Microchemical Journal 118 (2015) 158–165

Contents lists available at ScienceDirect

Microchemical Journal

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

Temporal variations of accumulated cesium in natural soils after an uncharacteristic external exposure

Hikaru Sawai [a,*], Ismail M.M. Rahman [a,b,*], Chao Lu [a], Yoshinori Tsukagoshi [a], Zinnat A. Begum [a], Teruya Maki [c], Hiroshi Hasegawa [c,*]

[a] Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan
[b] Department of Applied and Environmental Chemistry, Faculty of Science, University of Chittagong, Chittagong 4331, Bangladesh
[c] Institute of Science and Engineering, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

ARTICLE INFO

Article history:
Received 6 August 2014
Received in revised form 8 September 2014
Accepted 8 September 2014
Available online 16 September 2014

Keywords:
Cesium
Accidental exposure
Soil contamination
Solid-phase distribution
Sequential fractionation
Temporal variation

ABSTRACT

The accumulation behaviors and solid phase partitioning patterns of stable cesium, which have been recognized as an indicator of the long-term movement of radioactive cesium (^{137}Cs or ^{134}Cs) in ecosystems, were studied in typical and natural soils of Japanese origin, namely, red clay, leaf-mold and andosol soils. The retention and migration of soil-phase cesium have been explained relative to various factors, such as soil organic matter contents, competitive cation concentrations and the adsorption ratio of Cs to the solid phase. Cesium was adsorbed nearly quantitatively in the leaf-mold type soil, and the rate of Cs absorption increased as the particle size decreased in the red clay and andosol soils. The distributions of Cs within the soil solid phases were defined using the selective sequential extraction scheme and were used to explain its relative incorporation in the soil fractions. Solid phase fractionation indicated that nearly half of the total cesium concentrations in the soils were in the 'residual' fraction (representing the metal that was incorporated within the crystalline lattice of the soil and was difficult to extract). These findings are expected to provide information regarding suitable conditions for remediation, immobilization or the recovery of cesium from contaminated soils with excess cesium concentrations.

1. Introduction

Waste disposal operations or accidental releases due to nuclear-technology-related activities have resulted in the release of large amounts of radionuclides into the environment. The accidental release of radionuclides has been a topic of interest for years, beginning with the catastrophic nuclear accident that occurred on 26 April 1986 at the Chernobyl Nuclear Power Plant [1,2]. The Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident that resulted from an earthquake and subsequent tsunami on March 11, 2011 is the most recent example of such a catastrophe. Following the FDNPP accident, a large number (~500) of studies were published that covered the various aspects of the accident. Sorting these published articles by topic in the ISI-listed journals indicated that the studies mainly focused on radioactivity monitoring in places with foods. This trend becomes obvious when considering the importance of estimating the effects of fallout on human health. Approximately 80% of the FDNPP-generated fallout in the contamination zone affected agriculture, including forests [3]. However, very few publications have discussed the effects of fallout on agriculture, including soil contamination due to the extended radionuclide emissions [4–7].

Among the radioactive materials, the dispersion of radiocesium at elevated concentrations evokes concern due to its extended solubility characteristics as an alkaline metal ion, its comparatively longer half-life, and its easy incorporation into living beings [8–10]. The most notable radiocesium isotope is ^{137}Cs, which has a half-life of 30.2 years [11], is abundant in nuclear wastes and in radioactive fallout and can contaminate large areas of agricultural land [12–15]. The FDNPP accident resulted in an estimated atmospheric release of 1.3×10^{16} Bq of ^{137}Cs over four weeks (March 12 and April 6, 2011) [16]. Approximately 10–20% of the emitted radiocesium was deposited over the terrestrial soils in northeastern Japan [15,17]. The accumulated radiocesium in soils is a threat because plants can take up Cs [18]. Thus, it is important to understand the accumulation and dissemination patterns of radiocesium in the soil to assess the potential health risks of Cs contamination or its impacts on food production after over-exposure occurs. Moreover, radiocesium (particularly ^{137}Cs) is extremely useful for quantifying soil erosion and deposition risks in forested and agricultural areas where knowledge regarding diffusion processes is important [19,20].

The fate of radiocesium in the environment and its subsequent migration in soils depends on its physico-chemical form and commonly

---

* Corresponding authors. Tel./fax: +81 76 234 4792.
E-mail addresses: hikaru.sawai@gmail.com (H. Sawai), I.M.M.Rahman@gmail.com, I.M.M.Rahman@cu.ac.bd (I.M.M. Rahman), hhiroshi@se.kanazawa-u.ac.jp (H. Hasegawa).

http://dx.doi.org/10.1016/j.microc.2014.09.006
0026-265X/© 2014 Elsevier B.V. All rights reserved.

follows the behavior of its stable form [9,21,22]. For example, previous research indicated that the soil-to-plant transfer factor of ^{137}Cs follows a pattern that is similar to stable Cs [22–26]. In addition, analogous distributions of ^{137}Cs have been observed in different rice components relative to stable ^{133}Cs species [27,28].

The objective of this study is to investigate the cesium distribution in the operationally defined physico-chemical and particle size fractions of soils to understand the temporal variations of cesium after being released at an uncharacteristic rate.

2. Experimental

2.1. Instruments

The atomic absorption spectroscopy (AAS) technique was used to determine the stable cesium concentration in solution. An AAnalyst 600 (PerkinElmer, Waltham, MA) was used that was equipped with a transverse heated graphite atomizer with an integrated, pyrolytic graphite coated platform and a longitudinal Zeeman-effect background corrector. The light source was an electrodeless discharge lamp (EDL) that was powered by an EDL System II that was operated at 18 mA. The wavelength was set at the 852.1 nm resonance line and the monochromator spectral bandpass was set at 0.7 nm. In addition, a baseline offset correction time at 2.0 s was used with a read delay of 0.0 s. Argon was used as the purge gas at a flow of 250 mL min^{-1}. The temperature sequence was 110 (drying), 130 (drying), 750 (ashing) and 1900 °C (atomization), which were performed for 30, 30, 20 and 4 s, respectively. The loading volume was 20 μL, with 20 μL of the sample and matrix-modifier (1% H_2SO_4). Calibration was conducted thereby using three standard solutions that contained 0.01, 0.05 and 0.1 mg L^{-1} cesium.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to detect the co-existing trace metals (e.g., Al, Ca, Fe, K, Mg, Mn and Na) in solution. For this analysis, an iCAP 6300 instrument from Thermo Fisher Scientific (Waltham, MA) was used that included an EMT duo quartz torch, a glass spray chamber and a concentric glass nebulizer. A radio frequency power of 1.15 kW was used at the torch, the plasma, auxiliary and nebulizer gas flows were maintained at 12, 1 and 0.5 L min^{-1}, respectively, and an integration time of 30 s was used.

The microwave-assisted reaction was used to digest the soil samples. For this analysis, a Multiwave 3000 instrument from Anton Paar GmbH (Graz, Austria) was used that was equipped with an 8-position rotor and hydraulic pressurized sensing system for all vessels. The vessels (XF100) supported a controlled pressure of 6 MPa, a maximum operating pressure of 12 MPa and a maximum temperature of 240 °C.

A KDF S-8 muffle furnace from Kenis Scientific (Osaka, Japan), a Digiprep Jr block heater from SCP Science (Quebec, Canada) and a DX 600 oven from Yamato Scientific (Tokyo, Japan) were used for heating or drying.

Ultrapure water with a resistivity >18.2 MΩ cm was prepared using the Arium Pro UV water purification system from Sartorius Stedim Biotech GmbH (Göttingen, Germany). The pH measurements were performed using a Navi F-52 pH meter from Horiba Instruments (Kyoto, Japan).

Each instrumental measurement or treatment procedure was performed in three replicates and the resulting averaged value is reported.

2.2. Materials

2.2.1. Soil samples

The soil samples represented three soil types that are common in most regions of Japan (including the Fukushima), red clay, leaf-mold and andosol soils. A large amount (approximately 5 kg) of each soil type was collected from representative locations in Kanazawa, which is located on the Sea of Japan and is bordered by the Japanese Alps. The soil samples were dried for 24 h at 60 °C before separating into size fractions of 2000–212 μm (coarse sand; SF-1), 212–63 μm (fine sand; SF-2), and <63 μm (silt and clay; SF-3) with the use of grading sieves based on the ISO 14688-1 classification of soils [29].

2.2.2. Chemicals and laboratory wares

Analytical grade commercial products were used throughout the study. Cesium nitrate salt and the standard cesium solution (as CsCl) were obtained from Kanto Chemical (Tokyo, Japan) and were used to prepare the working standards. In addition, the HF, HNO_3, H_2SO_4, HCl and NaOH were obtained from Kanto Chemical (Tokyo, Japan) and were used for the decomposition experiments or as mentioned below. Magnesium chloride from Merck KGaA (Darmstadt, Germany), acetic acid from Tama Chemicals (Kanagawa, Japan), hydroxylamine chloride from Wako Pure Chemical (Osaka, Japan), and hydrogen peroxide from Kanto Chemical (Tokyo, Japan) were used during the extraction experiments. The HCl and NaOH solutions (1 mol L^{-1}) were used to adjust the solution pH. Working solutions were prepared from the stock solutions by diluting with ultrapure water on a weight basis.

Low-density polyethylene (PE) bottles from Nalge Nunc (Rochester, NY), screw-capped PE tubes from AS ONE (Osaka, Japan), conical polypropylene centrifuge tubes (Biologix Research, Lenexa, KS), and micropipette tips from Nichiryo (Tokyo, Japan) were used throughout the study. The laboratory equipment was washed by soaking in Scat 20X-PF alkaline detergent from Nacalai Tesque (Kyoto, Japan) overnight and then overnight in 4 mol L^{-1} HCl before rinsing with ultrapure water after each step.

2.3. Methods

2.3.1. Preparation of Cs-contaminated soil samples

The granulometric fractions of the dried soils (3 g) were spiked with 30 mL of a standard solution containing 5 mg L^{-1} cesium (as CsCl). The

Table 1
Chemical interpretation and the extraction conditions of the protocol that was used for fractionating the solid phase cesium from the soil.

Fraction	Chemical interpretation	Extraction conditions (for 0.25 g soil)			
		Extractants and other conditions	Duration	Temp.	Agitation
			h	°C	
F1	Exchangeable	1 M $MgCl_2$ (pH 7; 4 mL)	1	25 ± 2	Continuous
F2	Acid soluble [a]	1 M NaOAc (pH 5, adjusted with acetic acid; 4 mL)	5	25 ± 2	Continuous
F3	Reducible [a]	0.04 M $NH_2OH \cdot HCl$ in 25% (*v*/*v*) acetic acid (10 mL)	6	96 ± 3	Occasional
F4	Oxidisable [a]	0.02 M HNO_3 (3 mL) + 30% H_2O_2 (pH 2, adjusted with HNO_3; 2.5 mL)	2	85 ± 3	Occasional
		30% H_2O_2 (pH 2, adjusted with HNO_3; 1.5 mL)	3	85 ± 3	Intermittent
		3.2 M NH_4OAc in 20% (*v*/*v*) HNO_3 (2.5 mL)	0.5	85 ± 3	Continuous
F5	Residual	Microwave-assisted acid decomposition [b]	–	–	–

[a] The fraction names 'acid-soluble', 'reducible' and 'oxidisable' were originally called 'bound to carbonates', 'bound to iron and manganese oxides' and 'bound to the organic matter' by Tessier, et al. [30].

[b] The detailed microwave-assisted acid decomposition procedure for determining the soil cesium contents is available in Section 2.3.5.