**Isotopic determination of U, Pu and Cs in environmental waters**

**following the Fukushima Daiichi Nuclear Power Plant accident**

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**Abstract**

 Concentrations of transuranic nuclides, U and Pu, and Cs radioisotopes were measured in large volume water samples 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 Fukushima. Determinations of U, Pu and Cs isotopes were performed by accelerator mass spectrometry (AMS), inductively coupled plasma mass spectrometry (ICP-MS), and -ray spectrometry. The 236U/238U atom ratio was in the range 1.83-7.32 x 10-9 for fresh water and around 5.7 x 10-10 for sea water while the concentration of 236U was about 104-105 and 106-107 atoms/kg, respectively. Plutonium (239,240Pu) was detected in one riverine sample and marine samples at very low level and with large uncertainty. The concentrations of 137Cs in fresh riverine samples were 0.02-0.46 Bq/kg which is more than two to four orders of magnitude larger than the global fallout level. As for sea water samples within 80 km offshore of FDNPP, the concentration of 137Cs was 10-20 times higher than that of the Japan Sea water. Cs-134 also shows the nearly same concentration with 137Cs in all samples. The results showed that volatile and refractory nuclides such as Cs, U and Pu exist as dissolved phase, which can easily be taken by plants/humans. However the effect of Pu and U are much less so compared to the volatile radionuclide Cs and it seems no contribution from FDNPP in and around Fukushima area.

**INTRODUCTION**

 The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident occurred as a result of a magnitude 9.0 earthquake and tsunami in March 2011. As a consequence, the total amount of radionuclide discharge into the environment was more than 1019 Bq (METI 2011a). Especially volatile fission products, such as 137Cs (T1/2=30.2 years), 134Cs (T1/2=2.06 years) and 131I (T1/2=8.04 days), have been dispersed more than 1017 Bq (Chino et al., 2011) throughout the world contaminating the global environment. These nuclides have been monitored in the atmosphere (aerosol), soil and water to study the impact of the FDNPP accident (e.g. MEXT, 2011). Furthermore, there is concern that transuranic nuclides such as U and Pu isotopes 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 transuranic nuclides, there is a little data on the concentrations of Pu and U in and around the Fukushima area (Zheng et al., 2012).

 U-236 (T1/2=2.342×107 y) is mainly induced by the nuclear reaction 235U(n,) with thermal neutrons in reactors which use 235U fuel. The spent fuel contains about 0.4% of 236U and the isotope remains in nuclear waste for a long time due to its long half life. This anthropogenic U isotope has been used as a fingerprint of environmental contamination arising from use of U fuel, e.g. around nuclear reprocessing facilities and Chernobyl NPP (e.g. **Marsden** et al., 2001; Boulyga and Heumann, 2006). A small amount of 236U is also produced from the decay of 240Pu in Pu reactor fuel.

 In the case of Pu (238Pu T1/2=87.74 years; 239Pu 2.411×104 years; 240Pu 6.563×103 year; 241Pu T1/2=14.35 years) the isotopic composition is dependent on fuel burnup/burning-age. From recent data (METI, 2011b) on the 238Pu/239+240Pu activity ratio (about 2.0) in soil samples from the area of the FDNPP, the 240Pu/239Pu 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. (2012) found that the abnormal ratio of 240Pu/239Pu around 0.3 in the soil samples from northwest and south of the Fukushima DNPP in the 20–30 km zones. They also reported that the high activity ratio of 241Pu/239+240Pu (> 100) in these samples.

In this paper, we report 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 available from the recent work of Yamamoto et al. (2012, this issue). The present study serves as an aid to predict the fate of radionuclides in the natural environment, and to avoid the extra radiation for citizens, although the sampling sites for riverine water and sea water samples were limited.

**MATERIALS AND METHODS**

*Study area and sampling*

 The sampling sites and date, 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 biggest river in Fukushima. The Abukuma River discharges into the Pacific Ocean. Sites 7 and 9 of the Kuchibuto River are situated in Yamakiya-district (about 30 km from FDNPP), Kawamata-cho, a town next to Iitate-machi. These areas have been evacuation areas from May 2011 due to the highly contamination with radionuclides from FDNPP. All riverine water samples were collected in June to August 2011. The inflow and outflow water of the paddy-fields in the Yamakiya-district were collected in June.

 Sea water 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 also shown in Fig. 1 and Table 1.

 Water samples (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 a 180 mL of 16 M HNO3. A portion (about 100 mL) of the filtered water was sub-sampled for 238U measurement.

*Sample preparation and measurement of radionuclides*

 The filtered water sample was put into a polyethylene vessel. Plutonium-242, 133Cs (stable Cs) and iron (Fe) as Fe/HCl solution were added to the water as chemical yield tracers and carrier, respectively. The water sample was heated for three hours with stirring and then allowed to stand for 12 hours. After re-adjusting the pH of the water samples to approximately pH 1 with HNO3 and ammonia solution, 4 grams of ammonium-phosphomolybdate (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 enriched AMP powder was dried at 105°C for 12 hours, packed into a plastic bag (4.5 cm×4.5 cm) and measured for 137Cs (662 keV) and 134Cs (604 keV) by -ray spectrometry using a planer-type Ge detector (ORTEC, GEM-50195-P). The spectrometer was calibrated with a shelf-standard which was prepared by the Low Level Radioactivity Laboratory of Kanazawa University.

 Uranium and Pu were co-precipitated with Fe(OH)3at 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 adjusted to a concentration of 10 M HCl. Purification of U and Pu was performed as described by Sakaguchi et al. (2009, 2010). For the measurement of 236U and 239,240Pu with AMS, the cathode was prepared as U or Pu oxides in a Fe2O3 matrix. Details of the measurements of 236U and 239,240Pu with AMS are described in Steier et al. (2010) and Sakaguchi et al. (2010).

 A portion of the AMP powder was dissolved with 1.25% tetramethylammonium hydroxide (TMAH) to determine the concentration of 133Cs . For the measurement of 238U in seawater and 133Cs in solubilised AMP samples, an ICP-MS (Agilent 7700) with a high-matrix sample introduction system 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 Table 2-1 and 2-2. To see the spatial variation of radionuclides in river water, the samples were collected through the evacuation area, sites 7 and 9 at upper stream of the Kuchibuto River, to downstream of this river, and main stream of the Abukuma River. However, there were no specific spatial distribution through the upper to down river system in this sampling period. The concentrations of 137Cs in river water were 0.021-0.46 Bq/kg. These values are more than two to four orders of magnitude higher than the 137Cs concentrations (0.05-0.12 mBq/kg) in fresh water samples which were collected from Kuji River (Fukushima and Ibaraki Prefectures) before the FDNPP accident (Matsunaga et al., 1991). These samples were collected and estimated in 1988 when there was still frequent nuclear-testings (about 50 times/year), so the concentration of 137Cs in river water immediately before the FDNPP should have been quite low, less than 0.03-0.07 mBq/kg, given the decay of 137Cs (half-life, 30.2 years) and erosion of surface soil. The 137Cs concentrations of inflow and outflow water of paddy-fields were also high, 0.103 and 0.097 Bq/kg, respectively. However, as can be seen from these values, there is no difference of 137Cs concentration between in/out-flow of the paddy-field. This result may suggest that there is no large effect of Cs adsorption/adhention on soil in the paddy-field. Cs-134 (T1/2=2.06 years) was also detected in all water samples, and 134Cs/137Cs activity ratios which decay corrected to 11th March 2011 were around 1. This results are not contradicted with the estimated value of discharge from FDNPP and some previous reports (METI 2011a).

 The 236U/238U atom ratio was in the range 1.83-7.32 x10-9 for river water samples and the concentration of 236U was 0.66-4.48 ×105 atoms/kg. These uranium isotope results are about 100 times smaller than those of river water samples which were collected from Austria (Srncik et al., 2010). It was concluded that the waters from Austria might be affected by global fallout and/or Chernobyl fallout due to the high 236U/238U ratios compared to natural rock samples.

 The ratio of 236U/137Cs was 0.177-16.6 x 160 (atom/Bq) for riverine samples, and 6.80 x105 -10.1 x105 (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 x109 (Sakaguchi et al., 2009 and 2010). From above results, it is indicated that the global fallout value for 236U/137Cs was altered as a result of addition of 137Cs from FDNPP.

 Pu isotopes were measured only in one water sample from Abukuma River. The concentration of 239+240Pu for this sample was 3.14x10-6 Bq/kg. This is only slightly higher than the value for river water in Japan long time before the accident (Hirose et al., 1991). However, the significance of this concentration and the possible origin of Pu isotopes could not be identified due to the large measurement uncertainty.

*Sea water samples*

 The highly contaminated water from the drain of the FDNPP have been introduced to the ocean (Nuclear Emergency Response Headquarters Government of Japan), and serious contamination not only by fission products but also by fuel materials could have been induced into the sea around the FDNPP.

 After Povinec et al., (2005), the concentration of 137Cs in surface sea water of the north eastern Pacific Ocean due to global fallout was calculated as about 1 mBq/kg based on an average concentration of 137Cs (1.6 mBq/kg) in 2000 and an effective half life (14.4 years). This value is comparable with the concentration which was measured in surface water from the Japan Sea (CR58 and CR34, Table 2). In contrast, about one order of magnitude higher concentration of 137Cs was observed in sea water samples from offshore of the FDNPP (FSK1 and FSK2 in Table 2). Similar concentrations of 134Cs ,which decay corrected to 11th March 2011,were measured in the samples. It was also noted that the concentration of 137Cs decreased with distance from the FDNPP. Information on surface sea water circulation is not presented here. However, due to the detection of 134Cs and 134Cs/137Cs activity ratios are about 1 in these sea water samples, it can be presumed that the contamination by radioactive Cs originated from the FDNPP.

 The 236U/238U atom ratio and 236U concentration in the surface sea water samples were estimated as about 0.60x10-9 and 0.35x107 (atom/kg), respectively. This 236U/238U atom ratio value and the concentration of 236U were less than half of the value in the surface seawater samples from the Japan Sea (CR58 and CR34 in Table 2).Thus the low U isotopic ratio and concentration would suggest that the surface sea water samples have a relatively low potential for the contamination by the FDNPP accident.

 The 236U/137Cs ratio in the surface sea water samples was in the range of 1.56×108 to 2.82×108 (atom/Bq). These values are one to two orders of magnitude lower than that of the Japan Sea surface water. From consideration of the concentration of 236U, the 134Cs/137Cs and 236U/137Cs ratios in sea water from these sites has also been altered by the mixing of radio-Cs derived from the FDNPP.

 The Pu concentration and isotopic composition of the sea water samples were similar to that of the Japan Sea, the latter reflecting the global fallout value for Pu. The values observed were also comparable with the Pu isotope concentration and ratio, 239Pu= 1.07-8.07x106 atom/kg, 240Pu/239Pu=0.199-0.224, which have been reported for the Northwest Pacific Ocean (Yamada et al., 2006, 2007).

 The difference of the 239Pu/236U atom ratio between the Japan Sea and offshore of FDNPP might be due to the difference of scavenging rate of Pu with biological productivity. It means that Pu as a reactive element is much faster scavenged from the sea water column by particles than U (Kadokura, personal comn.). So, to discuss this ratio, the inventory of these elements in the water column is needed.

 In this study, we got above isotope information in the period of summer season (June to August). To see the temporal variation of nuclides in the environment, further observation should be continued.

**CONCLUSION**

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

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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: sea water samples of the Pacific Ocean, and CR34 and CR58: sea water samples of the Japan Sea. The information on sampling points is given in Table 1.*



