The situation of Ag and Pu radioisotopes in soil released from Fukushima Daiichi nuclear power plants

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The situation of Ag and Pu radioisotopes in soil released from Fukushima Daiichi nuclear power plants

H. Kimura[1], M. Uesugi[2], A. Muneda[3], R. Watanabe[1], A. Yokoyama[2], T. Nakanishi[4]

[1]Grad. School Nat. Sci. Tech., Kanazawa Univ., [2] Inst. Sci. Eng., Kanazawa Univ., [3]Col. Sci. Eng., Kanazawa Univ., [4]Adv. Sci. Res. Cent., Kanazawa Univ.

Corresponding author's e-mail address: yokoyama@se.kanazawa-u.ac.jp

1. Abstract

Massive radionuclides were released into the environment due to the Fukushima Daiichi nuclear power plant (FDNPP) accident in March 2011. The concentrations of Pu and ^{110m}Ag in a soil sample that was collected in Futaba-cho located at 4km north-west of FDNPP were measured by α-spectrometry and γ-spectrometry, respectively. The analytical result suggests that Pu isotopes are deposited in the soil as particles with high radioactivity (hot particles), although the ^{110m}Ag isotope is deposited uniformly like as Cs isotopes in a soil sample.

Keywords

Pu, ^{110m}Ag, hot particle, soil, Fukusima Daiichi, α-ray spectrometry

2. Introduction

Massive radionuclides were released into the environment due to the Fukushima Daiichi nuclear power plant (FDNPP) accident in March 2011. They were mainly volatile fission products such as ^{137}Cs, ^{134}Cs, ^{132}I and ^{131}I, but non-volatile radionuclides such as Pu and Ag isotopes were also emitted to a minor extent. The behavior of these released radionuclides changes in response to their chemical forms in the processes such as emission, diffusion, and deposition.

The volatile fission products were found to be distributed in Fukushima and its adjacent prefectures [1]. On the other hand, the non-volatile radionuclides such as Ag and Pu isotopes were distributed in high pollution area including FDNPP [2,3]. It was quite unlikely for them to disperse into the atmosphere like volatile nuclides because the non-volatile nuclides have high boiling points. These non-volatile nuclides would disperse with particles not through vaporization process.

The existence of such hot particles causes the radioactivity concentrations in soils to vary over a wide range, even if the samples are collected in one place [1]. Therefore, in this work, we focused the radioactive Cs, Ag and Pu, and decided to research for the dispersion behavior of Pu isotopes and ^{110m}Ag. Besides, we examined their chemical properties by dissolution experiments using with several kind of leaching solutions.

3. Sample

The following two samples were collected and prepared for the present work. Details of the samples are found elsewhere [4].

Soil 1 :

This soil sample was collected in Futaba-cho located at 4km north-west of FDNPP. Firstly, the sample was agitated by hand hundred times and dried at 105℃ overnight in a drying tumbler. Then it was crushed in a mortar and passed through a 2mm sieve. It was heated at 450℃ for 4 hours to decompose the organics in the soil sample.

Soil 2 :

This soil sample was collected from a side ditch in Namie-cho located in 24km northwest of FDNPP. The sample was subjected to drying, sieving and organics decomposition processes in the same way as above.

4 Experimental

4-1 Measurement of Pu radioactivity

Six aliquots of 10g were picked up from soil 1. After addition of ^{242}Pu tracer, six aliquots of 10g soil were leached on a hot plate at 90-100℃ with 40mL of 10 M HNO_3-0.1M HF for 4 hours. Then, after isolation and purification of Pu through anion exchange procedure [4,5], they were electrodeposited on a steel plate and measured by α-spectrometry.

4-2 Dissolution experiment of Pu with acids

Each of two aliquots of 10g was picked up to a teflon beaker from soil 2. One sample was leached on a hotplate with 40ml of 8M HNO_3 and the other was leached with 40ml of 10M HNO_3-0.1M HF for 2 hours, then they were filtered. The leaching operation was repeated.

Conc. HNO_3 and conc. HF acids were added to the two residues until they were completely decomposed. After isolation and purification of Pu, the Pu were electrodeposited on a stainless steel plate and subjected to α-spectrometry [4,5].

4-3 Measurement of ^{110m}Ag radioactivity

Many aliquots were prepared and picked up to 25ml vial bottles. They were subjected to γ-spectrometry to determine their radioactivity.

4-4 Dissolution experiments of ^{110m}Ag species

We used a column (0.5φ×5 cm) filled with 1g soil sample. To perform dissolution experiments, leaching solvents were passed through the column. Leaching solutions were used with several concentrations acids of HCl and HNO_3, pure water, seawater, conc. aqua ammonia, di-ammonium hydrogen citrate 25% solution, and 1M $Na_2S_2O_3$. These eluents were collected to 25ml vial bottles and measured by γ-spectrometry. Details of the chemical procedures are found elsewhere [4].

5. Results

The concentrations of ^{238}Pu and ^{137}Cs are shown in Figure 1. The results were obtained through the measurements with duplication analysis of a soil

sample.

The ^{137}Cs nuclides are generally suggested to be deposited uniformly in 10g of soil sample. The results of ^{137}Cs radioactivity for six samples were within 109-132Bq/g, and its standard deviation was 8.3. In the figure are also shown the concentrations of ^{238}Pu for six samples with the ratios of ^{238}Pu/$^{239+240}$Pu as a table. These ratios of ^{238}Pu/$^{239+240}$Pu are larger than the averaged ratio for global fallout around 0.03. The radioactivity of ^{238}Pu for one sample was clearly higher than the others and its ratio of ^{238}Pu/^{239,240}Pu was also higher as shown in the table with the figure. The existence of hot particles causes their radioactivity concentrations to vary over a wide range even if soil samples are well mixed. Therefore, these results suggest that the ^{238}Pu isotopes were released from FDNPP as particles with high radioactivity.

Tables 1 and 2 show the results of dissolution experiments. Rate of digestion with 10M HNO_3-0.1M HF was higher than that with 8M HNO_3 for first digestion, but both of the methods digested more than 90 percent of Pu in soil as a total of the first and second digestions. It is often noted that sintered Pu dissolves sparingly in HNO_3 [6]. The result suggests unexpectedly that the Pu species are not sintered and dissolve in nitric acid.

On the other hand, Fig. 2 shows a good correlation of concentrations of ^{137}Cs with ^{110m}Ag. The ^{110m}Ag isotope is deposited as same as the Cs isotopes. Table 3 shows the results of dissolution experiments. For soil 1, the ^{110m}Ag isotope was eluted from the soil column with conc. ammonia water and sodium thiosulfate solution. The dissolved Ag portions were 7 percent and 14

percent from soil 1. The chemical form of Ag is supposed to be mixture of metal simple substances and oxides.

6. Conclusion

It is suggested that the Pu isotopes have dissolvable chemical species in nitric acid and they are deposited in soil as hot particles. The Ag isotopes are suggested to be deposited with fine particles as same as the Cs isotopes in soil and their chemical forms may be a mixture of metal simple substances and oxides.

References

[1] Environment monitoring database for the distribution of radioactive substances released by TEPCO Fukushima Daiichi NPP accident (2014) Nuclear Regulation Authority, Ministry of Environmental, Japan, https://mapdb.jaea.go.jp/mapdb/portals/3/ Accessed 25 April 2014

[2] Environment monitoring database for the distribution of radioactive substances released by TEPCO Fukushima Daiichi NPP accident (2012) Nuclear Regulation Authority, Ministry of Environmental, Japan, https://mapdb.jaea.go.jp/mapdb/portals/201012/ Accessed 25 April 2014

[3] Yamamoto M, Takada T, Nagao S, Koike T, Shimada K, Hoshi M, Zhumadilov K, Shima T, Fukuoka M, Imanaka T, Endo S, Sakaguchi A, Kimura S (2012) An early survey of the radioactive contamination of soil due

to the Fukushima Dai-ichi Nuclear Power Plant accident, with emphasis on plutonium analysis, Geochem J 46:341-353

[4] Kimura H, Uesugi M, Muneda A, Watanabe R, Yokoyama A, Nakanishi T (2013) Particulates of Pu radioisotopes released from Fukushima Daiichi nuclear power plants, Proceedings of the 14th Workshop on Environmental Radioactivity :344-349

[5] The Pu analysis (1991) Japan's Ministry of Education, Culture, Sports, Science and Technology,

http://www.kankyo-hoshano.go.jp/series/main_pdf_series_12.html

(In Japanese) Accessed 25 April 2014

[6] Vajda N, Kim CK (2011) Determination of transuranium isotopes (Pu, Np, Am) by radiometric techniques: a review of analytical methodology, Anal Chem 83:4688-4719

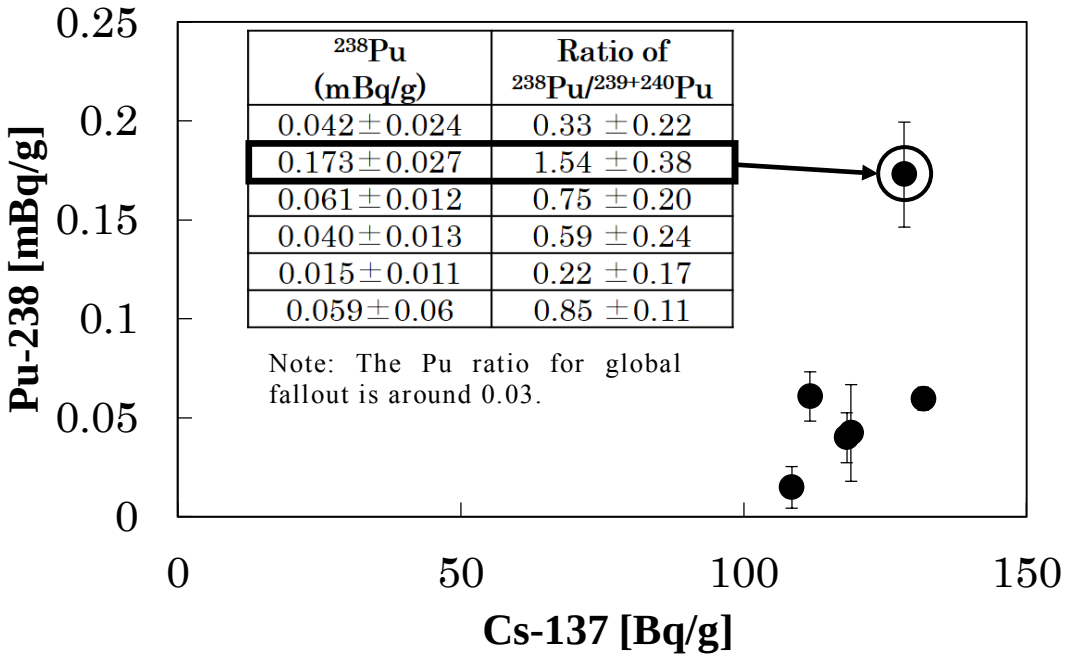
0.25
0.2
0.15
0.1
0.05
0
Pu-238 [mBq/g]
0
50
100
150
Cs-137 [Bq/g]
238Pu (mBq/g)
Ratio of 238Pu/239+240Pu
0.042±0.024
0.33 ±0.22
0.173±0.027
1.54 ±0.38
0.061±0.012
0.75 ±0.20
0.040±0.013
0.59 ±0.24
0.015±0.011
0.22 ±0.17
0.059±0.06
0.85 ±0.11
Note: The Pu ratio for global fallout is around 0.03.

Fig.1

Table 1 Dissolution of Pu in soil 2 with 8M HNO_3

Sample	^{238}Pu (Bq/kg)	$^{239+240}Pu$ (Bq/kg)	$^{238}Pu/^{239+240}Pu$	Dissolution (%)
First digestion	8.0±0.3	3.5±0.2	2.3±0.4	87
Second digestion	1.1±0.1	0.46±0.04	2.3 ±0.6	12
Complete Decomposition	0.07±0.01	0.038±0.005	2.0±0.7	1

Table 2　Dissolution of Pu in soil 2 with 10M HNO_3-0.1M HF

Sample	^{238}Pu (Bq/kg)	$^{239+240}Pu$ (Bq/kg)	$^{238}Pu/^{239+240}Pu$	Dissolution ratio（%）
First digestion	1.02±0.04	0.47±0.03	2.2 ±0.5	93
Second digestion	0.077±0.007	0.025±0.004	3.1 ±1.0	5
Complete Decomposition	0.033±0.005	0.012±0.003	2.8 ±1.3	2

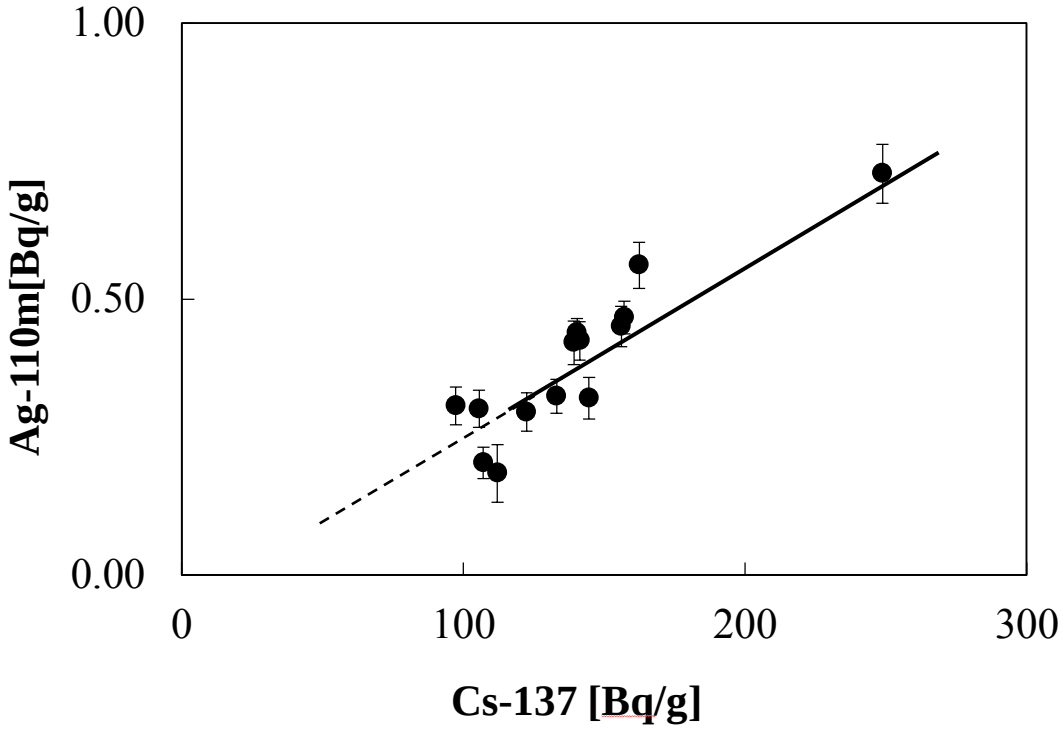

Fig. 2

Table 3　Elution of ^{110m}Ag from soils

Soil Sample	Water	Sea water	Ammonia water	25% Ammonium citrate soln.	1M Sodium thiosulfate	0.5M HCL	7M HNO_3
Soil 1	−	−	○(7 %)	−	○(14 %)	○	○
Soil 2	×	×	×	×	○	○	○

○: eluted, ×: not eluted, −: not applied

Figure captions

Fig.1　Correlation of ^{238}Pu and ^{137}Cs activities in soil 1

Fig.2　Correlation of ^{110m}Ag and ^{137}Cs activities in soil 1

Table captions

Table 1　Dissolution of Pu in soil 2 with 8M HNO_3

Table2　Dissolution of Pu in soil 2 with 10M HNO_3-0.1M HF

Table 3　Elution of ^{110m}Ag from soils