. The fraction of Pu from FDNPP in a given sample ($X_{FD,i}$) may be calculated as follows for any ^{i}Pu isotope (i = 239, 240, 241, and 242):

$$X_{FD,i} = \frac{A\left(^{i}Pu\right)_{Mes} - A\left(^{i}Pu\right)_{GF}}{A\left(^{i}Pu\right)_{FD} - A\left(^{i}Pu\right)_{GF}} \qquad (1)$$

Where $A\left(^{i}Pu\right)_{Mes}$, $A\left(^{i}Pu\right)_{GF}$, and $A\left(^{i}Pu\right)_{FD}$ are the ^{i}Pu isotopic abundances respectively in the Pu measured in the sample, from the global fallout, and from FDNPP. The standard uncertainty on $X_{FD,i}$ is calculated by using the propagation error formula.

Results obtained with the isotope ^{241}Pu are the most precise and are given in Table S3. Fractions of Pu originating from FDNPP calculated using ^{240}Pu and ^{241}Pu isotopes remained in relatively good agreement. However, results obtained with the ^{240}Pu isotopes have high standard uncertainties, especially for the samples for which both $^{240}Pu/^{239}Pu$ ratios are very close. Negative values were even obtained for FNS 140 and FOL 250 samples using the ^{240}Pu abundances as $^{240}Pu/^{239}Pu$ atom ratios in both samples were slightly lower than the value taken into account for characterizing the Pu isotopic composition of global fallout. Calculations with the ^{241}Pu abundances were performed with a higher precision and were referred to hereafter. If we consider the isotopic compositions derived from the values published by Nishihara et al.[12], the fractions of Pu from FDNPP in the analyzed soils range from ~1% for FNS 140 and FOL 250 samples to ~60% for FNL 034B sample. Again, this result is rather

surprising as the FNL 034B sampling site is the farthest from FDNPP (~45 km). However, these results are relatively consistent with previous findings. Schwantes et al.[10] observed that vented plutonium from Units 1 and 3 accounts for ~16% of the total plutonium present in surface soil located at up to 45 km from the source. Yamamoto et al.[14] calculated a proportion of FDNPP-originating Pu comprised between 2–44 % in surface soils collected ~25 km NW from FDNPP (Iitate-Mura). In addition, Zheng et al.[15] calculated that the percentage of Fukushima-derived Pu was 87% is surface soil samples collected in the J-village, 20 km south of FDNPP.

Overall, the additional Pu activity supplied by FDNPP accident to the soils and sediment of the region remains very low. However, the sample characterized by the Pu isotopic composition which is the closest to the global fallout signature – and which contains thus the lowest FDNPP Pu contribution – is also the one with the highest Pu concentration (FNS 140, 490±87 pg·g^{-1}). Total $^{239+240+241+242}$Pu activity concentrations in the six analyzed soil and riverine sediment samples range from 2.1 (FOL 250 and FNS 140) to 20.6 Bq kg^{-1} dry weight (FNL 034 B). ^{238}Pu activity was not considered, but its inclusion would not significantly modify these figures. It should be noted that the most part of this activity is due to the relatively short-lived ^{241}Pu isotope. Overall, the $^{239+240}$Pu activity concentrations are between 0.16 and 1.56 Bq kg^{-1} dry weight, within the range of the typical global fallout $^{239+240}$Pu activity of 0.15 to 4.31 Bq kg^{-1} dry weight reported in the literature[31]. ^{241}Pu activities measured in the samples range from 1.2 to 17.7 Bq kg^{-1}, in the same range as the high ^{241}Pu activities (from 4.5 to 34.8 Bq kg^{-1} dry weight) measured previously in surface soils and litters collected in the vicinity of FDNPP[15].

Future studies should focus on analyzing Pu isotope and atom ratio values on a large set of soils from the area located to the northwest of the exclusion zone in order to better understand its spatial distribution across the area and the succession of events (burn-up, release of radionuclides, etc.) that occurred at FDNPP in March 2011 and their consequences on Pu dispersion in the environment. Furthermore, similar analyses should be conducted on a larger set of river sediment samples collected in coastal rivers draining this area as this study showed their potential delivery to the Ocean. Our results show that the high ^{241}Pu/^{239}Pu atom ratio of the Fukushima accident sourced-Pu may particularly provide a relevant tracer of continental-originating material from Fukushima Prefecture to the Pacific Ocean.

Associated content

Supporting information. Figure displaying the location of the analyzed samples on a map of ^{110m}Ag:^{137}Cs activity ratio in soils of Fukushima Prefecture, and Tables detailing the Pu isotopic composition used for calculation of the fraction of Pu from FDNPP in the analyzed soil samples (Table S1) and the results of Pu isotopic measurements carried out on Japanese soil samples or atmospheric deposition samples in Japan (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author contributions

O.E., F.P. and Y.O. conceived the study. Fieldwork and sampling collection was conducted by O.E., C.C., H.L., I.L. and P.B. Then, O.E., H.L., I.L. and P.B. processed samples and conducted gamma spectrometry analyses, whereas plutonium analyses were performed by F.P., A.H. and A.C.P. The manuscript was written by O.E. and F.P., and was reviewed by Y.O., C.C., H.L., I.L., J.P.L., P.B. and S.A.

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Figures

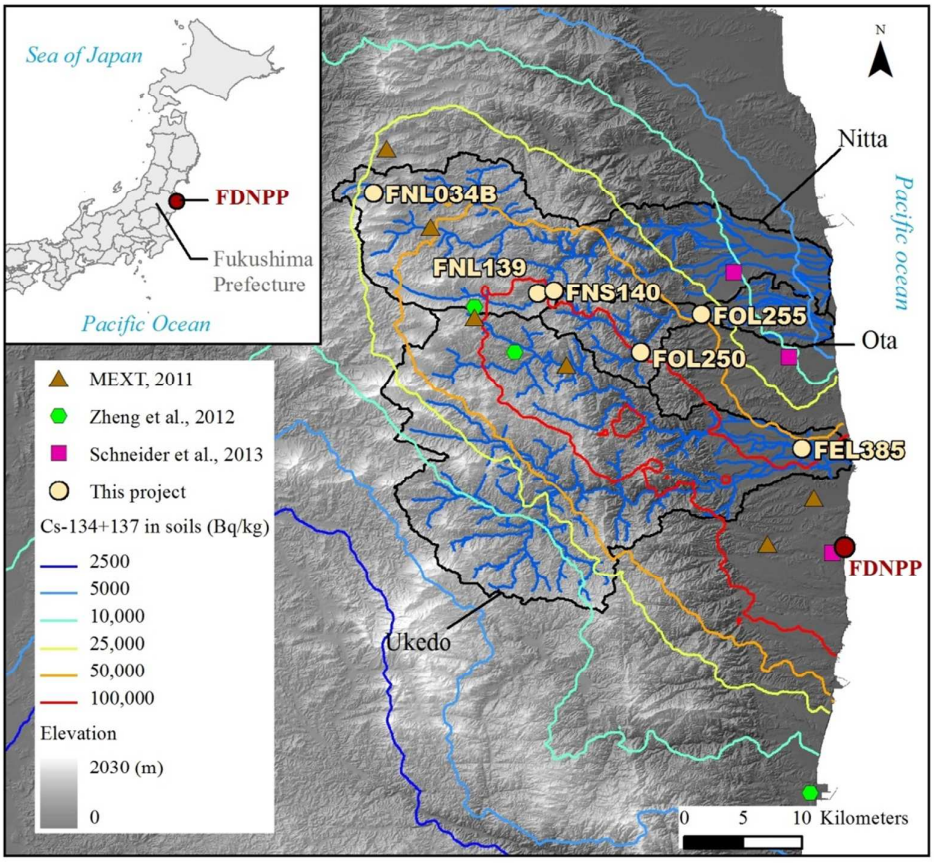

Figure 1. Location of the main inland radiocesium contamination plume in northeastern Japan (colored lines), the analyzed samples (white dots), and samples analyzed in other studies in which plutonium was detected (colored dots).

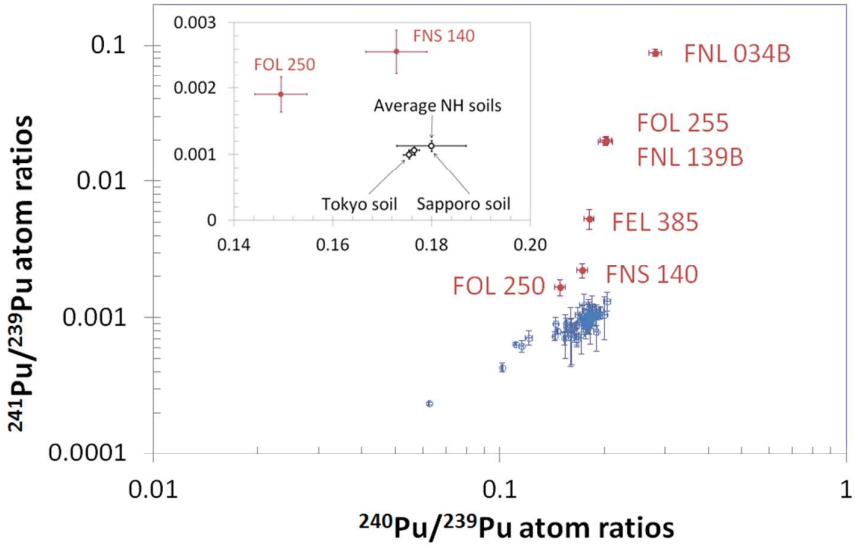

Figure 2. Plot of the $^{241}Pu/^{239}Pu$ atom ratios versus the $^{240}Pu/^{239}Pu$ atom ratios measured in the frame of this study (red plain circles) and by Hardy et al.[7], Krey et al.[8], and by Kelley et al.[26] (blue empty circles). Uncertainties are standard uncertainties (k=1). $^{241}Pu/^{239}Pu$ ratios are corrected from radioactive decay to the 15 March 2011. Note that log scales are used for both axes. Excerpt: zoom for FOL 250 and FNS 140 samples and previously published data for Japanese soils[22] and for average Northern Hemisphere soils (linear scale)[22].

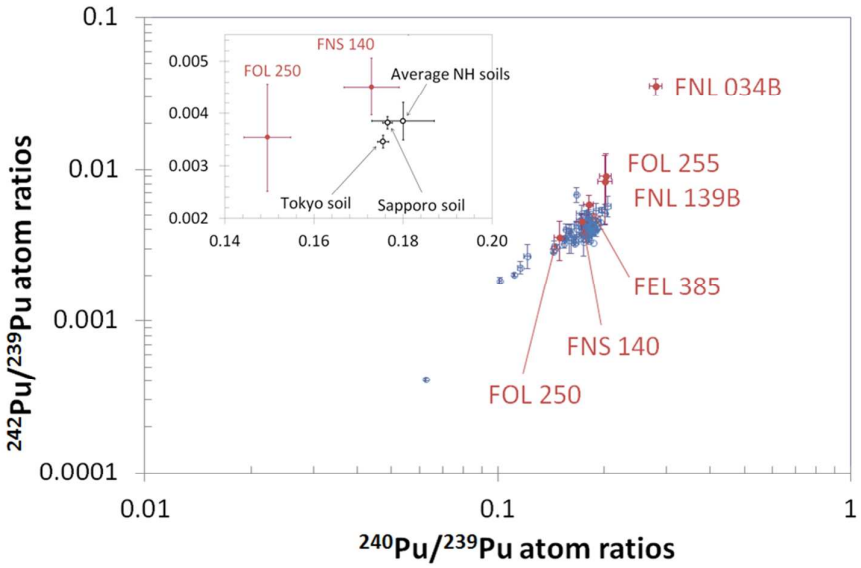

Figure 3. Plot of the $^{242}Pu/^{239}Pu$ atom ratios versus the $^{240}Pu/^{239}Pu$ atom ratios measured in the frame of this study (red plain circles) and by Hardy et al.[7], Krey et al.[8], and by Kelley et al.[26] (blue empty circles). Uncertainties are standard uncertainties (k=1). Note that log scales are used for both axes. Excerpt: zoom for FOL 250 and FNS 140 samples and previously published data for Japanese soils[22] and for average Northern Hemisphere soils (linear scale)[22].

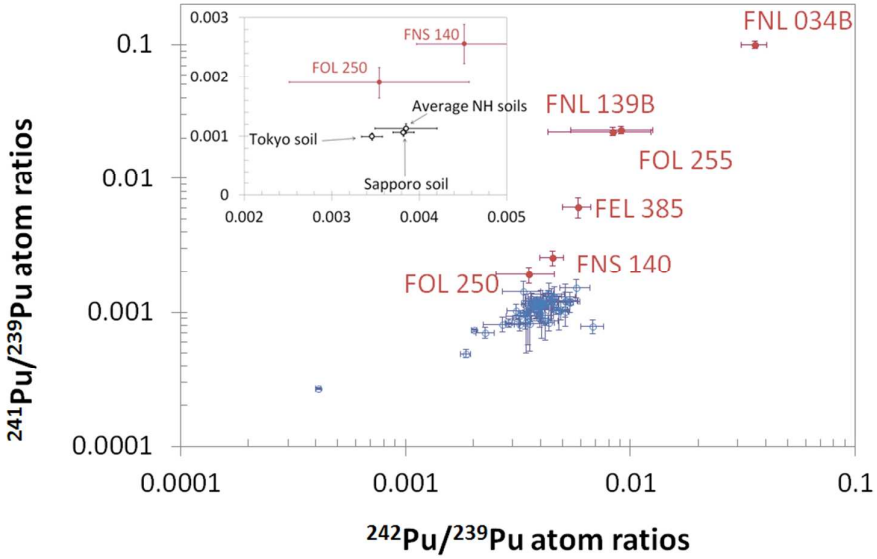

Figure 4. Plot of the $^{241}Pu/^{239}Pu$ atom ratios versus the $^{242}Pu/^{239}Pu$ atom ratios measured in the frame of this study (red plain circles) and by Hardy et al.[7], Krey et al.[8], and by Kelley et al.[26] (blue empty circles). Uncertainties are standard uncertainties (k=1). $^{241}Pu/^{239}Pu$ ratios are corrected from radioactive decay to the 15 March 2011. Note that log scales are used for both axes.

Tables

Table 1. Activity concentrations in radionuclides in the analyzed samples. ^{241}Pu activities are corrected from radioactive decay to 15 March 2011. Uncertainties are standard-uncertainties (given with a coverage factor of 1). Pu isotopic concentration activities are given in Bq per kg of dry weight material.

Sample	Date	^{239}Pu ($Bq \cdot kg^{-1}$)	^{240}Pu ($Bq \cdot kg^{-1}$)	^{241}Pu ($Bq \cdot kg^{-1}$)	^{242}Pu ($Bq \cdot kg^{-1}$)	^{137}Cs ($Bq \cdot kg^{-1}$)	^{110m}Ag ($Bq \cdot kg^{-1}$)
FNL 034B	Nov. 2011	0.121±0.013	0.125±0.013	20.3±2.4	0.00027±0.00005	715 780 ± 360	3 090 ± 120
FNL 139B	April 2012	0.094±0.010	0.069±0.008	3.5±0.9	0.00005±0.00003	172 370 ± 160	590 ± 70
FNS 140	April 2012	0.954±0.098	0.603±0.062	4.1±0.7	0.00027±0.00004	188 450 ± 200	1 040 ± 100
FOL 250	Nov. 2012	0.444±0.046	0.243±0.025	1.4±0.3	0.00010±0.00003	64 200 ± 200	650 ± 140
FOL 255	Nov. 2012	0.118±0.012	0.088±0.009	4.5±0.6	0.00007±0.00003	116 420 ± 340	600 ± 220
FEL 385	May 2013	0.497±0.051	0.330±0.034	5.1±1.0	0.00018±0.00003	102 430 ± 380	400 ± 240

Table 2. Pu concentration and atom ratios measured in this study. $^{241}Pu/^{239}Pu$ ratios are corrected from radioactive decay to 15 March 2011. Uncertainties are standard-uncertainties (given with a coverage factor of 1). Pu concentrations are given in pg per kg of dry weight material.

Sample	$^{240}Pu/^{239}Pu$ atom ratio	$^{241}Pu/^{239}Pu$ atom ratio	$^{242}Pu/^{239}Pu$ atom ratio	Pu ($pg \cdot kg^{-1}$)[a]
FNL 034B	0.281 ± 0.012	0.1006 ± 0.0065	0.0356 ± 0.0045	74 ± 12
FNL 139B	0.201 ± 0.010	0.0224 ± 0.0015	0.0083 ± 0.0040	50 ± 9
FNS 140	0.173 ± 0.006	0.0026 ± 0.0003	0.0045 ± 0.0005	490 ± 87
FOL 250	0.150 ± 0.005	0.0019 ± 0.0003	0.0035 ± 0.0010	223 ± 41
FOL 255	0.203 ± 0.008	0.0229 ± 0.0014	0.0090 ± 0.0036	63 ± 11
FEL 385	0.181 ± 0.006	0.0061 ± 0.0010	0.0058 ± 0.0009	258 ± 45

254x190mm (96 x 96 DPI)