Article

Isotopic compositions of 236U and Pu isotopes in "Black Substances" collected from roadsides in Fukushima Prefecture: fallout from the Fukushima Dai-ichi Nuclear Power Plant accident

Aya Sakaguchi, Peter Steier, Yoshio Takahashi, and Masayoshi Yamamoto

Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/es405294s • Publication Date (Web): 06 Mar 2014

Isotopic compositions of ^{236}U and Pu isotopes in "Black Substances" collected from roadsides in Fukushima Prefecture: fallout from the Fukushima Dai-ichi Nuclear Power Plant accident

Aya Sakaguchi[1*], Peter Steier[2], Yoshio Takahashi[1], Masayoshi Yamamoto[3]

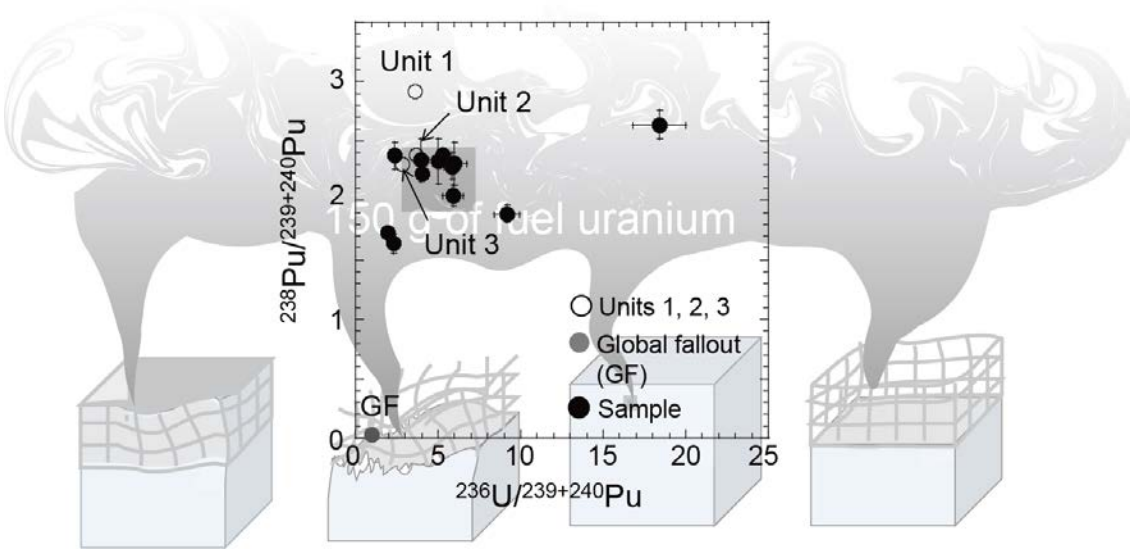
[1]Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8526, Japan

[2]VERA-Laboratory, Faculty of Physics, University of Vienna, Währinger Str. 17, A-1090 Vienna, Austria

[3]Low Level Radioactivity Laboratory, Kanazawa University, Ishikawa 923-1224, Japan

ABSTRACT

Black colored road dusts were collected in high radiation areas in Fukushima Prefecture. Measurement of ^{236}U and Pu isotopes and ^{134,137}Cs in samples was performed in order to confirm whether refractory elements such as U and Pu from the fuel core were discharged, and to ascertain the extent of fractionation between volatile and refractory elements. The concentrations of ^{134,137}Cs in all samples were exceptionally high, ranging from 0.43 to 17.7 MBq/kg, respectively. $^{239+240}$Pu was detected at low levels, ranging from 0.18 to 1.14 Bq/kg and with high ^{238}Pu/$^{239+240}$Pu activity ratios of 1.64 to 2.64. ^{236}U was successfully determined in the range 0.28 to 6.74 x10^{-4} Bq/kg. The observed activity ratios for ^{236}U/$^{239+240}$Pu were in reasonable agreement with those calculated for the fuel core inventories, indicating that trace amounts of U from the fuel cores were released together with Pu isotopes, but without large fractionation. The quantities of U and $^{239+240}$Pu, emitted to the atmosphere were estimated as 2.3x10^{9} Bq (150 g) and 3.9x10^{6} Bq (580 mg), respectively. Regarding U, this is the first report to give a quantitative estimation of the amount discharged. Appreciable fractionation between volatile and refractory radionuclides associated with the dispersal/deposition processes with distance from the Fukushima Dai-ichi Nuclear Power Plant was found.



INTRODUCTION

In the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident, which occurred following the Great East Japan Earthquake of March 11, 2011, large amounts of radionuclides, especially volatile species such as ^{131}I ($T_{1/2}$=8.02 d), ^{134}Cs ($T_{1/2}$=2.06 y) and ^{137}Cs ($T_{1/2}$=30.2 y), were released into the environment mainly from Units 1-3[1] of the plant. A possibility of radionuclide emission from the spent fuel pool of Unit 4, which had been shut down since Nobember 2010, has been discounted due to removal of fuel lods which commenced in November 2013. That is, damage to the spent fuel rods has not been serious and there has been minimal contribution of nuclide emissions from this source. Given this situation, there has been some public concern as to whether U and Pu isotopes in fuel were discharged to the environment, because some mixed U and Pu oxide fuel (MOX fuel) was used in Unit 3, and partial melt-down of the nuclear fuel cores occurred in Units 1-3. Due to the difficulty of measuring U and Pu radionuclides, data on the concentrations and the isotopic composition of U and Pu in the contaminated areas of Fukushima have been limited[2-7]. Zheng et al. (2012, 2013)[5,6] reported isotopic evidence for the release of Pu based on $^{241}Pu/^{239+240}Pu$ activity ratios in surface soil samples collected from the 30 km zone of FDNPP, where values were more than 100 compared with the global fallout value of about 1.2 in March 2011. Yamamoto et al. (2012, 2014)[4,7] also reported $^{238}Pu/^{239+240}Pu$ activity ratios one to two orders of magnitude higher than the global fallout value of ca. 0.03, found in surface soils from surrounding villages and towns. In fact, about a few % to 50% of $^{239+240}Pu$ found in these samples was estimated to have originated from the FDNPP accident, based on the activities and/or atom ratios of Pu isotopes. As for U released from the fuel cores, ^{235}U and ^{238}U

have been measured on soil samples collected around the contaminated areas, but no anomaly for ^{235}U associated with FDNPP fallout was observed because of the presence of a much larger quantity of natural U in soil[2]. Uranium-236 ($T_{1/2}$=2.342×10^7 y) is mainly produced via the nuclear reaction $^{235}U(n,\gamma)$ by thermal neutrons in reactors which use ^{235}U fuel. Unambigous detection of ^{236}U from the FDNPP accident, however, has not yet been achieved. Although Sakaguchi et al. (2012)[3] measured this nuclide in seawater samples, an assessment of the source was not possible. Thus, the characteristics of U and transuranic elements as refractory elements and emitted from the FDNPP have not been fully characterised in the environment, even two years after the accident.

Following the accident, road dust, blackish in color, has attracted the attention of citizens in the Fukushima and Tokyo areas, the dust being given the name "Black Substances". The material is composed of aerosol particles, asphalt and minute tire particles originating from traffic, residue of dried lichens, soil and other fine-grained environmental debris. The dust, which is blown by wind and rain into street corners and dips in the road, contains extremely high levels of radionuclides. Since there is less of a contribution of natural U and global fallout Pu in the matrix of these samples because of a reduced contribution of soil-derived materials, analysis of the road dust would seem appropriate for gaining new information on the isotopic compositions of U and transuranic elements released from the FDNPP.

In this paper, we report the concentration and isotopic compositions of ^{236}U and Pu isotopes (half-lives: ^{238}Pu 87.74 y; ^{239}Pu 2.411×10^4 y; ^{240}Pu 6.563×10^3 y), and $^{134,137}Cs$, in Black Substances from roadsides which are heavily contaminated by fallout from the FDNPP accident. The aims of research are (1) to gain new knowledge on the levels and isotopic compositions of the radionuclides released, (2) to compare values with those of nuclear fuel cores and further (3) to evaluate the fractionation effects between the volatile and refractory radionuclides which were released into the environment. Some focus is given to the measurement of ^{236}U to clarify whether U was released from the fuel cores. The present study serves as an aid not only to predict the fate of U and Pu in the environment but also to estimate, accurately and precisely, their inventories in the cores of the reactors.

MATERIAL AND METHODS

Sampling of road dust: "Black Substances"

The road dust samples were mainly collected from Minami-soma City and Namie Town from May to September, 2012 (Table 1 and Fig. 1). These regions were seriously contaminated by discharge of the radioactive plume due to the venting operations, hydrogen gas detonations and

breaches of the containment vessel on March 12-15, 2011, followed by scavenging of the nuclides in the atmosphere by precipitation in the form of rain and snow. The sampling points were located in the evacuation zone and show a relatively high radiation dose (>19 μSv/h) even one year after the accident[9]. The collected substances were air-dried, and sieved through a 2-mm mesh to remove pebbles and plant debris, then pulverized in an agate-mortar for a few hours to obtain homogeneous samples. The homogeneity of sample has been confirmed in previous papers[7,10].

Measurement of radionuclides

^{137}Cs and Pu isotope

Each sample (2-5g) was first packed into a plastic vessel of diameter 4 cm and height of 2 cm. Then, ^{134}Cs and ^{137}Cs were determined by γ-ray spectrometry using a Ge-detector (Princeton Gamma Tech, relative efficiency 40%) with measurement times of 600-1200 sec for each sample. The spectrometer was calibrated with a standard of the New Brunswick Laboratory (NBL) reference sample No. 42-1 (4.04% uranium), analytical grade KCl and a standard γ-ray reference sample for nuclides including ^{137}Cs from the JRIA (Japan Radioisotope Association). In addition, the ^{134}Cs concentration was corrected for cascade summing. The detection efficiency for ^{137}Cs (662 keV) was 5%, and the detection limit was 4.20 Bq for a 600 s measurement.

After γ-ray spectrometric analysis, plutonium analysis was carried out radiochemically[9, 10]. In brief, an aliquot of 30-50 g of the sample was calcinated at about 450°C overnight and Pu was leached twice with 250 ml of concentrated HNO_3 with a small amount of H_2O_2 on a hot plate, with the addition of a known amount of ^{242}Pu as a yield tracer. Plutonium was then separated from the main matrix and purified carefully by passing through an anion exchange resin column (diameter 1 cm x 10 cm height; Dowex 1-X8, 100-200 mesh). The purified Pu was electroplated onto a polished stainless steel disc, and activities (^{238}Pu, $^{239+240}$Pu and ^{242}Pu) were measured by α- spectrometry. As the α-particle energies of ^{239}Pu and ^{240}Pu are nearly the same, these nuclides could not be differentiated. Their activities were, therefore, presented as the sum ($^{239+240}$Pu) of ^{239}Pu and ^{240}Pu. The detection limit for Pu was 4.82×10^{-5} Bq for a 1 week measurement.

U isotope measurements

A portion (3-5 g) of the sample was decomposed with concentrated $HF+HNO_3+HClO_4$ (10 ml

soln. per 1 g sample) for 12 hours on a hot plate (150°C) with continual agitation. The total amount of solution leached was weighed and an aliquot was sub-sampled for determination by ICP-MS, of the total amount of ^{238}U leached. The remaining solution was used to determine the $^{236}U/^{238}U$ atom ratio by accelerator mass spectrometry (AMS).

Purification of U was conducted as described by Sakaguchi et al. (2009, 2010) [13,14]. For measurement of $^{236}U/^{238}U$ with AMS, the cathode was prepared as U oxides in a Fe_2O_3 matrix. Details of the measurements of ^{236}U with AMS are described in Steier et al. (2010) [15] and Sakaguchi et al. (2010)[14]. The detection limit is about 10^4 atoms of ^{236}U. ^{238}U was measured using ICP-MS (Agilent 7700) after appropriate dilution with 2% HNO_3. In this case, indium was used as an internal standard.

RESULTS AND DISCUSSION

Radionuclide composition of Black Substances

The results of the Cs, U and Pu isotope measurements are shown in Tables 2 and 3. The concentrations of ^{134}Cs and ^{137}Cs in all samples were exceptionally high, ranging from 0.43 to11.4 MBq/kg and 0.58 to 17.7 MBq/kg, respectively. These concentrations are two to three orders of magnitude higher than those of surface soil collected from the areas within the 20 km exclusion zone. These extremely high concentrations of radio Cs reflect a relative absence of soil matrix components and the fact that the sampling area where is heavily contaminated with radio Cs even at distance well removed from the FDNPP. Yoshida and Takahashi (2012)[16] have reviewed the reasons why a high radiation area exists far removed from FDNPP, and it is mainly due to the emission of highly radioactive plume combined with wet deposition associated with rain on the 15th of March. The $^{134}Cs/^{137}Cs$ activity ratios covered a narrow range of 0.60 to 0.76, depending mainly on the sampling date, and these values approached 1 when they were decay-corrected to the date on 11 March 2011 as reported in METI (2011) and other papers[1,4,7,10,17,18.] .

$^{239+240}Pu$ was detected at low levels in all the samples examined, ranging from 0.18 to 1.14 Bq/kg with $^{238}Pu/^{239+240}Pu$ activity ratios of 1.64 to 2.64. However, the concentrations of $^{239+240}Pu$ are higher than those of global fallout observed in Fukushima. Actually, the typical concentration of global fallout $^{239+240}Pu$ in surface soil of Fukushima[4,7], the samples being obtained from undisturbed and non-forested open flat land, is one to two orders of magnitude lower than other areas in Japan (about 1 Bq/kg)[11,14,19].

The ^{238}Pu activity concentrations in the Black Substances are well correlated with that of

$^{239+240}$Pu (R=0.99), and their correlation slope, that is the ratio, is two orders of magnitude higher than the global fallout value of 0.03. These values agree well with those (2.0±0.5) identified in several surface soil samples taken within the FDNPP site[20] and those calculated for the cores of Units 1-3 by the Japan Atomic Energy Agency (2.30-2.92)[21]. Cleary, it is very important to point out that almost all Pu in the black dust samples was originats from the FDNPP accident.

^{236}U was successfully measured in the range of (0.28 to 6.74) $\times 10^{-4}$ Bq/kg. The ^{236}U/^{238}U atom ratios were in the range of (0.25 to 2.60) $\times 10^{-7}$. For spent nuclear fuel, ratios above 10^{-3} are typical. The uranium in Black Substances was obviously diluted with natural ^{238}U in the environment. The atom ratios are comparable with those in soil samples collected from Mogilev, located more than 200 km north of the Chernobyl Nuclear Power Plant[22]. But the usefulness of this comparison is limited because of the difference in the ^{238}U content of soil and Black Substances. The observed ratios are clearly one to two orders of magnitude higher than those of global fallout values found in surface soil in Japan[13,14]. The activity ratios of ^{236}U/$^{239+240}$Pu were in the range of (1.96 to 18.4) x10^{-4} with a weighted mean value of 7.87x10^{-4}. This average value is about 7 times higher than that for the global fallout value for Japan[13,14].

Figure 2 shows a correlation of the concentration of the fuel burning products ^{238}Pu and ^{236}U in Black Substances. The concentrations of ^{238}Pu and ^{236}U are linearly well correlated. This implies that the deposited nuclides were well homogenized in the transportation process, or there is mainly one or two sources. Figure 3 shows the relationship between the ^{238}Pu/$^{239+240}$Pu and the ^{236}U/$^{239+240}$Pu activity ratios. The global fallout value is also plotted on this figure. Sample no. 1, which was collected from close to the FDNPP (3.43 km), is far from the other samples. The grey rectangle in Fig. 3 gives the one sigma (standard deviation) area of ^{238}Pu/$^{239+240}$Pu and ^{236}U/$^{239+240}$Pu (except for sample no. 1). By taking into consideration fact that the Pu in these samples was predominantly derived from the FDNPP, the ratios seem to represent the ratios for ^{236}U and ^{238}Pu released into the environment as a results of nuclear accident. The JAEA [21] reported core inventories for each radionuclide calculated mainly by using the ORIGEN2 code. By referring to those data, the ^{236}U/$^{239+240}$Pu activity ratios observed in Black Substances show a relatively good correlation with the estimated core ratios: 3.63 x10^{-4}, 3.66 x10^{-4} and 2.84x10^{-4} (activity ratio) in Units 1, 2 and 3, respectively (Fig. 3). If we pay attention to the details, the isotopic composition of U and Pu can be explained by mixing of core materials and global fallout for nos. 9, 10 and 11. The extra sources which has (1) high ^{238}Pu/$^{239+240}$Pu and high ^{236}U/$^{239+240}$Pu ratios and/or (2) low ^{238}Pu/$^{239+240}$Pu ratio but high ^{236}U/$^{239+240}$Pu ratio such as a low reprocessing fuel with low or no burn up, can be predicted

from this graph (broken lines 1 and 2). However, confirmation of this hypothesis has not been found in this study. In any case, it is reasonable to conclude that trace amounts of uranium from the fuel core was released into the environment together with Pu isotopes without large fractionation.

Calculation of the amount of Pu and U released

Using the averaged $^{137}Cs/^{239+240}Pu$ activity ratio observed in this study and the amount of ^{137}Cs released to the atmosphere ($1.5x10^{16}$ Bq)[1], the amount of $^{239+240}Pu$ released can be estimated as $2.3x10^{9}$ Bq. This value is smaller than that estimated by METI ($6.4x10^{9}$ Bq)[1]. The amount of $^{239+240}Pu$ dispersed to the atmosphere is $3.8x10^{-5}$% of the total amount in the cores of reactors 1-3[21]. In fact, this equates to about 590 mg of total plutonium (^{238}Pu, ^{239}Pu, ^{240}Pu). Our estimated values for the amount of $^{239+240}Pu$ released from the core and the ratio of the released $^{239+240}Pu$ to the total amount in the core are close to the range of calculated values (1.0 to $2.4x10^{9}$ Bq and 1.2 to $2.9x10^{-5}$%) by Zheng et al. (2013)[6], respectively.

In the same way, the amount of ^{236}U released as a result of the accident was estimated using the observed $^{236}U/^{239+240}Pu$ and $^{236}U/^{137}Cs$ activity ratio. The amount of ^{236}U released to the atmosphere was about $1.2x10^{6}$ Bq. This is about $6.1x10^{-5}$% of the ^{236}U inventories in cores 1-3 ($2.0x10^{12}$ Bq)[21]. This release ratio possibly applies also to the other uranium isotopes such as ^{234}U, ^{235}U and ^{238}U. From the uranium inventories in the cores 1-3[21], the total amount of uranium isotopes, ^{234}U, ^{235}U, ^{236}U and ^{238}U, dispersed in the atmosphere has been estimated to be about $3.9x10^{6}$ Bq. This equates to about 150 g of total uranium, which is four to five orders of magnitude smaller than that of Chernobyl[23-26]. In the FDNPP, the enrichment ratio of ^{235}U is about 1.7 to 1.9% for each reactor, and is obviously different from that of natural ^{235}U (0.72%). However, relatively high concentrations of natural uranium in Japanese soil (about 1-3 ppm) prevent identification of the ^{235}U fingerprint of uranium contamination from the FDNPP especially for the granitoid area in Fukushima. In this situation, ^{236}U is very appropriate for demonstrating anthropogenic uranium contamination in the surface environment. Summary for the calculation of the amount of Pu and U released is shown in Table 5.

Estimation of fractionation factor between refractory and volatile elements

It is of interest to evaluate the fractionation factor between refractory (R) and volatile (V) elements. The R/V factor is often used to predict the fate of radionuclides in the environment[26] and is an essential parameter to estimate radionuclide dispersion as a result of the venting operations, hydrogen detonations and breaches in containment. Here, three categories of R/V

factors were calculated based on the results for ^{137}Cs, $^{239+240}$Pu, ^{238}Pu and ^{236}U concentrations. The R/V factor are defined as:

R_{Pu}/V factor = (Measured ($^{239+240}$Pu/^{137}Cs) in the environmental sample)/(inventory ratio of ($^{239+240}$Pu/^{137}Cs) in the reactor)

R_{Pu8}/V factor = (Measured (^{238}Pu/^{137}Cs) in the environmental sample)/(inventory ratio of (^{238}Pu/^{137}Cs) in the reactor)

R_U/V factor = (Measured (^{236}U/^{137}Cs) in the environmental sample)/(inventory ratio of (^{236}U/^{137}Cs) in the reactor)

$^{239+240}$Pu/^{137}Cs (Bq/Bq), ^{238}Pu/^{137}Cs (Bq/Bq) and ^{236}U/^{137}Cs (Bq/Bq) in the core of Units 1, 2 and 3 were estimated using the calculation of Nishihara et al. (2012) [21] (Table 4). From the averages of these calculated values ($^{239+240}$Pu/^{137}Cs=8.54x10^{-3}, ^{238}Pu/^{137}Cs=2.12x10^{-2} and ^{236}U/^{137}Cs=2.78 x10^{-6}) and our measured data for each sample, the R/V factors were estimated to be nearly the same and in the range of (0.33 to 4.49) x10^{-5} for R_{Pu}/V, (0.18 to 1.76) x10^{-5} for R_{Pu8}/V and (0.38 to 8.21) x10^{-5} for R_U/V. These R/V values are of the same order of magnitude as data based on $^{239+240}$Pu/^{137}Cs found for surface soil/water samples contaminated with Pu derived from the FDNPP[3,4,7]. These R_{Pu}/V, R_{Pu8}/V and R_U/V values are clearly small, confirming that a much larger amount of volatile nuclides such as Cs and I have been dispersed and introduced into the surface environment compared to refractory elements such as U and Pu.

Surprisingly, the R/V factors, especially for samples with U and Pu isotopic compositions inside the gray rectangle in Fig. 3, increased with distance from the FDNPP (Fig. 4). This behavior was unexpected, since the refractory elements in Chernobyl were emitted as larger particles, and consequently should have been deposited more quickly than the volatile elements, which were emitted as gases and which accumulated on ambient aerosol particles with a typical size of 0.1 to 1 μm (accumulation or droplet mode[27]). Here in our results, different fractionation mechanism may operate to induce a preferential deposition of refractory elements at distances further from the FDNPP. However, the gradient of the regression curve for R_{Pu8}/V is different from that of R_{Pu}(R_U)/V. For two isotopes of the same element, ^{238}Pu and $^{239+240}$Pu, fractionation in the deposition process is no valid explanation. In addition as shown in Fig. 2, fractionation between ^{236}U and ^{238}Pu with the distance from the FDNPP is also not evident. Thus, it is expected that the increase of this R/V factor with distance is governed by a different source.

However, from these preliminary results it would be premature to draw firm conclusions on the relationships observed in Fig. 4. Inclusion of more sampling sites, a higher

time-resolution for the release history, different behaviors of the radionuclides after deposition and precipitation data could easily change the picture. In fact, no clear correlation between R/V factors, or with distance or precipitation has been found for a much larger data set for $^{239+240}Pu/^{137}Cs$ in about 150 environmental samples including surface soil and Black Substance[7,10].

.

AUTHOR INFORMATION

Corresponding author

*Tel: +81-82-424-7463, Fax: +81-424-0735, E-mail: ayaskgc@hiroshima-u.ac.jp

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the City Councilor in Minami-Souma, Mr. K. Oyama and research staff of the Low Level Radioactivity Laboratory, Kanazawa University, for their valuable help with the sampling. This work was supported by the distribution mapping project and a Grant-in-Aid for Scientific Research No.24110008 (Yamamoto 2012-2016) from the Ministry of Education, Culture, Sports, Science and Technology, MEXT, Japan.

REFERENCES

(1) Ministry of Economy, Trade and Industry, Data on the amount of released radioactive materials, 2011. http://www.meti.go.jp/press/2011/10/20111020001/20111 020001.pdf (accessed October 7, 2013, in Japanese).

(2) Takagai, 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. *Bunseki Kagaku.* **2011**, *12*, 947-957.(in Japanese)

(3) Sakaguchi, A.; Kadokura, A.; Steier, P.; Tanaka, K.; Takahashi, Y.; Chiga, H.; Matsushima, A.; Nakashima, S.; Onda, Y. Isotopic determination of U, Pu and Cs in environmental

waters following the Fukushima Daiichi Nuclear Power Plant accident, *Geochem. J.* **2012**, *46*, 355-360.

(4) Yamamoto, M.; Takada, T.; Nagao, S.; Koike, T.; Shimada, K.; Hoshi, M.; Zhumadiov, K.; Shima, T.; Fukuoka, M.; Imanaka, T.; Endo, S.; Sakaguchi, A.; Kimura, S. Early survey of radioactive contamination in soil due to the Fukushima Dai-ichi Nuclear Power Plant accident: with emphasis on Pu analysis, *Geochem. J.* **2012**, *46*, 341-353.

(5) Zheng, J.; Tagami, K.; Watanabe, S.; Uchida, S.; Aono, T.; Ishii, N.; Yoshida, S.; Kubota, Y.; Fuma, S.; Ihara, S. Isotopic evidence of plutonium release into the environment from the Fukushima DNPP accident. *Sci. Rep*. **2012**. *2*, doi:10.1038/srep00304.

(6) 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.

(7) Yamamoto, M.; Sakaguchi, A.; Ochiai, S.; Takada, T.; Hamataka, K.; Murakami, T.; Nagao, S.; Isotopic Pu, Am and Cm signatures in environmental samples contaminated by the Fukushima Dai-ichi Nuclear Power Plant accident. *J. Environ. Radioact.* (available online)

(8) Ministry of Education, Culture, Sports, Science and Technology, 2012, Mapping of radiatio Cs by MEXT (revised in 12/Aug/2012) http://radioactivity.nsr.go.jp/ja/contents/6000/5043/24/11555_0830.pdf (accessed3/Feb./2014, in Japanese)

(9) Ministry of Education, Culture, Sports, Science and Technology, 2012, Mapping of radiation dose by MEXT (revised in 12/Aug/2012), http://radioactivity.nsr.go.jp/ja/contents/6000/5045/24/5600_081218.pdf. (in Japanese)

(10) Yamamoto, M.; Sakaguchi, A.; Ochiai, Imanaka, T. Isotopic compositions of transuranic nuclides released by the Fukushima Dai-ichi Nuclear Power Plant accident: with emphasis on Cm isotopes. *J. Radioanal. Nucl. Chem.* (in press.)

(11) Yamamoto, M.; Komura, K.; Sakanoue, M. ^{241}Am and plutonium in Japanese rice-field surface soils. *J. Radiat. Res.* **1983**, *24*, 237–249.

(12) Yamamoto, M.; Tomita, J.; Sakaguchi, A.; Imanaka, T.; Fukutani, S.; Endo, S.; Tanaka, K.; Hoshi, M.; Gusev, B. I.; Apsalikov, A. N. Spatial distribution of soil contamination by ^{137}Cs and $^{239+240}$Pu in the village of Dolon near the Semipalatinsk Nuclear Test Site: New information of traces of the radioactive plume from the 29 August 1949 nuclear test. *Health Phys.* **2008**. *94*, 328–337.

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

(14) Sakaguchi, A.; Kawai, K.; Steier, P.; Imanaka, T.; Hoshi, M.; Endo, S.;, Zhumadilov, K.; Yamamoto, M. Feasibility of using ^{236}U to reconstruct close-in fallout deposition from the Hiroshima Atomic Bomb. *Sci. Total Environ.* **2010,** *408*, 5392-5398.

(15) Steier, P.; Dellinger, F.; Forstner, O.; Golser, R.; Knie, K.; Kutschera, W.; Priller, A.; Quinto, F.; Srncik, M.; Terras,i F.; Vockenhuber, C.; Wallner, A.; Wallner, G.; Wild, E.M. Analysis and application of heavy isotopes in the environment. *Nucl. Instr. Meth. Phys. Res. B.* **2010**, *268*, 1045-1049.

(16) Yoshida, N.; Takahashi, Y., 2012. Land-surface contamination by radionuclides from the Fukushima Dai-ichi Nuclear Power Plant accident. *Elements* **2010**, 8, 201-206.

(17) Kato, H.; Onda, Y.; Teramage, M. Depth Distribution of ^{137}Cs, ^{134}Cs, and ^{131}I in Soil Profile after Fukushima Daiichi 1 Nuclear Power Plant Accident. *J. Environ. Radioact.* **2012**, 110, 59-64.

(18) Endo, S.; Kimura, S.; Takatsuji, K.; Nanasawa, K.; Imanaka, T.; Shizuma, K. Measurement of soil contamination by radionuclides due to the Fukushima Dai-ichi Nuclear Power Plant accident and associated estimated cumulative external dose estimation. J *J. Environ. Radioact.* **2012**, 111, 18-27.

(19) Ohtsuka, Y.; Iyogi, T.; Kakiuchi, H.; Takaku, Y.; Hisamatsu, S.; Inaba, J., Evaluation of $^{239+240}Pu$, ^{137}Cs and natural ^{210}Pb fallout in agricultural upland fields in Rokkasho, Japan, *J. Radioanal. Nucl. Chem.* **2004**, *261*,625-630.

(20) Tokyo Electric Power Company (TEPCO) (2011) Result on radionuclides measured in soil within the site of Fukushima Dai-ichi nuclear power plant, Press Release March 28, 2011. http://www.tepco.co.jp/en/press/corp-com/release/11032812-e.html.

(21) Nishihara, K.; Iwamoto, H.; Suyama, K. Estimation of Fuel Compositions in Fukushima-Daiichi Nuclear Power Plant, JAEA-Data/Code 2012-018. 2012.

(22) Boulyga, S. F.; Heumann, K. G. Determination of extremely low $^{236}U/^{238}U$ isotope ratios in environmental samples by sector-field inductively coupled plasma mass spectrometry using high-efficiency sample introduction. *J. Environ. Radioact.* **2006**, 88, 1-10.

(23) Boulyga S. F.; Becker J. S. Determination of uranium isotopic composition and ^{236}U content of soil samples and hot particles using inductively coupled plasma mass spectrometry. *Fresenius J. Ana.l Chem.* **2001**, *370*, 612–617.

(24) Imanaka, T. Current Topics about the Radiological Consequences by the Chernobyl Accident, Recent research activities about the Chernobyl NPP accident in Belarus, Ukrain and Russia. KURRI KR-139, **2002**, 1-10. (http://www.rri.kyoto-u.ac.jp/NSRG/reports/kr79/KURRI-KR-79.htm)

(25) Imanaka, T. What happened at that time? Many-sided Approach to the Realities of the Chernobyl NPP Accident- Summing-up of the Consequences of the Accident Twenty Years After (II), KURRI KR-139, **2008**, 1-19. (http://www.rri.kyoto-u.ac.jp/NSRG/reports/kr139/KURRI-KR-139.htm)

(26) Izrael, Y.A. Radioactive Fallout after Nuclear Explosions and Accidents, Radioactivity in the environment vol. 3, Series editor: Baxter, M.S., 2002, pp. 165. Elsevier.

(27) Seinfeld, J. H.; Pandis, S. N. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Second Edition, John Wiley and Sons, NY, USA. 2006.

(28) Radke, L.; Hobbs, P.; Eltgroth, M.W. Scavenging of aerosol particles by precipitation. *J. Appl. Meteol.* **1980,** *19*, 715-722.

375

376

Table 1 Sampling locations of soil samples (Black Substances) including dust etc. collected mainly from the roadside

Sample No.	Lab.ID	Sampling date	Position (GPS data) N	E	distance from FDNPP (km)	Location	Remarks
1	12N-7	22-Sep-12	37°27'12.8"	141° 00'40.6"	3.43	Futaba	Side of the parking area at Futabakousei hospital
2	12N-17	22-Sep-12	37°28'02.4"	140° 55'51.0"	10.2	Namie	Roadsides (Route 253) in front of Matsunaga pottery
3	12N-23	22-Sep-12	37°28'14.6"	140° 55'59.2"	10.19	Namie	Space under the eaves of Yasuragi nursing home
4	12N-30	22-Sep-12	37°30'25.8"	140° 55'32.6"	13.11	Namie	Rooftop of a concrete house in Murohara (Route 114)
5	12R-7	23-Apr-12	37°32'59.6"	140° 56' 04.3"	16.16	Minami-soma	Side of a road near Odaka-chiku (Kanaya)
6	KURO-3	27-Mar-12	37°35'59.5"	140° 56' 21.5"	21.07	Minami-soma	Vicinity of the bsrvation deck of Yokokawa-dammu
7	12R-3	12-May-12	37°35'59.0"	140° 56'21.0"	21.07	Minami-soma	Vicinity of the bsrvation deck of Yokokawa-dammu
8	12K-12	5-Sep-12	37°33'23.0"	140° 52'27.7"	21.3	Minami-soma	Vicinity of the restricted area in Tetsuzan-dammu
9	12N-40	22-Sep-12	37°32'27.2"	140° 51'46.4"	19.74	Namie	Roadsides (Route 49) near Haranami tunnel
10	12N-37	22-Sep-12	37°34'00.6"	140° 47'55.6"	26.01	Namie	Rear U-shaped drainageway at the milk consolidating station in Tsushima (Route 114)
11	12K-18	6-Sep-12	37°33'34.0"	140° 45'39.9"	27.96	Namie	Roadsides (Route 114) before the checkpoint from Tsushima to Namie
12	12T-20	26-Mar-12	37°38'58.7"	140° 45'20.4"	34.59	Iidate	Roadsides near Yamabe hall

377

378

379

Table 2 The isotopic composition of Cs, U and Pu in Black Substances

Sample No.	Lab. code	Cs-134* (kBq/kg)	Cs-137* (kBq/kg)	U-238 (ppm)	U-236 (10^{-4} Bq/kg)	Pu-239+240 (Bq/kg)	Pu-238 (Bq/kg)
1	12N7	1408 ± 5	2337 ± 5	0.880 ± 0.004	5.21 ± 0.27	0.284 ± 0.019	0.749 ± 0.034
2	12N17	3276 ± 11	5021 ± 13	0.570 ± 0.003	1.43 ± 0.07	0.239 ± 0.026	0.552 ± 0.044
3	12N23	11410 ± 38	17670 ± 43	0.390 ± 0.009	2.40 ± 0.11	0.482 ± 0.026	1.122 ± 0.051
4	12N30	1434 ± 4	2150 ± 4	0.380 ± 0.004	1.04 ± 0.05	0.180 ± 0.012	0.411 ± 0.019
5	12R-7	2103 ± 8	2957 ± 8	0.670 ± 0.018	2.51 ± 0.16	0.273 ± 0.013	0.516 ± 0.019
6	KURO-3	4361 ± 9	5706 ± 9	1.35 ± 0.02	6.74 ± 0.57	1.14 ± 0.069	2.333 ± 0.102
7	12R-3	1809 ± 7	2492 ± 7	0.650 ± 0.013	2.83 ± 0.07	0.703 ± 0.019	1.571 ± 0.032
8	12K12	1593 ± 5	2318 ± 5	0.630 ± 0.009	2.21 ± 0.07	0.420 ± 0.015	1.001 ± 0.027
9	12N40	3282 ± 9	5053 ± 10	0.620 ± 0.004	1.56 ± 0.12	0.663 ± 0.036	1.576 ± 0.071
10	12N37	636 ± 2	947 ± 2	0.330 ± 0.001	0.45 ± 0.02	0.196 ± 0.012	0.321 ± 0.016
11	12K18	1834 ± 5	2697 ± 6	0.480 ± 0.001	0.28 ± 0.01	0.145 ± 0.005	0.252 ± 0.011
12	12T20	426 ± 3	582 ± 1	0.470 ± 0.007	0.87 ± 0.05	0.218 ± 0.021	0.508 ± 0.024

* The values are decay-corrected to the date of sampling
Error shows one sigma standard deviation from counting statistics

380

381

382

Table 3 The isotopic ratios use for Cs, U and Pu in Black Substances.

Sample No.	Lab. code	U-236/U-238 (10^{-7} atom ratio)	Pu-238/Pu-239+240 (activity ratio)	Pu-239+240/Cs-137 (10^{-8} activity ratio)	U-236/Cs-137 (10^{-11} activity ratio)	U-236/Pu-239+240 (10^{-4} activity ratio)
1	12N7	2.50 ± 0.13	2.64 ± 0.19	12.1 ± 0.81	22.3 ± 1.2	18.4 ± 1.6
2	12N17	1.06 ± 0.05	2.31 ± 0.27	4.75 ± 0.52	2.85 ± 0.14	5.99 ± 0.72
3	12N23	2.60 ± 0.10	2.33 ± 0.13	2.73 ± 0.15	1.36 ± 0.06	4.98 ± 0.35
4	12N30	1.16 ± 0.05	2.28 ± 0.16	8.36 ± 0.54	4.84 ± 0.23	5.81 ± 0.46
5	12R-7	1.58 ± 0.09	1.89 ± 0.11	9.24 ± 0.45	8.49 ± 0.54	9.17 ± 0.74
6	KURO-3	2.11 ± 0.17	2.04 ± 0.15	20.0 ± 1.22	11.8 ± 1.0	5.90 ± 0.61
7	12R-3	1.84 ± 0.02	2.23 ± 0.06	28.2 ± 0.76	11.4 ± 0.3	4.03 ± 0.14
8	12K12	1.48 ± 0.04	2.38 ± 0.09	18.1 ± 0.65	9.53 ± 0.30	5.26 ± 0.25
9	12N40	1.06 ± 0.08	2.38 ± 0.11	13.1 ± 0.71	3.09 ± 0.24	2.35 ± 0.22
10	12N37	0.57 ± 0.03	1.64 ± 0.11	20.7 ± 1.28	4.75 ± 0.21	2.27 ± 0.17
11	12K18	0.25 ± 0.01	1.73 ± 0.09	5.38 ± 0.19	1.04 ± 0.04	1.96 ± 0.10
12	12T20	0.78 ± 0.05	2.33 ± 0.14	37.4 ± 3.59	15.0 ± 0.9	3.98 ± 0.45

383

384

385

386

Table 4 The estimated core composition of Unit 1, 2 and 3 (Nishihara et al., 2013).

Unit No.	Pu-239+240/Cs-137 (10^{-3} activity ratio)	Pu-238/Cs-137 (10^{-2} activity ratio)	U-236/Cs-137 (10^{-6} activity ratio)
1	7.86	2.29	2.87
2	7.54	1.79	2.59
3	9.96	2.29	2.71
Average	8.45	2.12	2.72

387

388

389

390

391

392

393

Table 5 Summary of emission of Cs-137, Pu-239+240, U-236 and total U from FDNPP.

	Fuel composition (Bq)	Release to the atmosphere (Bq)	Release ratio (%)
Cs-137	7.0×10^{17}	1.5×10^{16}	2.10
Pu-239+240	5.9×10^{15}	2.3×10^{9}	3.9×10^{-5}
U-236	2.0×10^{12}	1.2×10^{6}	6.1×10^{-5}
Total U	6.4×10^{12}	3.9×10^{6} (150 g)	

394

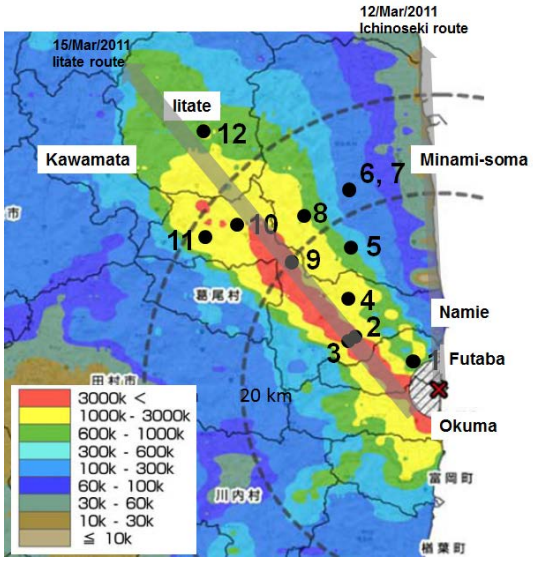
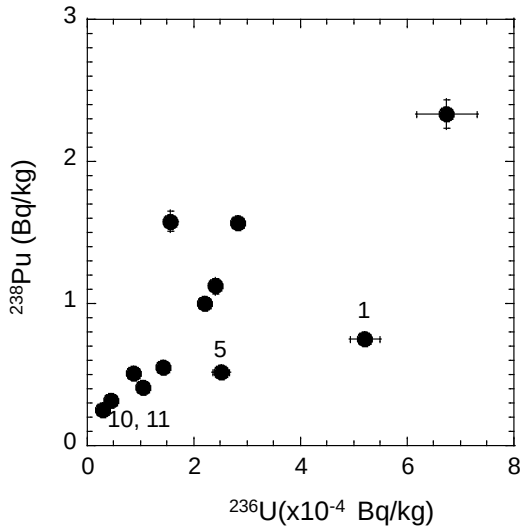


Fig. 1 Sampling sites of Black Substances in Fukushima Prefecture and inventory of Cs-137 (Bq/m^2)[8].

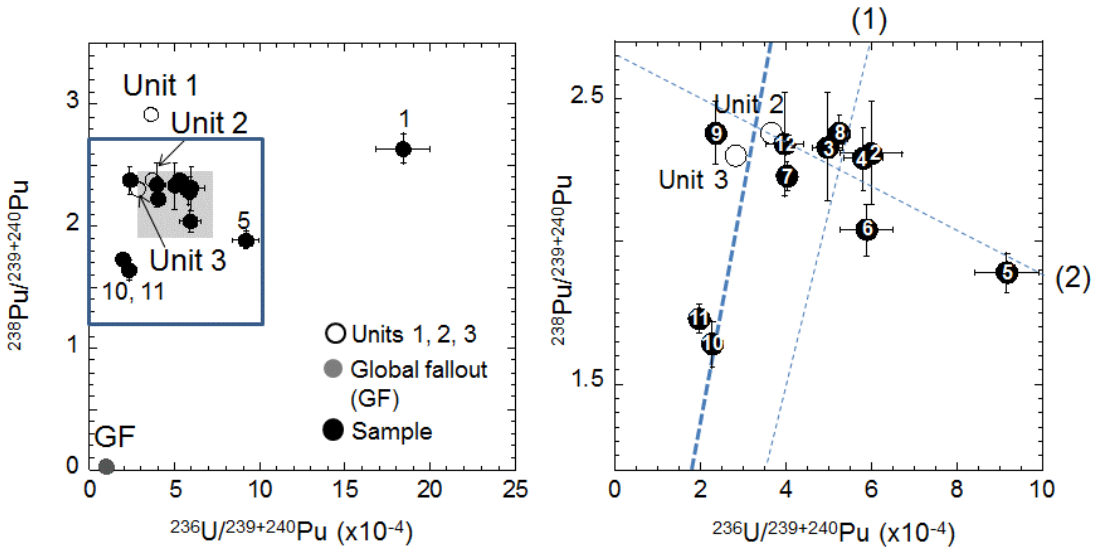
403

404



405 Fig. 2. Comparison between ^{238}Pu (Bq/kg) and ^{236}U (10^{-4} Bq/kg) in Black Substances.

406

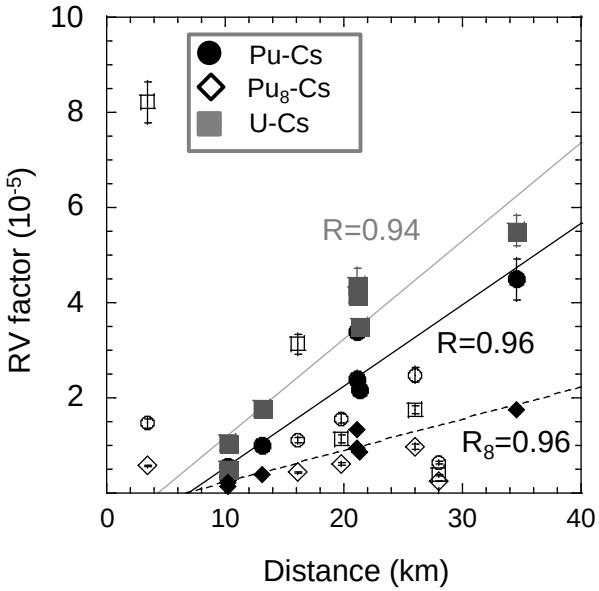


407

408 Fig. 3 Relationship between $^{238}Pu/^{239+240}Pu$ and $^{236}U/^{239+240}Pu$ activity ratios obtained from Black
409 Substances together with the isotopic composition of global fallout in Japan and the cores in
410 each Unit (Units 1-3) of FDNPP. Grey square represent the area of one sigma (standard
411 deviation) of $^{238}Pu/^{239+240}Pu$ and $^{236}U/^{239+240}Pu$ values which were calculated excluding sample no.
412 1. Right graph is close-up of open square in the left graph.

413

414



415

416 Fig. 4 Relationships of R_{Pu}/V, R_{Pu8}/V and R_U/V factors with distance from FDNPP to sampling
417 site (km). The solid symbols represent samples which are plotted in the grey square in Fig. 3.
418 The open symbols show other samples in Fig. 3.

419

420