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Plutonium isotopic signatures in soils and their variation (2011-2014) in sediment transiting a coastal river in the Fukushima Prefecture, Japan☆

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ABSTRACT

The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident resulted in a significant release of radionuclides that were deposited on soils in Northeastern Japan. Plutonium was detected at trace levels in soils and sediments collected around the FDNPP. However, little is known regarding the spatial-temporal variation of plutonium in sediment transiting rivers in the region. In this study, plutonium isotopic compositions were first measured in soils (n = 5) in order to investigate the initial plutonium deposition. Then, plutonium isotopic compositions were measured on flood sediment deposits (n = 12) collected after major typhoon events in 2011, 2013 and 2014. After a thorough radiochemical purification, isotopic ratios ($^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$) were measured with a Multi-Collector Inductively Coupled Mass Spectrometer (MC ICP-MS), providing discrimination between plutonium derived from global fallout, from atmospheric nuclear weapon tests, and plutonium derived from the FDNPP accident. Results demonstrate that soils with the most Fukushima-derived plutonium were in the main radiocaesium plume and that there was a variable mixture of plutonium sources in the flood sediment samples. Plutonium concentrations and isotopic ratios generally decreased between 2011 and 2014, reflecting the progressive erosion and transport of contaminated sediment in this coastal river during flood events. Exceptions to this general trend were attributed to the occurrence of decontamination works or the remobilisation of contaminated material during typhoons. The different plutonium concentrations and isotopic ratios obtained on three aliquots of a single sample suggest that the Fukushima-derived plutonium was likely borne by discrete plutonium-containing particles. In the future, these particles should be isolated and further characterized in order to better understand the fate of this long-lived radionuclide in the environment.

1. Introduction

The 2011 Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident released significant quantities of radioactive contamination into the environment. Although ~80% of the atmospheric fallout from the accident occurred over the ocean, the remainder was deposited on Japanese soils and formed a major radioactive pollution plume extending ~70 km northwest of the FDNPP (Evrard et al., 2015; Kawamura et al., 2011). Most of the research conducted after the accident has focused on gaseous radionuclides or radiocaesium isotopes (Bailly du Bois et al., 2012; Estournel et al., 2012; TEPCO, 2012). Other radionuclides, such as plutonium isotopes were also studied, although to a lesser extent (Steinhauser, 2014).

Plutonium is present in the Northern Hemisphere environment as a result of nuclear weapon tests (Yamamoto et al., 2014). ^{239}Pu ($T_{1/2} = 24{,}110$ y, alpha-decay) and ^{240}Pu ($T_{1/2} = 6563$ y, alpha-decay) are the most abundant isotopes in the environment on a

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global scale, while ^{238}Pu ($T_{1/2} = 88.74$ y, alpha-decay), ^{241}Pu ($T_{1/2} = 14.35$ y, beta-decay) and ^{242}Pu ($T_{1/2} = 376{,}000$ y, alpha-decay) are present in smaller concentrations (Hardy et al., 1973; Harley, 1979; Kelley et al., 1999; Yang et al., 2015). As the isotopic composition of plutonium is related to its origin, these isotopic ratios provide a powerful tool to discriminate between different sources of plutonium in the environment (Muramatsu et al., 2003). Specific isotopic signatures have been reported for the global fallout associated with nuclear weapon testing, local nuclear weapon tests (Chiappini et al., 1999), the Chernobyl accident (Ketterer et al., 2004) and the FDNPP accident (Evrard et al., 2014b).

Plutonium concentrations associated with the global fallout were shown to be heterogeneous in different aliquots (Kelley et al., 1999), due to the particulate form of deposition (Salbu, 2011). Contamination from the global fallout and the FDNPP have very different origins and their concentrations may evolve differently with time: global fallout contamination originated from the stratosphere, with many episodes spread over several decades, whereas the FDNPP fallout was supplied by a single local source at a much lower altitude, during a few days only. In contrast, plutonium isotopic ratios associated with the global fallout are homogeneous (Kelley et al., 1999) and ^{241}Pu/^{239}Pu isotopic ratios may be used in particular to calculate the respective plutonium concentrations originating from the FDNPP accident or the global fallout. Due to the relative short half-life of ^{241}Pu (14.35 y), the global fallout source of this isotope has decayed significantly, whereas plutonium released by the FDNPP accident contains abundant levels of ^{241}Pu (1.1×10^{11}–2.6×10^{11} Bq (Zheng et al., 2012)). Its detection in the environment therefore provides unambiguous evidence of the FDNPP release (Evrard et al., 2014b).

The plutonium isotopic composition in the fuel from the FDNPP was reconstructed at the moment of the accident based on simulations (Kirchner et al., 2012; Nishihara et al., 2012; Schwantes et al., 2012) (Table 1). The global fallout atom ratios were also quantified based on multiple sample analyses (Kelley et al., 1999; Muramatsu et al., 2003; Yang et al., 2015; Zhang et al., 2010) (Table 1). The fate of FDNPP-derived plutonium can therefore be investigated in the environment based on ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotopic ratios as demonstrated by Evrard et al. (2014b).

Zheng et al. (2013) published a comprehensive review of plutonium releases from the FDNPP accident. Since then, additional measurements reported by various authors on litter, soil, and river water samples collected in the Fukushima Prefecture after the accident indicated that some environmental samples contained plutonium from the FDNPP reactors (Kimura et al., 2015; Utsunomiya et al., 2012; Xu et al., 2016) (Table S1, Fig. 1). However, these studies were mainly based on measurements by alpha-spectrometry of the $^{239+240}$Pu and ^{238}Pu activities and of the ^{238}Pu/$^{239+240}$Pu isotopic ratio. Using alpha-spectrometry, FDNPP-derived plutonium was detected only in a few samples located near the plant, because alpha-spectrometry lacks in sensitivity and energy resolution to measure the ^{240}Pu/^{239}Pu isotopic ratio. As a beta-emitter, ^{241}Pu is not measurable by alpha-spectrometry and its analysis by beta-spectrometry has relatively poor detection limits (minimum of 10 mBq) (Rosner et al., 1992) compared to those obtained by mass spectrometry. ^{242}Pu has a very long half-life and cannot be measured efficiently by alpha-spectrometry at the ultra-trace level. Finally, ^{242}Pu is often used as an isotope dilution tracer for alpha spectrometry measurements.

In contrast, all plutonium isotopes, with the exception of ^{238}Pu (because of the presence of ^{238}U isotopes), can be measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with a high accuracy. As mentioned in the literature review by Zheng et al. (2013), and summarized in Table S1 and Fig. 1, ^{241}Pu and ^{242}Pu were only measured in a few studies, even though these isotopes are powerful tracers for identifying different sources of plutonium.

The objective of this current research was therefore to investigate the temporal variations of plutonium contamination in flood sediment in order to improve our understanding of plutonium dynamics in the FDNPP fallout-impacted region. As plutonium is strongly bound to the fine sediment mineral fraction (Kersting, 2013; Meusburger et al., 2016), plutonium may be eroded, deposited and remobilised during rainfall events (Ministry of Land Infrustructure and Transport, 2006; Yoshimura et al., 2005). In the Fukushima Prefecture, soil erosion and sediment transport were shown to be exacerbated during the typhoon season (Chartin et al., 2013; Evrard et al., 2013; Yamashiki et al., 2014).

Two types of samples were collected and analysed: i) recently deposited flood sediment collected at four sampling locations and in three different years to investigate the evolution of plutonium concentration and composition in a coastal catchment of the Fukushima Prefecture; and ii) soil samples collected at five sampling locations across the main radioactive plume to characterize the initial deposition of FDNPP-originating plutonium and compare its spatial pattern with that of the well-documented radiocaesium contamination plume (Chartin et al., 2013). To the best of our knowledge, this study represents the first attempt to characterise

Table 1
Estimates of the plutonium isotopic atom ratios in FDNPP at the time of the reactor shutdown and measured isotopic ratios of fallout plutonium in soils of the region representative of global fallout. Uncertainties associated with ratios of global fallout are extended with a confidence level of 95% (coverage factor of 2).

		^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu	^{242}Pu/^{239}Pu
FDNPP	Nishihara et al. (2012)			
	Reactor 1	0.344	0.1921	0.0662
	Reactor 2	0.320	0.1922	0.0630
	Reactor 3	0.356	0.1827	0.0620
	Schwantes et al. (2012)	0.447	0.1962	
	Kirchner at al. (2012)	0.395	0.1738	
Mean		0.373 ± 0.044	0.1874 ± 0.0081	0.0637 ± 0.0026
Global Fallout	Kelley et al. (1999)			
	Average - Northern Hemisphere soils (30°-71°N)	0.180 ± 0.014	0.0011 ± 0.0001	0.0039 ± 0.0007
	Sapporo, Japan	0.177 ± 0.002	0.0011 ± 0.0001	0.0038 ± 0.0002
	Tokyo, Japan	0.176 ± 0.002	0.0010 ± 0.0001	0.0035 ± 0.0002
	Zhang et al. (2010)	0.192 ± 0.003	0.0026 ± 0.0003	
	Zhang et al. (2010)	0.192 ± 0.004	0.0029 ± 0.0006	
	Muramatsu et al. (2003)	0.179 ± 0.001		
	Yang et al. (2015)	0.183 ± 0.011		
Mean		0.181 ± 0.005	0.0015 ± 0.0003	0.0037 ± 0.0005