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Isotopic determination of U, Pu and Cs in environmental waters following the Fukushima Daiichi Nuclear Power Plant accident

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Concentrations of the radionuclides, U, Pu, and Cs were measured in water samples (10–20 L) to study analyte dispersion and migration following the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident. A total of 8 water samples including oceanic water and paddy-field water were collected in the vicinity of the plant. Determinations of U, Pu and Cs isotopes were performed by accelerator mass spectrometry (AMS), inductively coupled plasma mass spectrometry (ICP-MS), and γ-ray spectrometry. The ^{236}U/^{238}U atom ratio was in the range $1.83–8.20 \times 10^{-9}$ for fresh water and around 0.57×10^{-9} for seawater while the concentration of ^{236}U was about 10^4–10^5 and 10^6 atoms/kg, respectively. Plutonium (^{239,240}Pu) was detected in one riverine sample and the marine samples at very low levels and with large uncertainty. The concentrations of ^{137}Cs in fresh riverine samples were 0.02–0.46 Bq/kg which are more than three orders of magnitude larger than the global fallout level. As for seawater samples within 80 km offshore of the FDNPP, the concentrations of ^{137}Cs were 10–20 times higher than that of the Japan Sea water. Also ^{134}Cs and ^{137}Cs were of similar concentrations in all samples. The results show that volatile and refractory nuclides such as Cs, U and Pu exist in the dissolved phase, which can be readily assimilated by plants/humans. However the environmental impact of Pu and U in the vicinity of the FDNPP is considered to be low in comparison to that of the volatile radionuclide Cs.

Keywords: uranium, plutonium, caesium, seawater, riverine water, Fukushima

INTRODUCTION

The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident occurred as a result of a magnitude 9.0 (Mw) earthquake and tsunami in March 2011. As a consequence, the total amount of radionuclide discharge into the environment was more than 10^{19} Bq (METI, 2011a). Especially volatile fission products and neutron activation products, such as ^{137}Cs ($T_{1/2}$ = 30.2 years), ^{134}Cs ($T_{1/2}$ = 2.06 years) and ^{131}I ($T_{1/2}$ = 8.04 days) of about 10^{17} Bq have been dispersed throughout the world contaminating the global environment (Chino *et al.*, 2011). These nuclides have been monitored in the atmosphere (aerosol), soil and water to study the impact of the FDNPP accident (e.g., MEXT, 2011; Tanaka *et al.*, 2012, Oura and Ebihara, 2012). Furthermore, there is concern that radionuclides such as U and Pu have also spread as a result of partial melt-down of the nuclear fuel core including the MOX fuel (mixed U and Pu oxide fuel) of unit 3 of the FDNPP. However, due to the relative difficulty of measuring actinide nuclides, there is a little data on Pu and U in and around the Fukushima area (Takagai *et al.*, 2011; Zheng *et al.*, 2012a, b).

Due to the difficulty of identify a small altered ratio of ^{235}U/^{238}U (^{235}U and ^{238}U are naturally occurring radionuclides at relatively high concentrations, average 3 ppm for ^{238}U, in soils) as a result of accidental discharge of spent nuclear fuel, ^{236}U has been used as an alternative fingerprint of environmental U contamination, e.g., around nuclear reprocessing facilities and Chernobyl NPP (e.g., Marsden *et al.*, 2001; Boulyga and Heumann, 2006). U-236 ($T_{1/2} = 2.342 \times 10^7$ years) is mainly induced by the nuclear reaction ^{235}U(n, γ) with thermal neutrons in reactors which use ^{235}U fuel. The spent fuel contains about 0.4% of ^{236}U and the isotope remains in nuclear waste for a long time due to its long half life. A small amount of

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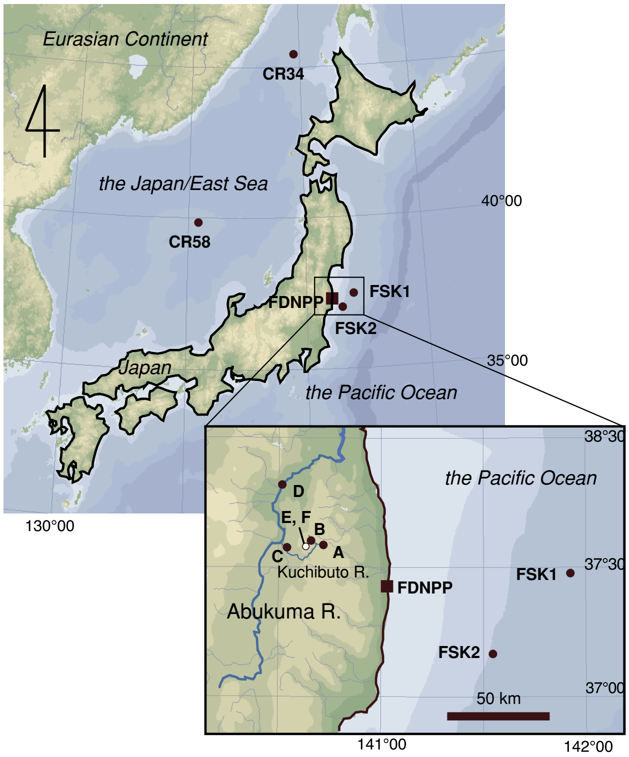

Fig. 1. Map showing sea and riverine water sampling locations. Filled circles on land : riverine water (A–C: Kuchibuto River, D: Abukuma River), open circle: inflow and outflow waters of paddy field (E and F). FSK1 and FSK2: seawater samples of the Pacific Ocean, and CR34 and CR58: seawater samples of the Japan Sea. The information on sampling points is given in Table 1.

^{236}U is also produced from the decay of ^{240}Pu in Pu reactor fuel.

In the case of Pu (half lives: ^{238}Pu 87.74 years; ^{239}Pu 2.411×10^4 years; ^{240}Pu 6.563×10^3 years; ^{241}Pu 14.35 years) the isotopic composition is dependent on fuel burnup/burning-age. From recent data (METI, 2011b) on the ^{238}Pu/$^{239+240}$Pu activity ratio (about 2.0) in soil samples from the area of the FDNPP, the ^{240}Pu/^{239}Pu atom ratio can be estimated to be more than 0.4. This value is different from the global fallout ratio, 0.176 (Krey *et al*., 1976), hence it might be possible to identify the origin of Pu in environmental samples using Pu isotopic ratio measurements. Actually, Zheng *et al*. (2012a) reported abnormal ratios for ^{240}Pu/^{239}Pu of around 0.3 in soil samples northwest and south of the FDNPP in the 20–30 km zones. They also observed high activity ratios for ^{241}Pu/$^{239+240}$Pu (>100) in these samples.

In this research we have measured the concentration and isotopic composition of U, Pu and Cs isotopes in water samples to understand the radiological situation for surface waters in the aftermath of the FDNPP accident. Additional data on Pu in soil samples are also available from the recent work of Yamamoto *et al*. (2012). This work and the afore-mentioned studies serve to clarify the extent and fate of potentially harmful radionuclides in the natural environment following the Fukushima accident.

MATERIALS AND METHODS

Study area and sampling

The sites and dates for sampling the Kuchibuto and Abukuma Rivers are shown in Fig. 1 and Table 1. The Kuchibuto River is one of the tributaries of the Abukuma River which is the largest river in Fukushima. The Abukuma River discharges into the Pacific Ocean. Sampling sites A and B of the Kuchibuto River are situated in the Yamakiya-district, Kawamata-cho (evacuation area about 30 km from FDNPP), and site C is a downstream of this river. All riverine samples were collected in June to August 2011. The inflow and outflow waters of the paddy-fields (E and F) were collected in June during the irrigation and plowing season before transplanting of rice seedlings. Seawater samples were collected on the cruise (KH11-07) of the *Research Vessel Hakuho-maru* in July to August 2011. The sampling sites, FSK1 and FSK2, are shown in Fig. 1 and Table 1.

Water samples (10–20 L) were filtered through 0.45 μm pore size membrane filter by using a pressurised pump system *in situ*. The filtrate was stored in polyethylene containers after addition of 180 mL of 16 M HNO_3. A portion (about 100 mL) of the filtered water was subsampled for ^{238}U measurement.

Sample preparation and measurement of radionuclides

The filtered water sample was transferred to a polyethylene container. Plutonium-242 (IRMM-085), ^{133}Cs (stable Cs) and iron (Fe) as Fe/HCl solution were added to the water sample as spike and carrier, respectively. The water sample was heated for three hours with stirring and then allowed to stand for 12 hours. After re-adjustment of the pH of the water sample to approximately pH 1 with HNO_3 and ammonia solution, 4 grams of ammonium molybdophosphate (AMP) powder were added to adsorb Cs. After stirring for 1 hour and standing for 24 hours at room temperature, the supernatant was removed first with a siphon and then by centrifugation (the supernatant was kept for U and Pu analyses). The AMP powder was dried at 105°C for 12 hours, packed into a plastic bag (4.5 cm × 4.5 cm) and measured for ^{137}Cs (662 keV) and ^{134}Cs (605, 796 keV) by γ-ray spectrometry using a planer-type Ge detector (ORTEC, GEM-50195-P). The spectrometer was calibrated with a standard, which was prepared by the Low Level Radioactivity Laboratory of Kanazawa University using NBL (New Brunswick Laboratory) Reference Material No. 42-1 (4.04 %

Table 1. The detail of water samples from river and ocean

Sampling site	Sample	Sampling date	Sampling site	
			N	E
A	Kuchibuto R. site 7	25/June/2011	37°35′80″	140°41′32″
B	Kuchibuto R. site 9	26/June/2011	37°35′27″	140°41′18″
C	Kuchibuto R. downstream	31/July/2011	37°34′52″	140°32′31″
D	Abukuma R.	10/July/2011	37°49′49″	140°31′80″
E	Inflow of paddy field	13/June/2011	37°35′26″	140°38′15″
F	Outflow of paddy field	13/June/2011	37°35′26″	140°38′15″
FSK1	Pacific Ocean 1	1/August/2011	37°27′47″	141°55′70″
FSK2	Pacific Ocean 2	1/August/2011	37°09′70″	141°32′29″
CR58*	Japan Sea 1	11/July/2010	40°25′35″	135°55′15″
CR34**	Japan Sea 2	4/July/2010	45°40′01″	139°59′47″

**Sakaguchi et al. (2012); **Kadokura (personal comm.).*
Sampling sites are shown in Fig. 1.

U), a γ-ray reference material including ^{137}Cs from JRIA (Japan Radioisotope Association) and analytical grade KCl. As for ^{134}Cs value, the count rates of the peaks corresponding to 605 and 796 keV were used for determination. The summing effect for these peaks was corrected by increasing the distance (30 cm) between the detector and the sample.

Uranium and Pu were co-precipitated with $Fe(OH)_3$ at pH 8 from the above supernatant. The supernatant was removed by siphon and centrifugation. The precipitated $Fe(OH)_3$ was re-dissolved with 12 M HCl and the solution was adjusted to a concentration of 10 M HCl. Purification of U and Pu was performed according to Sakaguchi *et al.* (2009, 2010). For the measurement of ^{236}U and ^{239,240}Pu with AMS, the cathode was prepared as U or Pu oxide in a Fe_2O_3 matrix. Details of the measurements of ^{236}U and ^{239,240}Pu with AMS are described in Steier *et al.* (2010) and Sakaguchi *et al.* (2012).

A portion of the AMP powder was dissolved with 1.25% tetramethylammonium hydroxide (TAMAPURE-AA) to determine the concentration of ^{133}Cs. For the measurement of ^{238}U in water and ^{133}Cs in solubilised AMP samples, an ICP-MS (Agilent 7700) was used. In this case, In and Re were used as on-line internal standards for U and Cs, respectively.

RESULTS AND DISCUSSION

Fresh water samples

The results for U, Pu and Cs isotopes in water samples are shown in Tables 2.1 and 2.2. To clarify the spatial variation of radionuclides in river water, samples were collected throughout the upstream of the Kuchibuto River (sites A and B in evacuation area), downstream of this river (site C), the main section of the Abukuma River (site D). However, no specific spatial distribution effects were noted for the upper to lower river systems for the sampling period. The concentrations of ^{137}Cs in river water were 0.02–0.46 Bq/kg. These values are more than three orders of magnitude higher than the ^{137}Cs concentrations (0.05–0.12 mBq/kg) in fresh water samples which were collected from the Kuji River (Fukushima and Ibaraki Prefectures) before the FDNPP accident (Matsunaga *et al.*, 1991). These samples were collected and analyzed in 1988, so the concentration of ^{137}Cs in river water immediately before the FDNPP (March, 2011) should have been quite low, less than 0.03–0.07 mBq/kg, due to the effect of decay and less supply of ^{137}Cs from surface soil. The ^{137}Cs concentrations of inflow and outflow water of paddy-fields (E and F) were also high, 0.10 Bq/kg for each sample. However, as can be judged from these values, there is no significant difference in ^{137}Cs concentrations between the in/out-flow waters of the paddy-field. This result suggests that there is minimal effect of Cs adsorption/retention on soil in the irrigation and plowing of the paddy-field. Cs-134 ($T_{1/2}$ = 2.06 years) was also detected in all water samples, and ^{134}Cs/^{137}Cs activity ratios which were decay-corrected to 11th March 2011 were around 1. These results are consistent with the estimated value of discharge from the FDNPP and some previous reports (e.g., METI, 2011a).

The ^{236}U/^{238}U atom ratio was in the range $2.57–8.20 \times 10^{-9}$ and the concentration of ^{236}U was $0.82–4.48 \times 10^5$ atoms/kg for river water samples. The values of ^{236}U/^{238}U and ^{236}U in in/out-flow waters of the paddy-field are nearly the same as those for riverine waters. A typical value of the global fallout for ^{236}U/^{238}U and ^{236}U concentrations in Japanese rivers has not been identified so far.

Table 2.1. The results for Cs, U and Pu isotopes in river water (A–F) and sea water (G–J) samples

Sampling site	Sample	^{238}U (10^{-9} g/kg)	^{236}U (10^{5} atom/kg)	^{137}Cs (Bq/kg)	^{134}Cs$^{\#}$ (Bq/kg)	^{239}Pu (10^{6} atom/kg)
A	Kuchibuto R. site 7	7.47 ± 0.34	0.82 ± 0.15	0.46 ± 0.01	0.52 ± 0.01	
B	Kuchibuto R. site 9	12.6 ± 0.5	1.10 ± 0.22	0.26 ± 0.01	0.26 ± 0.01	
C	Kuchibuto R. downstream	53.7 ± 1.2	3.49 ± 0.66	$0.02 \pm 0.00_1$	$0.05 \pm 0.00_2$	
D	Abukuma R.	21.6 ± 1.1	4.48 ± 0.61	0.25 ± 0.01	0.26 ± 0.01	1.62 ± 0.67
E	Inflow of paddy field	23.7 ± 0.6	1.10 ± 0.25	0.10 ± 0.01	0.11 ± 0.01	
F	Outflow of paddy field	3.54 ± 0.23	0.66 ± 0.23	0.10 ± 0.01	0.12 ± 0.01	
		(10^{-6} g/kg)	(10^{7} atom/kg)	(mBq/kg)	(mBq/kg)	
FSK1	Pacific Ocean 1	2.42 ± 0.04	0.35 ± 0.11	19.0 ± 0.5	26.1 ± 1.3	2.70 ± 0.79
FSK2	Pacific Ocean 2	2.38 ± 0.10	0.35 ± 0.08	12.4 ± 0.7	12.2 ± 0.7	2.85 ± 0.49
CR58*	Japan Sea 1	2.82 ± 0.28	0.98 ± 0.13	1.18 ± 0.08		1.76 ± 0.39
CR34**	Japan Sea 2	3.23 ± 0.24	1.08 ± 0.11	1.05 ± 0.07		3.82 ± 0.30

Table 2.2. The results for Cs, U and Pu isotopes in river water (A–F) and sea water (G–J) samples

Sampling site	Sample	^{236}U/^{238}U 10^{-9} (atom ratio)	^{134}Cs/^{137}Cs$^{\#}$ (activity ratio)	^{240}Pu/^{239}Pu (atom ratio)	^{236}U/^{137}Cs (10^{6} atom/Bq)	^{239}Pu/^{236}U (atom ratio)
A	Kuchibuto R. site 7	4.33 ± 0.74	1.12 ± 0.03		0.18 ± 0.03	
B	Kuchibuto R. site 9	3.43 ± 0.66	0.98 ± 0.06		0.42 ± 0.09	
C	Kuchibuto R. downstream	2.57 ± 0.49	0.93 ± 0.10		16.6 ± 3.2	
D	Abukuma R.	8.20 ± 1.05	1.03 ± 0.04	0.308 ± 0.176	1.81 ± 0.26	3.62 ± 1.56
E	Inflow of paddy field	1.83 ± 0.47	1.10 ± 0.06		1.07 ± 0.28	
F	Outflow of paddy field	7.32 ± 2.57	1.26 ± 0.10		0.68 ± 0.24	
					(10^{8} atom/Bq)	
FSK1	Pacific Ocean 1	0.57 ± 0.18	1.38 ± 0.10	0.218 ± 0.065	1.56 ± 0.49	0.77 ± 0.33
FSK2	Pacific Ocean 2	0.58 ± 0.13	0.98 ± 0.08	0.181 ± 0.051	2.82 ± 0.67	0.81 ± 0.23
CR58*	Japan Sea 1	1.37 ± 0.14		0.197 ± 0.053	83.1 ± 12.4	0.18 ± 0.05
CR34**	Japan Sea 2	1.32 ± 0.10		0.237 ± 0.032	103 ± 13	0.35 ± 0.05

**Sakaguchi et al. (2012); **Kadokura (personal comm.).*
$^{\#}$Decay corrected to 11/March/2011.
The analytical error is based on 1σ of counting statistics.
Sampling sites are shown in Fig. 1.

However, the uranium isotope ratios and concentrations are much smaller compared with those of Austrian river water samples which might be contaminated with global fallout and Chernobyl accident (Srncik *et al.*, 2010).

The ratio of ^{236}U/^{137}Cs was 0.18–16.6 × 10^{6} (atom/Bq) for riverine samples, and 0.68–1.07 × 10^{6} (atom/Bq) for inflow and out flow water of paddy-fields. These ratios are two to four orders less than the global fallout value, 3.40–5.34 × 10^{9} (Sakaguchi *et al.*, 2009, 2010). Given the results for ^{236}U/^{137}Cs and the concentrations of ^{137}Cs, it is concluded that the global fallout value for ^{236}U/^{137}Cs was simply affected as a result of additional input of ^{137}Cs from the FDNPP accident. Consequently, the input of uranium isotope from FDNPP is negligibly small in these samples.

Pu isotopes were measured in one water sample (D) from the Abukuma River. The concentration of ^{239}Pu for this sample was 1.62 × 10^{6} atom/kg (as $^{239+240}$Pu: 3.14 × 10^{-6} Bq/kg). This is only slightly higher than the value for river water in Japan measured some time before the Fukushima accident (Hirose *et al.*, 1990). However, the significance of this concentration and the possible origin of Pu isotopes could not be identified due to the large measurement uncertainty.

Seawater samples

Highly contaminated water from the drains of the FDNPP were introduced to the ocean (Nuclear Emergency Response Headquarters Government of Japan, 2011), resulting in potentially serious contamination of the marine environment not only by fission/activation products but also by fuel materials.

The concentration of ^{137}Cs in surface seawater of the north eastern Pacific Ocean due to global fallout was calculated as about 1.5 mBq/kg based on an average concentration of ^{137}Cs (2.4 mBq/kg) in 2000 and an effective half life (16.5 years) (Povinec *et al*., 2005). This value is comparable with the concentration which was measured in surface water from the Japan Sea before the accident (CR58 and CR34). In contrast, about one order of magnitude higher concentration of ^{137}Cs was observed in seawater samples from offshore of the FDNPP (FSK1 and FSK2). Similar concentrations of ^{134}Cs (values being decay-corrected to 11th March 2011) were also measured in the seawater samples. These values are in the range of radio Cs concentrations, which were reported after the FDNPP accident, in seawater samples from the Pacific Ocean (e.g., Honda *et al*., 2012; Inoue *et al*., 2012). Although we cannot infer a direct correlation between the Cs isotope concentration and distance from the FDNPP due to the complicated surface currents around this area, it is assumed that the elevated radioactive Cs originated from the FDNPP through detection of ^{134}Cs and the ^{134}Cs/^{137}Cs activity ratios.

The ^{236}U/^{238}U atom ratio and ^{236}U concentration in the surface seawater samples (FSK1 and FSK2) were estimated as about 0.60×10^{-9} and 0.35×10^{7} (atom/kg), respectively. These ^{236}U/^{238}U atom ratio values and concentrations of ^{236}U were less than half the values in the surface seawater samples, which were measured before the FDNPP accident, from the Japan Sea (CR58 and CR34). Thus the low ^{236}U/^{238}U and ^{236}U concentrations suggest that the surface seawater samples (FSK1 and FSK2) exhibited a relatively low potential for contamination as a result of the FDNPP accident.

The ^{236}U/^{137}Cs ratios in the seawater samples (FSK1 and FSK2) were 1.56×10^{8} and 2.82×10^{8} (atom/Bq), respectively. From consideration of the concentrations of ^{236}U and ^{137}Cs, and the ^{134}Cs/^{137}Cs in seawater from the FSK1 and FSK2 sites, ^{236}U/^{137}Cs ratios have been altered by the mixing of radio Cs derived from the FDNPP with global fallout ^{236}U/^{137}Cs ratio.

The Pu concentration and isotopic composition of the seawater samples (FSK1 and FSK2) were similar to those of the Japan Sea (CR58 and CR34), the latter reflecting the global fallout value for Pu. The values observed were also comparable with the Pu isotope concentrations (^{239}Pu = $1.07\text{–}8.07 \times 10^{6}$ atom/kg) and ratios (^{240}Pu/^{239}Pu = 0.199–0.224) reported for the Northwest Pacific Ocean (Yamada *et al*., 2006, 2007).

The difference of the ^{239}Pu/^{236}U atom ratio between the Japan Sea and offshore of FDNPP might reflect a difference in the scavenging rate of Pu due to biological productivity. This means that Pu, as a reactive element, is more readily scavenged from the seawater column by particles than U (Kadokura, personal communication). Clearly for an in-depth discussion of this topic a full inventory of these elements in the water column throughout the whole year is needed.

CONCLUSION

Fresh riverine/paddy-field water samples and seawater samples from the Fukushima area were analysed for actinide nuclides, U and Pu isotopes, together with Cs isotopes. Significant contamination of fresh surface waters and seawater with radio-Cs has been confirmed, as previously reported (e.g., MEXT, 2011). Moreover, the concentration and isotopic compositions of U and Pu isotopes in the waters were consistent with minimal dispersal of these elements from the FDNPP.

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