Chapter 3
Isotopic Ratio of ^{135}Cs/^{137}Cs in Fukushima Environmental Samples Collected in 2011

Takumi Kubota, Yuji Shibahara, Tomoko Ohta, Satoshi Fukutani, Toshiyuki Fujii, Koichi Takamiya, Satoshi Mizuno, and Hajimu Yamana

Abstract The isotopic ratios of radioactive cesium derived from the Fukushima accident were determined by γ-spectrometry and thermal ionization mass spectrometry (TIMS). In order to ascertain the initial ratios at the time of the accident, environmental samples collected during 2011 were used for the analysis. Soil, litter, and seaweed were incinerated, and the cesium contained therein was adsorbed into ammonium phosphomolybdate powder. The cesium in the seawater was adsorbed into AMP-PAN resin (Eichrom Technologies, LLC); its recovery ratio was almost one without the carrier being added. Incinerated samples and the AMP-PAN resin were then measured by γ-spectrometry. The cesium solution recovered from adsorbers was subjected to TIMS measurements. The isotopic ratios of ^{134}Cs/^{137}Cs and ^{135}Cs/^{137}Cs were found to be independent of the type of sample in question, as well as the sampling location; the ratios were 0.07 and 0.36 (decay correction: 11 March 2011), respectively, which differ from the results of atmospheric nuclear tests (i.e., 0 and 2.7, respectively). This difference in the ratio of ^{135}Cs/^{137}Cs will contribute to estimations of the origin of radioactive contamination in the future.

Keywords Thermal ionization mass spectrometry • Fukushima accident • Environmental samples • Isotopic ratio of ^{135}Cs/^{137}Cs and ^{134}Cs/^{137}Cs

3.1 Introduction

The Fukushima Daiichi Nuclear Power Plant (FDNPP) disaster gave rise to the release of a large amount of radioactive material into the environment [1–3]. Radioactive cesium nuclides were spread and stored in east Japan because of

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T. Kubota (✉) • Y. Shibahara • S. Fukutani • T. Fujii • K. Takamiya • H. Yamana
Research Reactor Institute, Kyoto University, Kumatori, Osaka 590-0494, Japan
e-mail: t_kubota@rri.kyoto-u.ac.jp

T. Ohta
Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

S. Mizuno
Nuclear Power Safety Division, Fukushima Prefectural Government, Fukushima 960-8043, Japan

their high volatility and long half-life. However, global fallout from atmospheric nuclear tests was the main contaminant source before the Fukushima accident [4]. Yellow sand, which flies from China in the spring, is known to contain radioactivity from atmospheric nuclear tests [5]. In addition to this periodic input, it is possible that radioactive contaminants from the Fukushima accident may be present. Even though the radioactive materials are found somewhere in the future, the environment can be considered to be the same situation before the Fukushima accident as long as they originate from the global fallout; in other words, the environment is not contaminated by the Fukushima accident. The migration of contaminants from the Fukushima accident is an important factor in resolving the Fukushima accident. It is natural that radioactive materials will be found even in locations far from Fukushima, such as west Japan, because of the global fallout. It is therefore important, from the perspective of future studies on Fukushima, to determine whether such contaminants originate from the Fukushima accident or not.

The use of nuclear energy, both in terms of nuclear reactors and nuclear weapons, provides several radioactive cesium nuclides in its products. The different production history in the two processes, however, results in different isotopic ratios of cesium. ^{134}Cs is produced as a result of neutron irradiation of ^{133}Cs, which can originate as a fission product. On the other hand, the production amount of ^{134}Cs in nuclear tests can be ignored because nuclear reactions and neutron irradiation cease after an extremely short period of time. Accordingly, ^{134}Cs is considered to be contaminant in nuclear reactors. Although ^{135}Cs and ^{137}Cs are produced as direct fission products, the production of ^{135}Cs is affected by neutron irradiation conditions. Because ^{135}Xe, which is the parent nuclide of ^{135}Cs, has a large neutron capture cross section, the production of ^{135}Cs is suppressed in long periods of neutron irradiation; this results in the isotopic ratio of ^{135}Cs/^{137}Cs from nuclear reactors being different from that of nuclear tests. In this way, the isotopic ratios of Cs (e.g., ^{134}Cs/^{137}Cs and ^{135}Cs/^{137}Cs) can reveal the origin of contaminants in the environment.

Isotopic ratios can be determined in two ways: γ-spectrometry and mass spectrometry. It is easy to measure ^{134}Cs and ^{137}Cs by γ-spectrometry, a nondestructive analysis method. However, the ^{135}Cs of pure beta emitter cannot be measured, and the decay of ^{134}Cs (with a relatively short half-life) prohibits the isotopic analysis. On the other hand, mass spectrometry can determine the presence of ^{134}Cs, ^{135}Cs, and ^{137}Cs nuclides after chemical and/or physical purification. The measurement of ^{135}Cs permits isotopic analysis even after the ^{134}Cs has decayed out. Mass spectrometry can potentially be hindered by isobar nuclides; however, thermal ionization mass spectrometry (TIMS) with a high signal-to-noise ratio sufficiently suppresses the isobar effect. In the ionization process, isobar nuclides (in this study, cesium and barium) are separated according to their different ionization energies. We investigated various environmental samples by using TIMS [6], which is suitable for determining the isotopic ratios of radioactive cesium in the environment for long periods of time.

The isotopic ratio of ^{135}Cs/^{137}Cs determined by TIMS can estimate the origin of contamination in environmental samples; this process requires the ratio at the time

of Fukushima accident to be used as the initial value. The initial values in various samples – not only soil and litter but also seawater and seaweed – are important factors in discussing the migration and mixing of radioactive cesium released in the Fukushima accident, other accidental releases, and atmospheric nuclear tests. In this study, the isotopic measurement of the various samples collected from May to September 2011 was conducted by γ-spectrometry and TIMS.

3.2   Materials and Methods

The environmental samples were collected in Fukushima prefecture from May to September 2011, and four of them were subjected to analysis. A litter sample was collected along Route 399 in Iitate village, where severe contamination was observed. Seawater and seaweed samples were collected at the Matsushita beach in Iwaki city. A soil sample was collected in Hinoemata village, which is one of the Fukushima local government's sampling plots.

Before analyzing the specific activity and isotopic ratios of cesium, the samples collected were treated as follows. The soil sample was dried at 105 °C and sieved through a 2 mm screen in order to remove pebbles, tree roots, and leaves; it was then incinerated at 450 °C in order to disintegrate organic matter. The litter sample was dried, cleaned by hand, and then incinerated. The seaweed sample was dried and incinerated without cleaning. An aliquot of these incinerated samples was dissolved in HNO_3 and then purified with ammonium phosphomolybdate (AMP) [6] in order to recover the cesium fraction. The seawater sample was treated with AMP-PAN in order to concentrate the cesium, which was eluted with NH_4OH.

The radioactivity of ^{134}Cs and ^{137}Cs in incinerated samples and AMP-PAN was measured by γ-spectrometry. The radioactivity was measured with a HPGe semiconductor detector, which was calibrated with a standard radioactive source of ^{137}Cs (662 keV) and ^{60}Co (1132 and 1337 keV) [7]. Each sample was placed apart from the detector, thereby reducing the coincidence summing effect in the determination of ^{134}Cs. In this case, the lower detection limit would rise; however, the radioactivity in samples was sufficiently high and could therefore be determined in this study. The isotopic ratios of ^{134}Cs/^{137}Cs and ^{135}Cs/^{137}Cs in the purified cesium fraction were measured by TIMS. The isotopic ratios of ^{134}Cs/^{137}Cs and ^{135}Cs/^{137}Cs were determined by TIMS, and a TaO activator was used to enhance the counting efficiency. The effect of isobaric barium can be ignored owing to the fact that it has a different ionization energy than cesium does [6].

3.3   Results and Discussion

In the analysis of radioactive cesium nuclides in seawater by γ-spectrometry, the natural cesium carrier is ordinarily added into the recovery process of cesium because of its low concentration. The addition of the carrier in mass spectrometry

Table 3.1 Specific activity of ^{137}Cs in AMP-PAN resin and the ^{137}Cs recovery ratio

	Weight (g)	Radioactivity of [137]Cs (Bq)	Specific activity (Bq/kg)	Recovery ratio
1st column	0.87	16.4 ± 0.2		
2nd column	1.49	12.8 ± 0.2		
Total (15 kg seawater)		29.2 ± 0.3	1.95 ± 0.02	0.97 ± 0.10
Initial [7]			2.0 ± 0.2	

Table 3.2 Radioactivity of [134]Cs and ^{137}Cs as determined by γ-spectrometry

Sample	Dry weight (g)	Radioactivity		Radioactivity ratio of [134]Cs/[137]Cs	Collection date	Location
		[134]Cs (Bq)	[137]Cs (Bq)			
Soil	12.98	3.4 ± 0.3	4.0 ± 0.1	0.87 ± 0.07	15 September 2011	Hinoemata
Litter	15.90	6562 ± 57	6194 ± 43	1.06 ± 0.01	23 May 2011	Iitate
Seaweed	17.78	10.4 ± 0.5	10.7 ± 0.2	0.97 ± 0.05	25 August 2011	Iwaki
Seawater	AMP-PAN	28.9 ± 0.9	29.2 ± 0.3	0.99 ± 0.03	25 August 2011	Iwaki

could prevent to detection of the signal isotopes of interest by isotope dilution, thereby decreasing isotopic ratios below detection limit and covering with large signal from the carrier added. A seawater sample of known concentration was used in order to confirm qualitative recovery without adding the carrier. The seawater sample was treated with HNO_3 to pH 1 and then passed through two columns, connected in series and filled with AMP-PAN, at a rate of 5 kg/d. The specific activity of ^{137}Cs and the recovery ratio onto the AMP-PAN resin, listed in Table 3.1, show that an AMP-PAN resin of about 2.5 g is sufficient for completely extracting cesium isotopes from 15 kg of seawater.

The specific activity in environmental samples (as determined by γ-spectrometry) and the activity ratio of [134]Cs/^{137}Cs are listed in Table 3.2. The specific activity depends on the type of sample in question and the distance of the collection point from the FDNPP. However, the activity ratio shows that the contamination was derived from the Fukushima accident, although the activity ratio for soil collected at Hinoemata village is slightly low. The activity ratios were converted to isotopic ratios, which were then compared to the results of TIMS (see below).

The results of TIMS measurements are listed in Table 3.3, where the isotopic ratios evaluated from the results of γ-spectrometry are also listed. Among the four samples – litter, soil, seaweed, and seawater – only the litter sample yielded isotopic ratios for both [134]Cs/^{137}Cs and [135]Cs/[137]Cs. In particular, the intensity of the signal from the soil sample was too low to evaluate both isotopic ratios. Other elements obviously interfered with the mass spectrometry measurements of the seaweed sample, and thus neither isotopic ratio was evaluated. Both evaluation failures were probably caused by inadequate processes and/or the shortcomings of the purification

Table 3.3 Isotopic ratio of ^{134}Cs/^{137}Cs and ^{135}Cs/^{137}Cs as determined by γ-spectrometry and thermal ionization mass spectrometry (TIMS)

Sample	Isotopic ratio of ^{134}Cs/^{137}Cs		Isotopic ratio of ^{135}Cs/^{137}Cs	Distance from FDNPP	Reference
	γ-spectrometry	TIMS			
Soil	0.059 ± 0.005	Not detected	Not detected	WSW, 160 km	This work
Litter	0.073 ± 0.001	0.0691 ± 0.0014	0.3574 ± 0.0020	NW, 34 km	
Seaweed	0.067 ± 0.003	Not evaluated	Not evaluated	SSW, 55 km	
Seawater	0.068 ± 0.003	Not evaluated	0.3617 ± 0.0051	SSW, 55 km	
Grass	0.069 ± 0.009	0.0722 ± 0.0004	0.3622 ± 0.0006	NW, 42 km	[6]
Bark	0.067 ± 0.002	0.0698 ± 0.0005	0.3663 ± 0.0005	NNW, 3 km	
Root	0.069 ± 0.001	0.0684 ± 0.0008	0.3586 ± 0.0008	WNW, 8 km	
Moss	0.070 ± 0.000	0.0713 ± 0.0003	0.3663 ± 0.0007	SSW, 2 km	

process, which first requires the purification of cesium. The mass spectrometry of the seawater sample shows that the ^{134}Cs signal overlapped with the tail of the ^{133}Cs signal (see Fig. 3.1); nevertheless, the isotopic ratio of ^{135}Cs/^{137}Cs can be obtained. Despite the fact that it is based on only one result of the litter sample, the isotopic ratio of ^{134}Cs/^{137}Cs evaluated from TIMS is in good agreement with that from γ-spectrometry, thereby demonstrating the validity of both measurement methods. The isotopic ratios of ^{135}Cs/^{137}Cs of the litter and the seawater sample collected in 2011 were both 0.36 (decay correction: 11 March 2011).

The results obtained in this study are now compared to those of other references. Those of the previous work [6] are listed in Table 3.3. The isotopic ratio of ^{134}Cs/^{137}Cs in the samples (evaluated from both γ-spectrometry and TIMS) agrees with the results of the other study; however, the ratio of soil from Hinoemata is slightly lower. Furthermore, the isotopic ratios of ^{135}Cs/^{137}Cs in land samples are in good agreement with that in the seawater sample, which did not yield an isotopic ratio for ^{134}Cs/^{137}Cs. In another study [8], the isotopic ratios of ^{135}Cs/^{137}Cs in litter, lichen, and soil samples were determined with inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) to be 0.333–0.375, depending on location and distance from the FDNPP. These three studies showed that the environmental samples (both land and marine samples) collected from the area remarkably contaminated by the Fukushima accident had isotopic ratios of ^{134}Cs/^{137}Cs of 0.07 and ^{135}Cs/^{137}Cs of 0.36, which are quite different from the values that arise from global fallout; such values were mainly the result of atmospheric nuclear tests and were almost 0 and about 2.7, respectively [6]. The radioactivity of ^{134}Cs will decrease to 1/30 of its initial value 10 y after the Fukushima accident, which will lead to difficulties in detecting ^{134}Cs. However, ^{135}Cs and ^{137}Cs can be sufficiently detected by TIMS at that time, and thus the isotopic ratio of ^{135}Cs/^{137}Cs related to the Fukushima accident and global fallout will become 0.44 and 3.4, respectively. The value of the isotopic ratio in environmental samples collected in the future can therefore demonstrate the origin of radioactive cesium by TIMS.

a

b
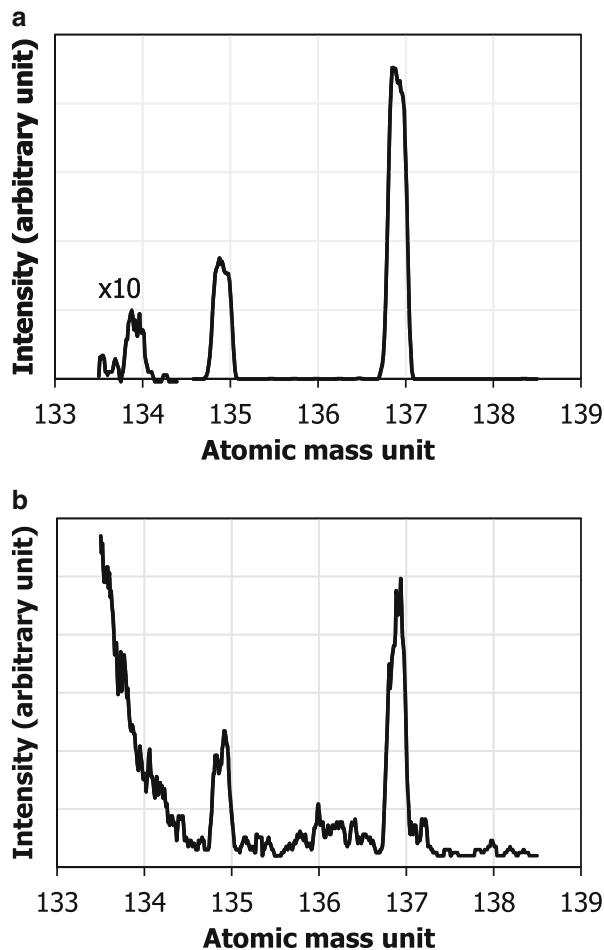
Fig. 3.1 Mass spectrometry measurements obtained by thermal ionization mass spectrometry (TIMS) for (**a**) litter and (**b**) sea water

3.4   Conclusion

In order to obtain the initial isotopic ratios of cesium at the time of the Fukushima accident, environmental samples were collected in Fukushima prefecture during 2011. The samples were treated with AMP and AMP-PAN in order to purify and recover the cesium; using the latter technique, the cesium contained in seawater was almost completely recovered. The isotopic ratios of cesium were determined by γ-spectrometry and TIMS. These results were in good agreement with each other (i.e., the results were independent of the determination method used) and with other studies as well. However, further development in the purification of the

seaweed sample is required. On the basis of the initial isotopic ratio derived from the Fukushima accident, the isotopic ratio of cesium in environmental samples collected in the future can be expected to estimate the contribution of the accident through comparisons with the effects of global fallout.

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