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Airborne Plutonium and Non-Natural Uranium from the Fukushima DNPP Found at 120 km Distance a Few Days after Reactor Hydrogen Explosions

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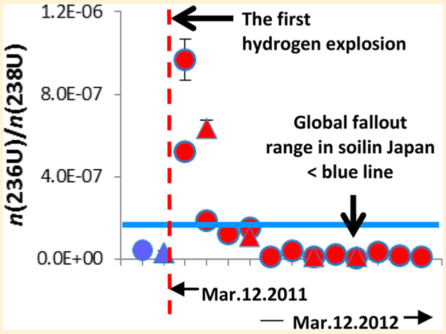
Ⓢ *Supporting Information*

ABSTRACT: Plutonium (Pu) and non-natural uranium (U) originating from the Fukushima Daiichi Nuclear Power Plant (FDNPP) were identified in the atmosphere at 120 km distance from the FDNPP analyzing the ratio of number of atoms, following written as *n*(isotope)/*n*(isotope), of Pu and U. The $n(^{240}\text{Pu})/n(^{239}\text{Pu})$, $n(^{241}\text{Pu})/n(^{239}\text{Pu})$, $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ in aerosol samples collected before and after the FDNPP incident were analyzed by accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICPMS). The activity concentrations of ^{137}Cs and ^{134}Cs in the same samples were also analyzed by gamma spectrometry before the destructive analysis. Comparing the time series of analytical data on Pu and U obtained in this study with previously reported data on Pu, U, and radioactive Cs, we concluded that Pu and non-natural U from the FDNPP were transported in the atmosphere directly over a 120 km distance by aerosol and wind within a few days after the reactor hydrogen explosions. Effective dose of Pu were calculated using the data of Pu: (130 ± 21) nBq/m^3, obtained in this study. We found that the airborne Pu contributes only negligibly to the total dose at the time of the incident. However the analytical results show that the amount of Pu and non-natural U certainly increased in the environment after the incident.



INTRODUCTION

A large scale earthquake (moment magnitude 9.0) occurred on March 11, 2011 in the northwest Pacific generating the tsunami which seriously damaged the Fukushima Daiichi Nuclear Power Plant (FDNPP). Further hydrogen explosions occurred in the Unit 1 and 3 reactors on March 12 and 14, respectively. On March 15, white smoke was observed at the Unit 2 and 4 reactors. Following the FDNPP incident, numerous data on radioactive nuclides released into the environment were published mainly focusing on the activity of ^{134,137}Cs and ^{131}I,[1−7] because of their high concentrations in the atmosphere and high dose effect on human beings. They can be analyzed rapidly by gamma spectrometry without chemical treatment, which may be another reason for their extensive publication. Actinides, such as plutonium (Pu) and uranium (U) are also important nuclides from the point of view of environmental contamination, and for ingestion and inhalation dose assessments as studied after the Chernobyl accident.[8] Plutonium release from the damaged FDNPP was confirmed analyzing surface soil at the reactor site and observing a rapid decrease of Pu with the distance from the facility.[9] Reports on Pu atom ratios in litter and soil samples collected around the FDNPP were published,[10,11] presenting a comparison of the ratio of number of atoms, following written as "*n*(isotope)/*n*(isotope)", the $n(^{240}\text{Pu})/n(^{239}\text{Pu})$ and the $n(^{241}\text{Pu})/n(^{239}\text{Pu})$ among litter samples near from the FDNPP, Chernobyl data and global fallout in Japan. As a conclusion, the report confirmed that Pu was released from the FDNPP. In another publication,[12] the $n(^{235}\text{U})/n(^{238}\text{U})$ in soil samples from the 7−80 km zone around the FDNPP were reported as natural U composition. However, it is likely that the non-natural U emitted was strongly diluted by the large amount of natural U present in the soil, and thus its characteristic was obscured.

Due to the trace amount of Pu and non-natural U present in the atmosphere, and difficulties of sample collection and analysis, the release of Pu and U from the FDNPP to the atmosphere is still not well-known. We analyzed the isotopic compositions of Pu and U in aerosol samples collected at monitoring and sampling stations at 120 km south−southwest

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(Tokai-mura) of the FDNPP, before and after the reactor hydrogen explosions, using accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICPMS) after chemical separation. The results obtained in this study are compared with the Pu data on the litter samples from the 20−30 km zone around the FDNPP[10,11] and Chernobyl,[13−15] and the data on global fallout of U[16] and Pu[17,39] in Japan.

MATERIALS AND METHODS

Sample Collection. The sampling locations, MS-3 (vegetable field) and MS-4 (rice field) are located in Tokai-mura (Figure 1). The place of MS-3 is 5 km to the southeast of MS-4. The sampling filters are made of 70% cellulose and 30% glass fiber (HE-40TA, Toyo Roshi Kaisha, Ltd.). The active sampling area of the filters was 50 mm in diameter. The sampling duration was typically one week and a total about 1000 m^3 of aerosol was collected for each sample. Only for one sample at MS-4 (March 7−21), the total about 1500 m^3 aerosol was collected in two weeks because of a power failure (March 11, 14:50−13, 21:30) due to the earthquake. The sampling height was 1 m above ground and the air flow rate of the vacuum system was 100 L/min. The particle collection efficiency is more than 87% for dispersed oil particles with a size of 0.07−1.0 μm under the condition that the face velocity is 20−130 cm/s.[18]

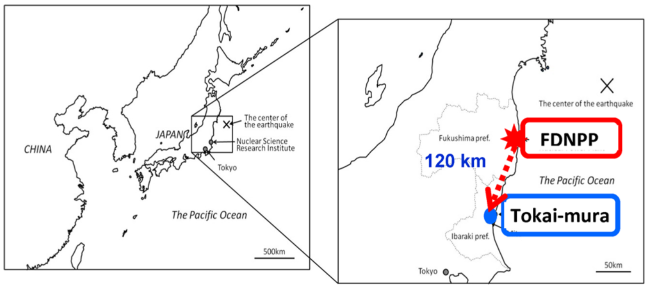

Figure 1. Monitoring and sampling stations in Tokai-mura (blue point) and FDNPP (red star).

Analysis of ^{137}Cs, ^{134}Cs, and Isotopic Composition of Pu and U. The activity concentration of ^{137}Cs and ^{134}Cs was measured by gamma spectrometry using high-purity germanium detectors. After the gamma-ray measurements, the filter samples were divided into several parts for atom ratio analysis and quantitative analyses. The filter was ashed at ca. 550 °C and Pu and U compounds were leached from the filter and decomposed with nitric acid, hydrochloric acid and hydrogen peroxide. Plutonium and U were then separated from the matrix using commercially available ion exchange and ion chromatographic resins. The analytical procedures are described in detail elsewhere.[19,20] After chemical separation of U and Pu, each nuclide in the fraction was coprecipitated with $Fe(OH)_3$ using ammonium hydroxide. The precipitate was washed with high purity water and prepared as Pu and U oxides by heating at to 550 °C for 10 h. The Pu and U oxide was then mixed with about 3 mg of Fe powder and pressed into an aluminum sample holder. During the measurements, the solid sample is sputtered with a Cs$^{\pm}$ beam, negative sample ions, U^{16}O$^-$ and Pu^{16}O$^-$, are extracted, and $n(^{240}\mathrm{Pu})/n(^{239}\mathrm{Pu})$, $n(^{241}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ and $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ are measured. After a first mass separation, the ions are accelerated in the first stage of a Tandem accelerator to an energy of 1.65 MeV. In the high-voltage terminal the ions are stripped to positive charge states in a helium gas cell. Since almost no molecular ions can exist in the 3+ charge state, the atomic ^{236}U^{3+} and Pu^{3+} ions can be sorted out in a second mass spectrometer after acceleration to 6.7 MeV in the second stage of the tandem accelerator. The recently discovered rare ^{235}UH^{3+} ions are destroyed due to collisional breakup by increasing the helium pressure.[20] The choice of the 3+ charge state and helium results in the unusually high yield of 20%, which is four times higher than the 5% previously achieved for the 5+ charge state with oxygen. The second mass spectrometer consists of four electric/magnetic separators to fully suppress background from charge exchange along the beamline.[21]

The $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ is determined by counting ^{236}U^{3+} with a gas ionization detector in sequence with measuring the ^{238}U^{5+} beam current in a Faraday cup. To increase the precision of the current measurement, the integration time for ^{238}U^{5+} was extended up to 1s. Where the uranium content was still too low, ^{234}U^{3+} and ^{235}U^{3+} were measured with the ionization chamber. The natural abundances of these isotopes were used to estimate the $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$. This is a valid approximation considering our measurement precision and the isotopic ratios obtained by ICPMS. The advantage of AMS to measure isotopic ratios of small number of Pu atoms and ^{236}U (about 10^6) is the complete suppression of isobaric hydrogen compound like ^{235}UH and ^{239}PuH, and a low detection limit for the $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ which can be as low as 10^{-13}.[21−24] The detection limit of plutonium isotopic ratios is only limited by the number of atoms present. At the level of sensitivity needed for this work, traces of other Pu isotopes in a ^{242}Pu spike could compromise the detection limits. Therefore no Pu spike was added to the sample for isotopic ratio analysis by AMS but for one sample, the ^{239}Pu concentration was measured with the isotope dilution method using the ^{242}Pu spike, IRMM-085.[25]

For the ICPMS measurements, the final fraction was dissolved in 2% nitric acid and the $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ in the aerosol samples were analyzed by sector-field inductively coupled plasma mass spectrometry (SF-ICPMS) without spike. The final results were obtained after reagents and filter blanks and mass bias correction using a linear law,[26] and impurity measurements.[27] The U concentration in the aerosol samples was determined using a split filter with the isotopic dilution method using the ^{233}U spike, IRMM-057.[28]

RESULTS AND DISCUSSION

Cs-137 and Uranium in Aerosol Samples. The U concentration in the aerosol samples ranged from 3.2 to 22 pg/m^3 (Table 1) and this corresponds to a previous observation of (14 ± 10) pg/m^3 at Tsukuba, Japan, about 70 km distance from the monitoring stations of this study.[29] However, an obvious signal is visible in the activity concentration of ^{137}Cs (7.81 ± 0.17 Bq/m^3), and $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$: 0.00790 ± 0.00019 and $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$: 0.000100 ± 0.000028 in sample 4, which was collected soon after the first hydrogen explosions (Figure 2A, B, C). The sudden increase of the radiocesium concentration was accompanied by an activity ratio ^{137}Cs to ^{134}Cs close to unity,[30] which shows that the origin was from the FDNPP. The activity concentrations and behavior of ^{137}Cs and ^{134}Cs observed at MS-4 are close to those of MS-3. Emission of spherical cesium-bearing particles collected at Tsukuba, Japan on March 14−15 was investigated by another group.[31] They found that the particles coexist with Fe, Zn and possibly other elements,

Table 1. Sampling Period and the Corresponding Sample Name (Arabic Number: MS-3; Alphabet Character: MS-4), and the Concentration of U. –: Not Analyzed

sample name	sampling period in 2011	U concentration ± uncertainty, (k = 1) [pg/m^3] MS-3	U concentration ± uncertainty, (k = 1) [pg/m^3] MS-4
1	Jan. 3–10	3.22 ± 0.65	
2	Jan. 31–Feb. 7	9.7 ± 2.6	
A	Feb. 28–Mar. 7		3.60 ± 0.39
3	Mar. 7–14	3.79 ± 0.67	–
4, B	**Mar. 14–21, 7–21**	**17.6 ± 4.4**	**9.9 ± 1.2**
5, C	Mar. 21–28	22.0 ± 4.2	–
6, D	Mar. 28–Apr. 4	–	4.6 ± 0.67
7, E	Apr. 4–11	–	5.4 ± 1.1
8, F	Apr. 11–18	–	3.85 ± 0.97
9, G	Apr. 18–25	–	–
10, H	Apr. 25–May 2	17.6 ± 4.3	3.59 ± 0.61
11, I	May 2–9	–	–
12	May 9–16	–	–
13, J	May 30–Jun. 6	–	20.2 ± 1.9
K	Jul. 4–11		–
14	Aug. 15–22	–	
L	Nov. 14–21		–
M	Mar. 5–12 (2012)		

insoluble in water, and mainly fell onto the ground by dry deposition. The diameters of the particles they studied are approximately 2 μm.

The observation of enriched U in this study, however, cannot necessarily be associated with the FDNPP. For example, a previous accident, which occurred at the JCO Company Limited in Tokai-mura in 1999, released enriched U into the environment. Uranium isotopic ratios in soil samples at the JCO campus in Tokai-mura indicate that atom of $n(^{235}U)/n(^{238}U)$ ranged from 0.0076 to 0.0162.[32] Such enriched U particles may have been resuspended to the atmosphere as previously observed in the Chernobyl area[33] and trapped by our sampling filters. However, we think that an origin from the FDNPP is a more plausible explanation referring to the sudden increase of the activity concentration of radio-cesium and the $n(^{236}U)/n(^{238}U)$ (Figure 2D) in the sample collected in the same period.

In the weeks immediately after the reactor hydrogen explosion, a higher $n(^{236}U)/n(^{238}U)$ than before was observed by AMS (Figure 2D), corresponding to the behavior of ^{137}Cs, and the $n(^{235}U)/n(^{238}U)$ and the $n(^{234}U)/n(^{238}U)$. The two data points of samples B_1 and B_2 are obtained with two different aliquots of the filter. The ratios decreased over time and after one month they settled to the global fallout level in Japan. From the observed time trend and the atom ratios, we conclude that the U on the filter with increased $n(^{236}U)/n(^{238}U)$ are affected by the FDNPP but strongly diluted by natural U, whose isotopic abundances are ^{234}U: 0.0055%, ^{235}U: 0.720% and ^{238}U: 99.274%.[34] The isotope ^{236}U does not exist in the nature above $n(^{236}U)/n(^{238}U) \sim 10^{-10}$, except for contamination from nuclear facilities and weapon tests.

If a radioactive particle of reactor fuel as observed after the Chernobyl accident[35−38] had been trapped on the filter, the ratio would be several orders of magnitude higher than observed. The highest value of the $n(^{236}U)/n(^{238}U)$ observed in

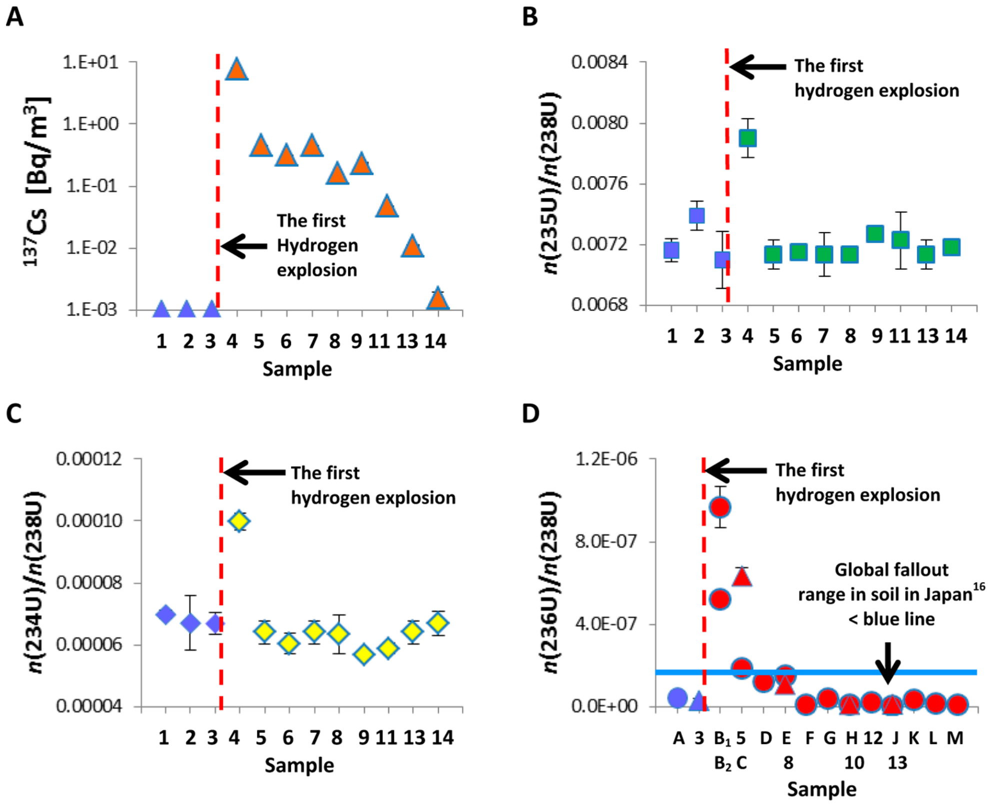

Figure 2. The symbols in blue color indicate the analytical results of the samples collected before incident. (**A**): Activity concentration of ^{137}Cs and (**B**): $n(^{235}U)/n(^{238}U)$, (**C**): $n(^{234}U)/n(^{238}U)$ and (**D**): $n(^{236}U)/n(^{238}U)$ in aerosol samples collected at 120 km south−southwest of the FDNPP. The triangle and circle symbols indicate the data from MS-3 and MS-4, respectively. The bars indicate uncertainty (k = 1).

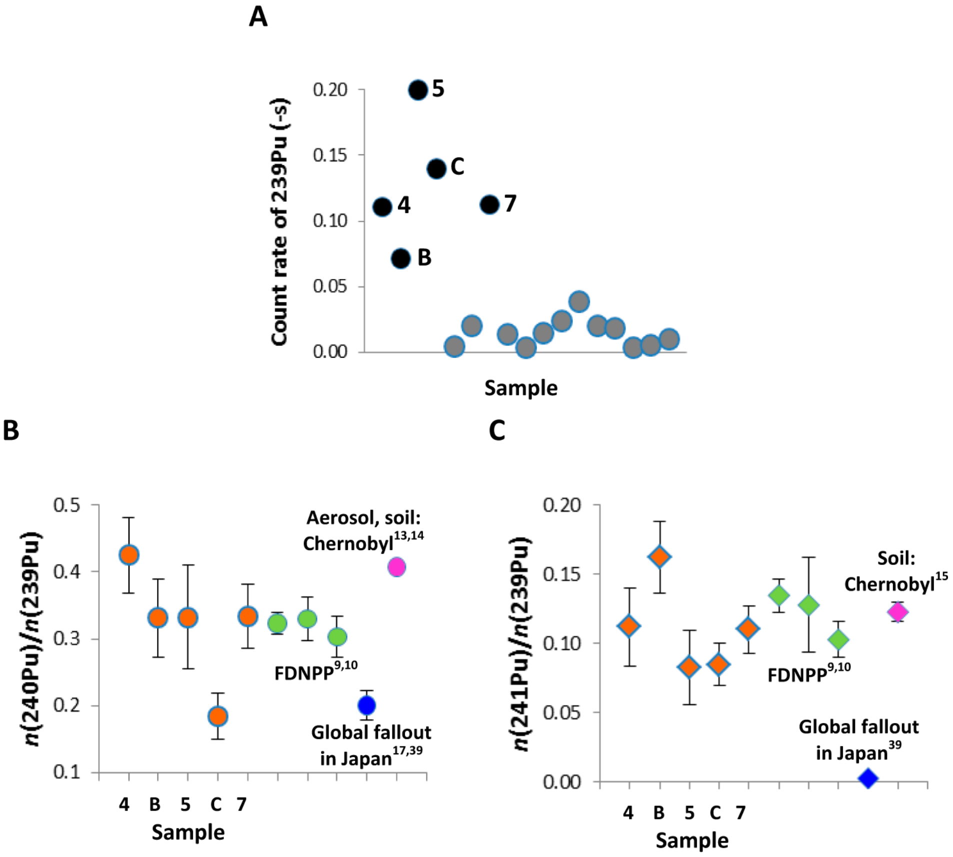

Figure 3. (**A**) Count rate of ^{239}Pu in the sample sources. The data with sample name is used for further discussion, (**B**) $n(^{240}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ and (**C**) $n(^{241}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ in the aerosol samples. The orange, green, blue, and pink colors indicate the data obtained in this study, in the litter samples in the 20−30 km zone around the FDNPP,[9,10] global fallout in Japan[17] and in Chernobyl samples,[13−15] respectively. The bars indicate uncertainty ($k = 1$) except for (B), (C) Global fallout in Japan. The bar of Global fallout in Japan indicates the range of the analytical results. (B) Global fallout in Japan: 0.17 − 0.25,[17,39] (C) Global fallout in Japan: 0.00255−0.00314.[39]

sample B (Figure 2D) is diluted by natural U by a factor of 10^4, taking into account that the fuel contains a few % of ^{236}U as typical. The content of ^{236}U in this sample aliquot is $(2.53 \pm 1.1) \times 10^7$ atoms. For sample 5, a content of $(2.83 \pm 0.38) \times 10^7$ atoms of ^{236}U was obtained. Assuming that ^{236}U is distributed over the whole filter homogeneously, the concentration of ^{236}U in the atmosphere was calculated as (0.128 ± 0.053) nBq/m^3 and (0.43 ± 0.16) nBq/m^3 for sample B_1 and 5, respectively.

Uranium concentrations of blank filters were determined by the isotope dilution method and ICPMS. The average amount of U in five blank filters was (88 ± 16) pg in quarter pieces of each filter, which size we mainly used for the analysis. The maximum contribution to the U content of the aerosol samples is about 4%. The concentration of total U in the aerosol samples was calculated correcting the U amount present in the blank filter and reagent blanks. The blank value for the atom ratio analysis was in the range of 0.1−1.5%, and the influence of this on the results is smaller than the uncertainties.

Plutonium in Aerosol Samples. Under similar measurement conditions, the AMS detector count rate is roughly proportional to the Pu concentration of the sample in the ion source, and thus allows a relative comparison of the samples from one measurement, although this estimate has uncertainty of at least a factor two. Five samples show a significantly enhanced count rate of ^{239}Pu of more than 0.07 cps. The other samples yield between 0.02 and 0.04 cps. The two process blanks showed less than 0.003 cps (Figure 3A). The content of ^{239}Pu in sample 5 determined by isotope dilution was $(8.9 \pm 1.4) \times 10^6$ atoms in the analyzed sample aliquot. Assuming that Pu is distributed homogeneously on the filter, the activity concentration of ^{239}Pu was calculated as (130 ± 21) nBq/m^3.

The activity of ^{241}Pu was decay corrected to the March 15, 2011 (Figure 3C). The results of $n(^{240}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ and $n(^{241}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ in five Pu-rich samples analyzed by AMS in this study are clearly different from the global fallout in Japan, and correspond to the ratio observed in the litter sample near the FDNPP (Figures 3B and 3C). While the lower $n(^{240}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ value of sample C might indicate mixing with Pu from global fallout, the observed $n(^{241}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ does not support such an assumption. We have presently no explanation for this deviation. The atom ratios obtained for the 12 samples with low ^{239}Pu count rate are $n(^{240}\mathrm{Pu})/n(^{239}\mathrm{Pu})$: 0.141 ± 0.032 and $n(^{241}\mathrm{Pu})/n(^{239}\mathrm{Pu})$: 0.0224 ± 0.0084 which are in agreement with global fallout in Japan during 1999−2000[17] as well as 1963−1979[39] within uncertainties.

The data obtained in this study strongly suggest that this series of unusual Pu and U were transported from the FDNPP over 120 km distance after the incident.

Wind Direction and Transport of Radionuclides. The wind direction from the FDNPP on March 12−17, 2011 was computed with the NOAA-Hysplit Model program (http://ready.arl.noaa.gov/HYSPLIT_traj.php) (Figure 4). The first explosion of the Unit 2 and 3 reactors occurred on March 12 at

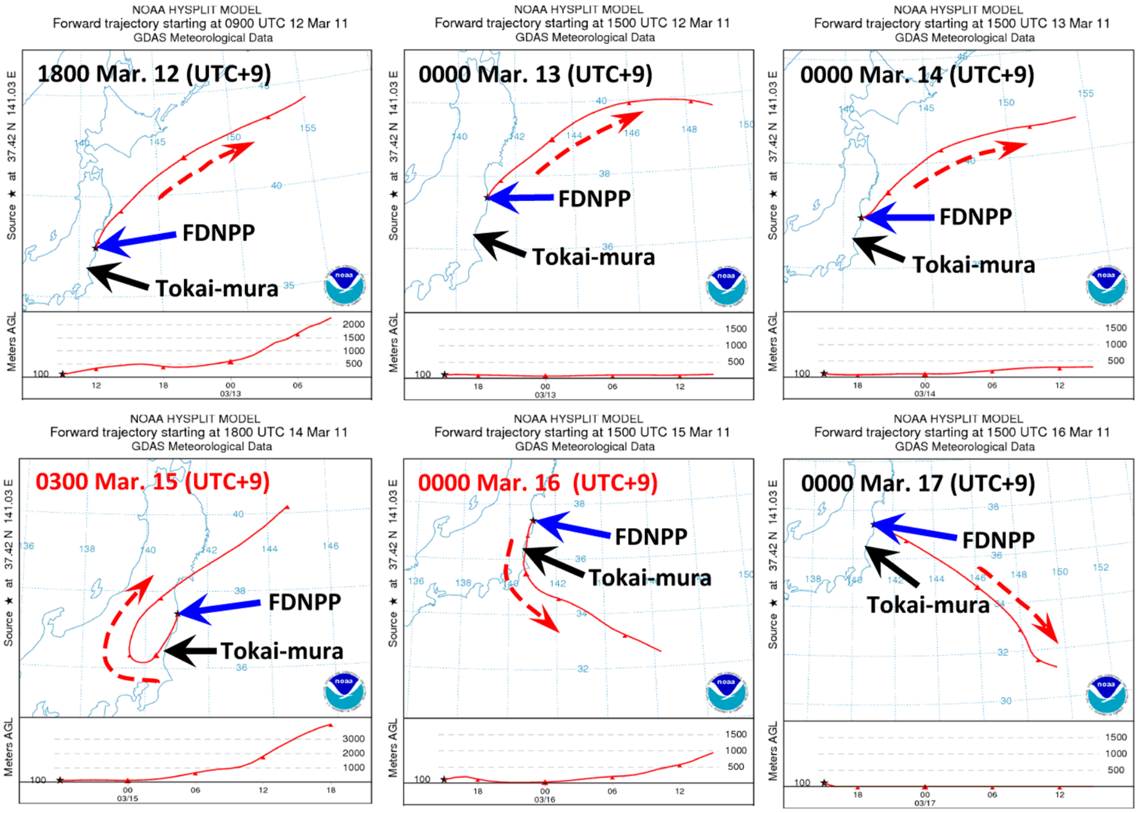

Figure 4. Wind direction on March 12−17, 2011 from the FDNPP.

Table 2. Effective Dose of Pu Calculated for Public/Adult for the FDNPP Accident Using Dose Coefficients Recommended by the ICRP and Assuming a Concentration of Pu in the Atmosphere of 130 nBq/m^3 (This Work)[a]

isotope	concentration [Bq/m^3]	inhalation rate[43] [m^3/h]	dose coefficient [Sv/Bq]	exposure time [h]	effective dose [Sv]
^{239}Pu	1.3×10^{-7}	0.925	5.0×10^{-5}	1	6.0×10^{-12}
^{240}Pu	1.5×10^{-7}	0.925	5.0×10^{-5}	1	6.9×10^{-12}
^{241}Pu	2.5×10^{-5}	0.925	9.0×10^{-7}	1	2.1×10^{-11}

[a] Activity median aerodynamic diameter (AMAD): 1 μm; Absorption type: moderate.[40,44] Exposure time: 1 h by way of an example.

around 15:36 (Unit 1) and 14 at around 11:01 (Unit 3). However no influence of radioactive material was found in the aerosol samples collected on March 7−14. This is likely related to the fact that the direction of the wind on March 12−14 was not toward Tokai-mura. Most probably the Pu and the non-natural U found in this study were transported by wind on March 15 and 16 together with the plume of the hydrogen explosion in the Unit 3 reactor, which was equipped with a mixed core of uranium fuel, and mixed uranium and plutonium oxides (MOX). Gamma-ray dose rate monitored by a NaI(Tl) scintillation detector at 1 km west of the sampling stations indicate that the gamma-ray dose rate began to increase on March 15 at 01:00 and the highest value was observed on the same day at 08:00.[40,41] This observation together with the wind direction allow us to assume that the unusual Pu and U were transported with this plume from the FDNPP over 120 km distance on March 15, in a few days after the hydrogen explosions occurred on March 12 and 14. After the Chernobyl accident, at a distance of 480 km a large number of radioactive particles (up to 10,000 particles per m^3) were found containing ^{233}U, ^{234}U, ^{235}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Cm, ^{244}Cm and other radionuclides.[37] It was also reported that hot particles derived from Chernobyl were found widely in Europe.[38] The trace amount of Pu and U detected in this study were presumably small particles from the fuel removed by some process and transported over long distance by wind. To our knowledge, this is the first verification using the analytical data of Pu and non-natural U that the fuel materials from the FDNPP were transported in the atmosphere over a distance of 120 km.

Effective Dose of Plutonium. In the following, we assume that the concentration of Pu of FDNN origin in aerosol was 130 nBq/m^3 (7 in Figure 4) with an isotopic ratio $n(^{240}\text{Pu})/n(^{239}\text{Pu}) = 0.318 \pm 0.10$ and $n(^{241}\text{Pu})/n(^{239}\text{Pu}) = 0.117 \pm 0.032$ (average of samples 4, B, 5, and C ± standard deviation). With this assumption, effective dose for each Pu isotope was calculated using the exposure condition for the members of the public recommended by the International Commission on Radiological Protection (ICRP)[40] (Table 2). The main activity and dose are from ^{241}Pu: half-life (14.325 ± 0.006) *a*,[41,42] which decays into ^{241}Am: half-life (432.6 ± 0.6) *a*.[41] The alpha emitter ^{241}Am gives an even larger radiation risk in the environment. The results show that airborne Pu on site contributes only negligibly to the total effective dose evaluated with radioactive Cs and iodine at the same location on March 13 − May 23, 2011 by another group.[43]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of materials and analytical method of AMS, ICPMS and gamma spectrometry. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Masson, O.; et al. Tracking of airborne radionuclides from the Damaged Fukushima Dai-Ichi nuclear reactors by European Networks. *Environ. Sci. Technol.* **2011**, *45*, 7671−7677.

(2) Buesseler, K.; Aoyama, M.; Fukasawa, M. Impacts of the Fukushima nuclear power plants on marine radioactivity. *Environ. Sci. Technol.* **2011**, *45*, 9931−9935.

(3) Parache, V.; Pourcelot, L.; Roussel-Debet, S.; Orjollet, D.; Leblanc, F.; Soria, C.; Gurriaran, R.; Renaud, Ph.; Masson, O. Transfer of ^{131}I from Fukushima to the vegetation and milk in France. *Environ. Sci. Technol.* **2011**, *45*, 9998−10003.

(4) Bossew, P.; Kirchner, G.; De Cort, M.; de Vries, G.; Nishev, A.; de Felice, L. Radioactivity from Fukushima Dai-ichi in air over Europe; part 1: Spatio-temporal analysis. *J. Environ. Radioact.* **2012**, *114*, 22−24.

(5) Yoshida, N.; Kanda, J. Tracking the Fukushima radionuclides. *Science* **2012**, *336*, 1115−1116.

(6) Wetherbee, G. A.; Gay, D. A.; Debey, T. M.; Lehmann, C. M. B.; Nilles, M. A. Wet deposition of fission-product isotopes to North America from the Fukushima Dai-ichi Incident, March 2011. *Environ. Sci. Technol.* **2012**, *46*, 2574−2582.

(7) Thakur, P.; Ballard, S.; Nelson, R. An overview of Fukushima radionuclides measured in the northern hemisphere. *Sci. Total Environ.* **2013**, *458*−*460*, 577−613.

(8) Garger, E. K.; Sazhnyuk, A. D.; Odintzov, A. A.; Paretzke, H. G.; Roth, P.; Tschiersch, J. Solubility of airborne radioactive fuel particles from the Chernobyl reactor and implication to dose. *Radiat. Environ. Biophys.* **2004**, *43*, 43−49.

(9) Schwantes, J. M.; Orton, C. R.; Clark, R. A. Analysis of a nuclear accident: Fission and activation product releases from the Fukushima Daiichi nuclear facility as remote indicators of source identification, extent of release, and state of damaged spent nuclear fuel. *Environ. Sci. Technol.* **2012**, *46*, 8621−8627.

(10) Zheng, J.; Tagami, K.; Watanabe, Y.; Uchida, S.; Aono, T.; Ishii, N.; Yooshida, S.; Kubota, Y.; Fuma, S.; Ihara, S. Isotopic evidence of plutonium release into the environment from the Fukushima DNPP accident. *Sci. Rep.* **2012**, *2* (304), 1−8.

(11) Zheng, J.; Tagami, K.; Uchida, S. 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.* **2013**, *47*, 9584−9595.

(12) Takagai, Y.; Furukawa, M.; Nagahashi, Y.; Takase, T.; Shikino, O.; Kameo, Y. Isotope ratio analysis of ^{235}U and ^{238}U nuclide using a microwave digestion associated with ICP-MS and the large areal soil survey related to Fukushima Daiichi Nuclear disaster. *BUNSKI KAGAKU* **2011**, *60*, 947−957 (abstract in English).

(13) Lujanienė, G.; Aninkevicius, V.; Lujanas, V. Artificial radionuclides in the atmosphere over Lithuania. *J. Environ. Radioact.* **2009**, *100*, 108−119.

(14) Muramatsu, Y.; Rühm, W.; Yoshida, S.; Tagami, K.; Uchida, S.; Wirth, E. Concentrations of ^{239}Pu and ^{240}Pu and their isotopic ratios determined by ICP-MS in soils collected from the Chernobyl 30-km Zone. *Environ. Sci. Technol.* **2010**, *34*, 2913−2917.

(15) Ketterer, M. E.; Hafer, K. M.; Mietelski, J. W. Resolving Chernobyl vs. global fallout contributions in soils from Poland using plutonium atom ratios measured by inductively coupled plasma mass spectrometry. *J. Environ. Radioact.* **2004**, *73*, 183−201.

(16) Sakaguchi, A.; Kawai, K.; Steier, P.; Quinto, F.; Mino, K.; Tomita, J.; Hoshi, M.; Whitehead, N.; Yamamoto, M. First results on ^{236}U levels in global fallout. *Sci. Total Environ.* **2009**, *407*, 4238−4242.

(17) Hirose, K.; Igarashi, Y.; Aoyama, M.; Kim, C. K.; Kim, C. S.; Chang, B. W. Recent trends of plutonium fallout observed in Japan: Plutonium as a proxy for desertification. *J. Environ. Monit.* **2003**, *5*, 302−307.

(18) Kinouch, N.; Onodera, J.; Zoshino, T.; Murata, M.; Yamazaki, T. Performance of improved cellulose-glass fiber filter paper for radioactive aerosol sampling. *Hokenbutsuri* **1995**, *30*, 303−314 (abstract in English).

(19) Shinonaga, T.; Aigner, H.; Klose, D.; Spinder, P.; Fröschl, H.; Donohue, D. Recommended Values of ^{239}Pu, ^{240}Pu and $^{239+240}$Pu concentrations in reference material IAEA-315 (marine sediment) estimated by thermal ionisation mass spectrometry, inductively coupled plasma-mass spectrometry and alpha spectrometry. *Geostand. Geoanal. Res.* **2008**, *32*, 93−101.

(20) Shinonaga, T.; Donohue, D.; Aigner, H.; Bürger, S.; Klose, D.; Kärkelä, T.; Zilliacus, R.; Auvinen, A.; Marie, O.; Pointurier, F. Production and characterization of plutonium dioxide particles as a quality control material for safeguards purposes. *Anal. Chem.* **2012**, *84*, 2638−2646.

(21) Lachner, J.; Christl, M.; Vockenhuber, C.; Synal, H. A. Detection of UH^{3+} and ThH^{3+} molecules and ^{236}U background studies with low-energy AMS. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2013**, *294*, 364−368.

(22) Vockenhuber, C.; Ahmad, I.; Golser, R.; Kutschera, W.; Liechtenstein, V.; Priller, A.; Steier, P.; Winkler, S. Accelerator mass spectrometry of heavy long-lived radionuclides. *Int. J. Mass Spectrom.* **2003**, *223*−*224*, 713−732.

(23) Steier, P.; Richler, M.; Keith, L.; Golser, R.; Kutschera, W.; Priller, A.; Quinto, F.; Richter, S.; Srncik, M.; Terrasi, P.; Wacker, L.; Wallner, A.; Wallner, G.; Wilcken, K. M.; Wild, E. M. Natural and anthropogenic ^{236}U in environmental samples. Nucl. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2008**, *206*, 2246−2250.

(24) Steier, P.; Dellinger, F.; Forstner, O.; Golser, R.; Knie, K.; Kutschera, W.; Priller, A.; Quinto, F.; Srncik, M.; Terrasi, F.; Vockenhuber, C.; Wallner, A.; Wallner, G.; Wild, E. M. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2010**, *268*, 1045−1049.

(25) Spike Isotopic Reference Material IRMM-085. Geel, Belgium. March 2009.

(26) Bayne C. K. Statistical design of mass spectrometry calibration procedure. ORN/TM-13341, ISPO391 1996.

(27) Becker, J. S.; Dietz, H. J. Application of double-focusing sector field ICP mass spectrometry with shielded torch using different nebulizers for ultratrace and precise isotope analysis of long-lived radionuclides. *J. Anal. At. Sepctrom.* **1999**, *14*, 1493−1500.

(28) Spike Isotopic Reference Mateiral IRMM-057. Geel, Belgium. February 2003.

(29) Hirose, K.; Sugimura, Y. Concentration of uranium and the activity ratio of 234U/238U in surface air: Effect of atmospheric burn-up of cosmos-954. *Pap. Meteorol. Geophys.* **1981**, *32*, 317−322.

(30) Tagami, K.; Uchida, S.; Uchihori, Y.; Ishii, N.; Kitamura, H.; Shirakawa, Y. Specific activity and activity ratios of radionuclides in soil collected about 20 km from the Fukushima Daiichi Nuclear Power Plant: Radionuclide release to the south and southwest. *Sci. Total Environ.* **2011**, *409*, 4885−4888.

(31) Adachi, K.; Kajino, M.; Zaizen, Y.; Igarashi, Y. Emission of spherical cesium-bearing particles from an early stage of the Fukushima nuclear accident. *Sci. Rep.* **2013**, *3* (2554), 1−5.

(32) Yoshida, S.; Muramatsu, Y.; Tagami, K.; Uchida, S.; Ban-nai, T.; Yonehara, H.; Sahoo, S. Concentrations of uranium and $^{235}U/^{238}U$ ratios in soil and plant samples collected around the uranium conversion building in the JCO campus. *J. Environ. Radioact.* **2000**, *50*, 161−172.

(33) Wagenpfeil, F.; Tschiersch, J. Resupension of coarse fuel hot particles in the Chernobyl area. *J. Environ. Radioact.* **2001**, *52*, 5−16.

(34) De Laeter, J. R.; Böhlke, J. K.; De Biévra, P.; Hidaka, H.; Peiser, H. S.; Rosman, K. J. R.; Taylor, P. D. P. Atomic weight of the elements: Review 2000 (IUPAC Technical Report) Pure. *Appl. Chem.* **2003**, *75*, 683−800.

(35) Krivokhatsky, A. S.; Dubasov, Yu. V.; Smirnova, E. A.; Skovorodkin, N. V.; Savonenkov, V. G.; Alexandrov, B. M.; Levedev, E. L. Actinides in the near release from the Chernobyl NPP Accident. *J. Radioanal. Nucl. Chem.* **1991**, *147*, 141−151.

(36) Lujanienė, G.; Valiulis, D.; Byčenkien, S.; Sakalys, J.; Povinec, P. P. Plutonium isotopes and ^{241}Am in the atmosphere of Lithuania: A comparison of different source terms. *Atmos. Environ.* **2012**, *61*, 419−427.

(37) Lujanas, V.; Mastauskas, A.; Lujanienė, G.; Spirkauskaitė, N. Development of radioation in Lithuania. *J. Environ. Radioact.* **1994**, *23*, 249−263.

(38) Pöllänen, R.; Valkama, I.; Toivonen, H. Transport of radioactive particles from the Chernobyl accident. *Atmos. Environ.* **1997**, *31* (21), 3575−3590.

(39) Zhang, Y. S.; Zheng, J.; Yamada, M.; Wu, F. C.; Igarashi, Y.; Hirose, K. Characterization of Pu concentration and its isotopic composition in a reference fallout material. *Sci. Total Environ.* **2010**, *408*, 1139−1144.

(40) Smith, H., Ed. *ICRP (International Commission on Radiological Protection), ICRP Publication 72, Annals of the ICRP*; Elsevier Science Ltd., 1996; Vol. *26*(1).

(41) Tuli, J. K. *Nuclear Wallet Cards (October 2011)*; National Nuclear Data Center. Brookhaven National Laboratory: Upton, NY,2011; pp 11973−5000.

(42) Wellum, R.; Verbruggen, A.; Kessel, R. A new evaluation of the half-life of ^{241}Pu. *J. Anal. At. Spectrom.* **2009**, *24*, 801−807.

(43) Takeyasu, M.; Nakano, M.; Fujita, H.; Nakada, A.; Watanabe, H.; Sumiya, S.; Furuta, S. Results of environmental radiation monitoring at the Nuclear Fuel Cycle Engineering Laboratories, JAEA, following the Fukushima Daiichi Nuclear Power Plant accident. *J. Nucl. Sci. Technol.* **2012**, *49* (3), 281−286.

(44) Smith, H., Ed.; *ICRP (International Commission on Radiological Protection), ICRP Publication 66, Paragraph 170, Annals of the ICRP*; Elsevier Science Ltd., 1994; Vol. *24*(1−3).