Applied Geochemistry 85 (2017) 194–200

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Radionuclide pollution inside the Fukushima Daiichi exclusion zone, part 2: Forensic search for the “Forgotten” contaminants Uranium-236 and plutonium

Stephanie Schneider [a], Stefan Bister [a], Marcus Christl [b], Mayumi Hori [d], Katsumi Shozugawa [c], Hans-Arno Synal [b], Georg Steinhauser [a], Clemens Walther [a, *]

[a] *Leibniz Universität Hannover, Institut für Radioökologie und Strahlenschutz, D-30419 Hannover, Germany*
[b] *Laboratory of Ion Beam Physics, ETH Zürich, CH-8093 Zürich, Switzerland*
[c] *Graduate School of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo, Japan*
[d] *Komaba Organization for Educational Excellence (KOMEX), The University of Tokyo, Meguro-ku, Tokyo, Japan*

ARTICLE INFO

Article history:
Received 30 January 2017
Received in revised form
26 May 2017
Accepted 27 May 2017
Available online 29 May 2017

Keywords:
Fukushima nuclear accident
Plutonium
Uranium-236
Accelerator mass spectrometry

ABSTRACT

In the course of the Fukushima Daiichi nuclear accident (March 2011), large quantities of radionuclides, mainly of the volatile elements such as cesium and iodine were released to the environment. In small amounts non-volatile elements such as plutonium and uranium have also been released. For this study vegetation, litter and soil drill core samples were taken in 2013 and 2015 in the contaminated area in Fukushima prefecture. In 2015 the samples were taken as close to the sampling locations of the 2013 campaign as possible. To investigate the origin of plutonium and uranium the isotopic ratios ^{240}Pu/^{239}Pu and ^{236}U/^{238}U were measured using accelerator mass spectrometry. While the determined ^{240}Pu/^{239}Pu ratios indicate global fallout as the plutonium source for most samples, reactor plutonium of the reactors of Fukushima Daiichi is identified unambiguously in some vegetation and litter samples. This assumption is corroborated by the detection of ^{236}U. None of the samples contained higher plutonium activity concentrations than in the rest of Japan, caused by global fallout. This holds even for the samples where the reactors were identified as the source from the isotope ratios. This and the strong localization, even for neighboring sampling sites, indicate that the overall small quantities of plutonium were most likely released in the form of particulate matter.

1. Introduction

On March 11, 2011 the earthquake and the following tsunami at the east coast of Japan caused serious damage of the Fukushima Daiichi nuclear power plant (NPP). During venting operations and several hydrogen explosions in the course of the accident at the Fukushima Daiichi NPP large amounts of radionuclides were released and contaminated parts of the Japanese landscape and the Pacific Ocean. Mainly volatile fission products such as ^{131}I, ^{132}Te, ^{134}Cs, and ^{137}Cs were released (Steinhauser et al., 2014). The release of non-volatile elements including the actinides (especially plutonium) was of public concern, because of the large radiological risk caused by plutonium mainly upon inhalation (ICRP, 2012; Steinhauser, 2014).

For the determination of the sources of the actinides uranium and plutonium in the environment, it is important to distinguish these from the other possible sources. Plutonium and the anthropogenic uranium isotope ^{236}U were released mostly during the atmospheric nuclear explosions up to the 1960s and were spread globally and can be detected in the environment. The isotopic ratios ^{240}Pu/^{239}Pu and ^{236}U/^{238}U can be used as a fingerprint and are helpful to distinguish between global fallout or releases from a nuclear reactor or other possible sources (Buesseler, 1997; Sakaguchi et al., 2012; Steier et al., 2008; Cagno et al., 2014).

In several previous studies, the release of plutonium isotopes (Zheng et al., 2012; Schneider et al., 2013; Yamamoto et al., 2012; Xu et al., 2016; Yamamoto et al., 2014; Imanaka et al., 2012; Tanaka et al., 2014; Steinhauser et al., 2015) and ^{236}U (Sakaguchi et al., 2014; Shinonaga et al., 2014; Yang et al., 2016) from the Fukushima Daiichi NPP into the environment was exemplified.

---

* Corresponding author.
E-mail address: walther@irs.uni-hannover.de (C. Walther).

http://dx.doi.org/10.1016/j.apgeochem.2017.05.022

Characteristic isotopic ratios of reactor plutonium were determined by Zheng et al. (2012) mainly in litter samples or in upper soil layers and especially in black dust samples investigated by Sakaguchi et al. (2014) and Yamamoto et al. (2014). Also in their investigations most samples contained mainly or exclusively global fallout plutonium. The activity concentrations showed no relevant increase compared to the background activity concentrations measured in surface soil samples collected around the 1970s in central-eastern Japan prior to the accident in a range of 0.004–1.46 Bq/kg (Yang et al., 2015). This is true even for samples taken at the site of the Fukushima Daiichi Power Plant with elevated plutonium isotope ratios demonstrating the reactor as the source (Yamamoto, 2012). In previous investigations ^{236}U activity concentrations up to 6.74 * 10^{-4} Bq/kg were determined in black substances (Sakaguchi et al., 2014). Publications on ^{236}U, are very sparse and show values of ^{236}U/^{238}U = 10^{-8} to 10^{-7}. Only in aerosol filters, higher ratios of ^{236}U/^{238}U = 10^{-6} could be measured by Shinonaga et al. (2014) in the days after the accident. These investigations lead to the assumption that plutonium and uranium were released during the same events in small quantities. That (a) gross Pu activity concentrations remain at the level of global fallout even when the isotope ratio clearly indicates presence of reactor Pu and (b) the reactor Pu is distributed rather inhomogenously hints at a release in particulate form (Schneider et al., 2013).

In this study we investigated the isotopic ratio and the activity concentrations of the plutonium isotopes ^{239}Pu and ^{240}Pu and the uranium isotope ^{236}U in soil, litter and vegetation samples. These samples were taken in different years but at the same places, so it is possible to compare the values at the same sampling sites and to obtain an overview about the behavior in the environment of the investigated isotopes, especially of the migration in the soil using soil drill cores.

2. Materials and methods

2.1. Samples

The samples were taken at several sites in the vicinity of the damaged power plant in June 2013 and May 2015, see Fig. 1. In 2015 samples were taken as close to the sampling location of 2013 as possible. Exact locations are given in Table 1. At each sampling site vegetation and litter samples and a soil drill core up to a depth of about 15 cm were taken. Each soil drill core was sliced into six nearly equal parts with a thickness of about 2.5 cm, each.

2.2. Sample preparation

All samples were dried at 105 °C. The activity concentrations are referring to this dry mass. Before further processing larger stones with diameters more than 0.5 cm were removed from the litter and soil samples. Additionally, in the soil samples of 2015 the soil skeleton was removed. For the γ−ray spectrometric measurements (only for the samples taken in 2015) the homogenized sample material was pressed into Petri dishes with a diameter of 5.5 cm for the soil samples and 8.5 cm for the litter samples. After the measurement of γ−ray emitting nuclide, the dried material of the soil and litter samples were incinerated at temperatures of up to 450 °C and the vegetation samples at up to 600 °C. The choice of the right incineration temperature of geological samples was shown to be a possible source of error previously (Wang et al., 2015). For further investigations, we used about 10 g ash of the litter and soil samples and approx. 1 g ash of the plant samples. Each sample was spiked with 5 pg ^{242}Pu and 5 pg ^{233}U. For the digestion, concentrated nitric acid and concentrated hydrofluoric acid were used. After the digestion, the samples were filtered. The chemical separation of plutonium was performed by extraction chromatography using Eichrom® TEVA resin (Bisinger et al., 2010). In this step the uranium was separated from the plutonium. To remove interfering isotopes in the uranium fraction, a second extraction chromatography was performed using Eichrom® UTEVA resin. For the purification of the plutonium fraction, a second separation step was applied to optimize the separation of uranium and plutonium. The plutonium and uranium samples were co-precipitated by ferric hydroxide. To remove perturbing compounds, a centrifuge step was implemented and the residue was washed with methanol. The washed residue was transferred into porcelain crucibles and converted into ferric oxide by heating up to 800 °C. Finally, the plutonium and uranium samples, respectively were mixed with niobium powder in a ratio of 1:1 and pressed into aluminum AMS target holders.

2.3. AMS measurement

U and Pu samples were measured at the compact low energy AMS system Tandy at ETH Zurich. The measured ^{236}U/^{238}U and ^{233}U/^{238}U ratios were normalized to the ETH Zurich in-house standard ZUTRI, with nominal values of $(4055 \pm 200) \times 10^{-12}$ and (33.17 ± 0.83) x 10^{-9}, respectively (Christl et al., 2013). The estimated instrumental background for ^{236}U/^{238}U analyses at ETH Zurich is at the level of 10^{-14} (Christl et al., 2015). The ^{236}U data was corrected for ^{236}U impurities carried by the ^{233}U spike.

The measured Pu-isotopic ratios were normalized to the ETH in-house standard CNA (Christl et al., 2013). No background corrections had to be applied for ^{239}Pu due to the high abundance sensitivity (suppression of ^{238}U tailing) of the AMS system. The reported activity concentrations and ^{240}Pu/^{239}Pu ratios were corrected for ^{239}Pu and ^{240}Pu impurities carried by the ^{242}Pu spike.

3. Results

3.1. Plutonium

The AMS results of the isotopic ratio ^{240}Pu/^{239}Pu of both sampling campaigns and the activity concentration $^{239+240}$Pu of the samples taken in 2013 are listed in Table 1 in the Supporting Information. For signals below the detection limit but above the decision threshold, no value for the activity concentration could be determined and consequently only upper limits for the ratios are given. These upper limits were only calculated if the signals were below the detection limit but above the decision threshold. In this case the value of the detection limit was used for the calculation of the ratio as an upper limit. Depth profiles of the isotopic ratio and the activity concentration for the samples taken in 2013 are shown in Fig. 2 and Fig. 3, sorted by each sampling spot. The depth profile of the ratio of the samples taken in 2015 is shown in Fig. 4.

For most samples of both campaigns the ^{240}Pu/^{239}Pu ratio ranges from 0.17 to 0.19, which represents a typical signature for global fallout. Only eight samples show higher ratios of ^{240}Pu/^{239}Pu = 0.27 to 0.48. These values are considerably higher than the omnipresent fallout from the nuclear weapon tests and characteristic for plutonium derived from a nuclear reactor (ca. 0.32–0.36 (Nishihara et al., 2012)). The activity concentrations $^{239+240}$Pu measured for the samples taken in 2013 show values in the range of 0.01–2.34 Bq/kg. This is similar to and even lower than the range of plutonium of global fallout of 0.15–4.31 Bq/kg which was measured in Japan before the Fukushima accident (Zheng et al., 2012). Fig. 3 shows clearly very low activities. For most samples the highest activity was measured in the top 7.5 cm of the soil samples at Spot F, which was taken at the main gate of the Fukushima Daiichi nuclear power plant. No correlation between the activity concentrations and the isotopic ratios was identified.