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Tritium and iodine-129 concentrations in precipitation at Tsukuba, Japan, after the Fukushima Daiichi Nuclear Power Plant accident

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The earthquake off the Pacific coast of Japan and the subsequent tsunami on March 11, 2011, triggered a series of accidents in the Fukushima Daiichi Nuclear Power Plant (FNPP1). The accidents caused the release of a mixture of radioactive substances into the environment. This study measured the concentration of tritium (^{3}H) and iodine-129 (^{129}I) in rainwater samples collected at Tsukuba, 170 km southwest of the plant, during the year following the accident. High ^{3}H concentrations were observed in the rainwater samples collected within one month after the FNPP1 accident. ^{3}H concentrations decreased steadily over time and returned to the levels before the accident. Concentrations of ^{129}I also decreased over time. However, pulses of high ^{129}I concentrations were observed at several other times following the accident. The ^{129}I concentrations were found to be correlated with iron concentrations in rainwater. It is likely that iron oxide, which can absorb iodate ions (IO_3^-), was the carrier of radiogenic iodine. This study concludes that ^{129}I and also ^{131}I, which is one of the most harmful radionuclides produced in nuclear reactors, can be redistributed to the atmosphere in the months following the deposition of radiogenic iodine on the ground.

Keywords: Fukushima Daiichi Nuclear Power Plant accident, volatile radionuclides, tritium, radioactive iodine, accelerator mass spectrometry

INTRODUCTION

The earthquake off the Pacific coast of Japan and the subsequent tsunami on March 11, 2011, triggered a series of accidents in the Fukushima Daiichi Nuclear Power Plant (FNPP1). Radioactive substances were subsequently released into the environment. These substances were produced in the nuclear reactors and were stored in the spent-fuel (e.g., Hirose, 2012; Steinhauser, 2014).

In light water nuclear reactors, which is the type of reactors used at FNPP1, ^{3}H ($t_{1/2}$ = 12.32 y; Lucas and Unterwerger, 2000) is formed from the ternary fission of nuclear fuels and from neutron activation of lithium and boron. The total amount of ^{3}H stored in FNPP1 was calculated to be 1.81×10^{13} Bq (Schwantes *et al*., 2012). Matsumoto *et al*. (2013) reported a decrease in ^{3}H concentration in rainwater samples, with increasing distance, at sites ranging from 170 to 700 km from FNPP1. Based on the observed distance relationship, the atmospheric ^{3}H level at source during the early stage of the accident was estimated to be approximately 1500 Bq/m^3. This implies that significant amounts of ^{3}H were released from the FNPP1 and were deposited on the ground via precipitation. Measuring ^{3}H concentrations in rainwater can improve our understanding of the emission and dispersal of volatile radioactivity after a nuclear accident.

Iodine-131(^{131}I) ($t_{1/2}$ = 8.0252 days; Khazov *et al*., 2006) is one of the most harmful radionuclides produced in nuclear reactors; therefore, the activity of ^{131}I around the accident site should be precisely evaluated to assess the impact of radioactivity on public health (e.g., Miyake *et al*., 2012; Doi *et al*., 2013). Some studies have used Iodine-129 (^{129}I) ($t_{1/2} = 1.57 \times 10^7$ y; Timar *et al*., 2014) to estimate the distribution of ^{131}I (e.g., Muramatsu *et al*., 2015). ^{129}I is used because it has a longer half-life than ^{131}I, which is no longer detectable after a few months. ^{131}I and ^{129}I are mobilized together, and therefore, their distribution and behavior in the environment will be similar.

In this paper, we report on measured concentrations of ^{3}H and ^{129}I from the precipitation samples collected at Tsukuba, 170 km southwest from the FNPP1 in the year

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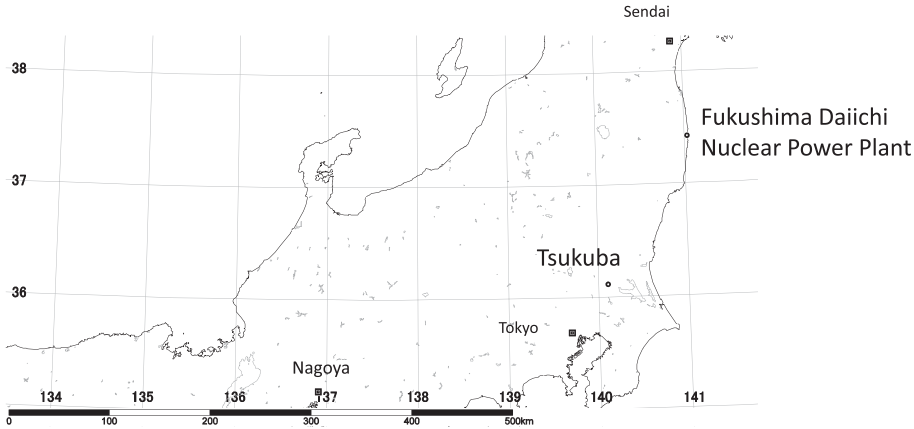

Fig. 1. Map of the sampling locality and the FNPP1.

following the accident. The purpose of this study is to improve the understanding of the behavior of these volatile radionuclides.

SAMPLING AND ANALYSIS

Rain samples were collected at University of Tsukuba, Tsukuba City, Japan, (Fig. 1) over the first year after the accident. Individual rain samples were collected in pan-shaped containers.

^{3}H concentrations were measured using about 500 ml rainwater samples and the residual rainwater (if a sufficient amount of rainwater could be collected) was used for cation and ^{129}I analysis. ^{3}H analysis was carried out in the Isotope Hydrology Laboratory of the International Atomic Energy Agency (IAEA) by electrolytic enrichment followed by liquid scintillation spectrometry with a detection limit of about 0.1 TU (Gröning *et al*., 2009; Matsumoto *et al*., 2013).

Concentrations of ^{129}I were determined using accelerator mass spectrometry (AMS) at MALT (Micro Analysis Laboratory, Tandem accelerator) in the University of Tokyo (Matsuzaki *et al*., 2007). The standard used for the determination of ^{129}I/^{127}I ratios was Z94-0596 prepared by Prime Lab., University of Purdue. We also determined the ^{129}I/^{127}I ratio of the KI solution (Kanto Chemicals Co.) in order to examine the carrier blank value (^{129}I/^{127}I ratio: 1.8×10^{-13}). About 150 ml of rainwater was used for ^{129}I analyses of samples collected after May 2011. Smaller amounts of rainwater (1 to 40 ml) were used for samples collected in March and April of 2011 because these samples had higher concentrations of ^{129}I.

The concentrations of cations (K, Na, Ca, Mg, Al, Fe, and Mn) and ^{127}I were determined using ICP-MS/MS (Agilent 8800; Agilent Technologies, Tokyo, Japan). The analyses were conducted at Gakushuin University by comparing the results to a set of standard samples of known concentration. The water samples were filtered using a membrane filter with a pore size of 0.45 μm before ^{129}I measurements and chemical analysis.

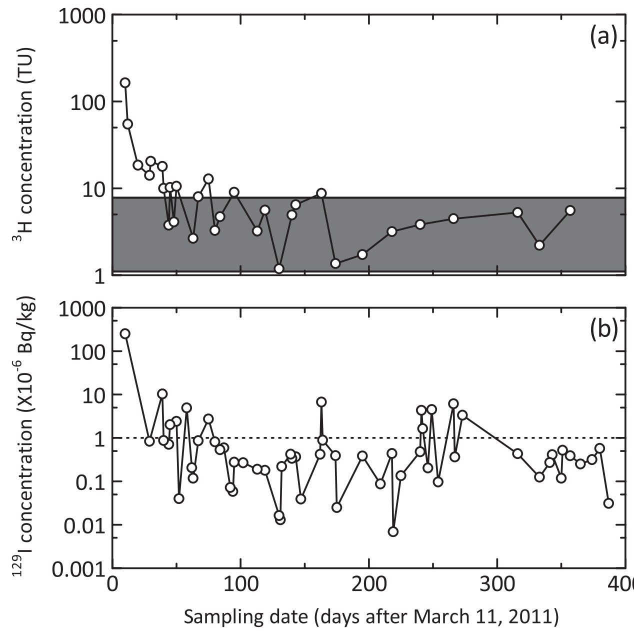

Fig. 2. Concentrations of ^{3}H (a) and ^{129}I (b) for individual rainfall occurences. Gray area in (a) represents pre-accident ^{3}H levels ranging from 1.1 and 7.8 TU, which were minimum and maximum ^{3}H concentrations, respectively, obtained by monthly analyses during 2001 and 2002 at Tsukuba (Yabusaki et al., 2003). Dotted line in (b) represents the threshold (10^{-6} Bq/kg) between high and low concentrations of ^{129}I used in this study.

RESULTS AND DISCUSSION

Concentrations of ^{3}H, ^{127}I, ^{129}I, cations and ^{129}I/^{127}I

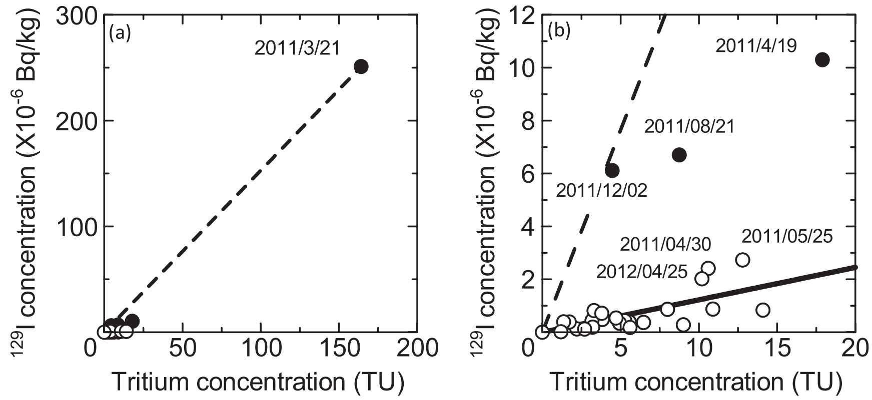

Fig. 3. Concentrations of ^{129}I plotted against those of tritium (a), enlarged in (b). Dashed lines in (a) and (b) connect data point from March 21, 2011, to the origin. Solid line in (b) represents the regression line determined as passing the origin. The regression line were determined using data of open circle symbols (R^2 = 0.48). Numbers near the data points indicate sampling dates.

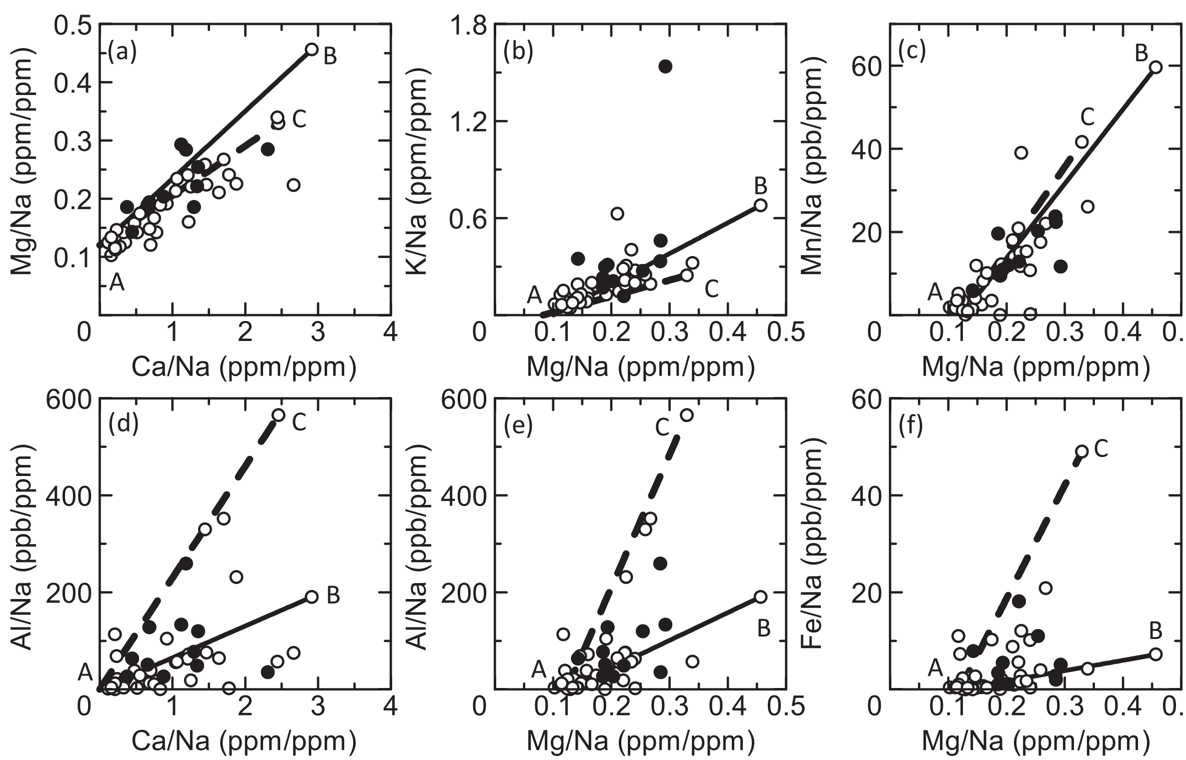

Fig. 4. Cation compositions of the rain water samples: (a) Mg/Na vs. Ca/Na (b) K/Na vs. Mg/Na (c) Mn/Na vs. Mg/Na (d) Al/Na vs. Ca/Na, (e) Al/Na vs. Mg/Na, and (f) Fe/Na vs. Mg/Na. Three endmembers were proposed. Component "A" represents sea salt composition. "B" and "C" represent for the chemical compositions for rainwater samples collected on May 17 and 13, 2011, respectively. Solid and dashed lines connect data points of the components "B" and "C", respectively, to that of component "A". Closed and open circles represent data points for samples with high (>10^{-6} Bq/kg) and low (<10^{-6} Bq/kg) ^{129}I concentrations, respectively.

ratios from rainwater samples are given in Table 1. Higher ^{3}H concentrations were observed in the rainwater samples collected within one month after the FNPP1 accident (Fig. 2a). The ^{3}H concentrations of subsequent rainwater samples decreased steadily with time and returned to pre-accident levels (1.1–7.8 TU in Tsukuba; Yabusaki *et al*., 2003). This indicates that the Fukushima-derived ^{3}H was washed out from the atmosphere by precipitation within a month.

Concentrations of ^{129}I also decreased over time after

Table 1. Analytical results for ^{127}I, ^{129}I, tritium, cations in rainwater samples collected at Tsukuba, Japan, after the Fukushima Daiichi Nuclear Power Plant accident

Sampling date	^{127}I (ppb)	^{129}I/^{127}I ($\times10^{-6}$)	^{129}I ($\times10^{-6}$ Bq/kg)	^{3}H (TU)	Na (ppm)	Mg (ppm)	Al (ppb)	K (ppm)	Ca (ppm)	Mn (ppb)	Fe (ppb)	Direction of prevailing winds #	Average wind speed # (m/s)	Precipitation # (mm)	Average temperature # (°C)
2011/3/21	0.831 ± 0.015	46.2	251 ± 12	164.2 ± 8.0*								NE	2.7	21	8
2011/3/23				54.9 ± 2.7*								NNE	1.8	14	6
2011/3/31				18.5 ± 1.4								NNE → NW	2.8	3	9
2011/4/9 †	0.922 ± 0.014	0.139	0.836 ± 0.034	14.1 ± 0.7*	3.527 ± 0.046	0.6672 ± 0.0059	0.73 ± 0.05	0.6741 ± 0.0076	2.941 ± 0.045	0.078 ± 0.005	0.16 ± 0.01	SSW	3.6	6	14
2011/4/10 ‡				20.5 ± 1.0*								SSW	3.6	6	14
2011/4/19 †	0.963 ± 0.018	1.636	10.30 ± 0.27	17.9 ± 0.9*	0.789 ± 0.009	0.1494 ± 0.0020	39.96 ± 0.81	0.2354 ± 0.0029	0.520 ± 0.004	7.47 ± 0.16	1.08 ± 0.03	NE	3.5	23	9
2011/4/20 ‡	0.421 ± 0.009	0.318	0.874 ± 0.028	10.0 ± 0.6*	0.698 ± 0.009	0.1637 ± 0.0024	39.71 ± 0.48	0.2821 ± 0.0026	0.742 ± 0.010	10.69 ± 0.12	1.20 ± 0.02	NE	3.5	23	9
2011/4/24	1.638 ± 0.007	0.067	0.713 ± 0.024	3.8 ± 0.2*	1.597 ± 0.029	0.2132 ± 0.0056	5.83 ± 0.23	0.1216 ± 0.0021	0.258 ± 0.004	1.38 ± 0.01	0.54 ± 0.04	S	4.1	27	16
2011/4/25	1.951 ± 0.027	0.159	2.020 ± 0.052	10.2 ± 0.5*	2.732 ± 0.032	0.5071 ± 0.0041	71.84 ± 0.62	0.6262 ± 0.0081	1.032 ± 0.017	26.88 ± 0.32	2.80 ± 0.08	ENE	2.8	3	14
2011/4/28				4.1 ± 0.3*								S → NE	4.6	11	18
2011/4/30	2.042 ± 0.017	0.181	2.410 ± 0.060	10.6 ± 0.6*	2.092 ± 0.020	0.5942 ± 0.0073	542.2 ± 5.9	0.6964 ± 0.0086	2.483 ± 0.042	49.69 ± 0.50	5.83 ± 0.06	ENE	2.4	5	13
2011/5/2	0.044 ± 0.004	0.138	0.040 ± 0.002		0.436 ± 0.007	0.1481 ± 0.0032	24.92 ± 0.66	0.1407 ± 0.0026	1.066 ± 0.017	11.37 ± 0.57	1.85 ± 0.02	SSW	4.3	1	17
2011/5/8	4.805 ± 0.133	0.157	4.93 ± 0.12		7.454 ± 0.096	1.5152 ± 0.0404	196.7 ± 2.2	1.5619 ± 0.0178	6.554 ± 0.144	89.18 ± 3.31	8.02 ± 0.31	NW	1.9	1	16
2011/5/12	1.758 ± 0.015	0.018	0.206 ± 0.007		0.143 ± 0.002	0.0315 ± 0.0007	2.65 ± 0.03	0.0410 ± 0.0020	0.179 ± 0.006	2.98 ± 0.02	0.80 ± 0.38	WNW → NE	1.5	36	16
2011/5/13	2.370 ± 0.049	0.008	0.118 ± 0.006	2.7 ± 0.2*	0.023 ± 0.001	0.0076 ± 0.0001	13.08 ± 0.34	0.0057 ± 0.0001	0.057 ± 0.001	0.96 ± 0.03	1.13 ± 0.05	NE → ESE	2.0	27	16
2011/5/17	3.045 ± 0.037	0.043	0.863 ± 0.020	8.0 ± 0.2*	0.919 ± 0.011	0.4194 ± 0.0053	175.1 ± 3.8	0.6237 ± 0.0073	2.678 ± 0.034	54.77 ± 0.99	6.62 ± 0.11	S	2.0	12	16
2011/5/25	0.595 ± 0.026	0.703	2.730 ± 0.067	12.8 ± 0.3*	0.167 ± 0.001	0.0475 ± 0.0003	5.87 ± 0.08	0.0767 ± 0.0027	0.385 ± 0.004	3.73 ± 0.04	0.33 ± 0.01	N	1.9	19	13
2011/5/30	0.506 ± 0.007	0.247	0.815 ± 0.020	3.3 ± 0.1*	0.147 ± 0.002	0.0208 ± 0.0001	0.41 ± 0.18	0.0158 ± 0.0006	0.076 ± 0.002	0.88 ± 0.01	<0.001	ENE	2.4	67	18
2011/6/3	2.296 ± 0.016	0.036	0.535 ± 0.013	4.7 ± 0.4	1.835 ± 0.010	0.2687 ± 0.0036	125.9 ± 1.2	0.1406 ± 0.0011	0.428 ± 0.002	7.46 ± 0.13	4.88 ± 0.05	NNE	1.3	15	15
2011/6/6	1.319 ± 0.019	0.069	0.592 ± 0.026									S	2.1	34	21
2011/6/11	1.543 ± 0.046	0.007	0.072 ± 0.003									SSE	1.9	30	21
2011/6/13	0.452 ± 0.015	0.020	0.059 ± 0.006		0.163 ± 0.006	0.0342 ± 0.0008	10.45 ± 0.08	0.1019 ± 0.0031	0.267 ± 0.005	2.93 ± 0.06	1.43 ± 0.02	SE	2.0	29	20
2011/6/14	2.263 ± 0.019	0.019	0.276 ± 0.017	9.0 ± 0.3								ENE	2.3	2	20
2011/6/21	1.794 ± 0.020	0.023	0.268 ± 0.008									S	2.3	2	24
2011/7/2	1.251 ± 0.013	0.023	0.189 ± 0.006	3.2 ± 0.2	0.389 ± 0.004	0.0648 ± 0.0015	4.07 ± 0.03	0.0777 ± 0.0024	0.292 ± 0.009	3.94 ± 0.06	0.14 ± 0.01	E	1.9	40	26
2011/7/8	0.374 ± 0.008	0.073	0.179 ± 0.019	5.6 ± 0.2								S → SSE	2.1	9	26
2011/7/19	0.623 ± 0.009	0.004	0.016 ± 0.001	1.2 ± 0.2	0.061 ± 0.001	0.0139 ± 0.0002	14.23 ± 0.32	0.0188 ± 0.0006	0.115 ± 0.003	2.40 ± 0.05	0.74 ± 0.15	SE	2.4	34	26
2011/7/20 †	1.427 ± 0.012	0.001	0.013 ± 0.001									SSE	2.9	25	25
2011/7/21 ‡	0.997 ± 0.029	0.034	0.220 ± 0.017									SSE	2.9	25	25
2011/7/28	1.184 ± 0.014	0.055	0.422 ± 0.013		0.444 ± 0.007	0.1071 ± 0.0052	0.98 ± 0.07	0.1224 ± 0.0051	0.789 ± 0.030	0.10 ± 0.01	0.17 ± 0.10	NE	1.7	33	25
2011/7/29	0.221 ± 0.006	0.235	0.339 ± 0.019	4.9 ± 0.2								WNW	1.5	18	24

Sampling date	^{127}I (ppb)	$^{129}I/^{127}I$ ($\times10^{-6}$)	^{129}I ($\times10^{-6}$ Bq/kg)	^{3}H (TU)	Na (ppm)	Mg (ppm)	Al (ppb)	K (ppm)	Ca (ppm)	Mn (ppb)	Fe (ppb)	Direction of prevailing winds #	Average wind speed # (m/s)	Precipitation # (mm)	Average temperature # (°C)
2011/8/1	0.273 ± 0.006	0.206	0.368 ± 0.011	6.5 ± 0.5	0.635 ± 0.010	0.1214 ± 0.0057	66.2 ± 2.1	0.0804 ± 0.0033	0.586 ± 0.027	7.75 ± 0.36	1.33 ± 0.11	NE	2.3	25	23
2011/8/5	1.505 ± 0.010	0.004	0.039 ± 0.004		0.046 ± 0.003	0.0110 ± 0.0004	2.87 ± 0.15	0.0091 ± 0.0003	0.055 ± 0.002	0.49 ± 0.02	0.46 ± 0.04	SSE	2.4	17	27
2011/8/20	0.204 ± 0.005	0.316	0.420 ± 0.013		0.399 ± 0.009	0.0458 ± 0.0006	4.87 ± 0.11	0.0252 ± 0.0007	0.085 ± 0.002	1.39 ± 0.05	0.19 ± 0.04	ENE	2.4	92	23
2011/8/21	2.647 ± 0.013	0.388	6.700 ± 0.262	8.8 ± 0.5	0.127 ± 0.004	0.0236 ± 0.0010	9.81 ± 0.29	0.0215 ± 0.0014	0.164 ± 0.010	2.49 ± 0.06	0.43 ± 0.05	N	1.8	5	20
2011/8/22	2.694 ± 0.010	0.050	0.886 ± 0.042		0.405 ± 0.007	0.0476 ± 0.0018	45.8 ± 2.2	0.0611 ± 0.0058	0.085 ± 0.004	2.09 ± 0.06	4.44 ± 0.18	ENE	1.6	22	21
2011/9/1	1.419 ± 0.035	0.042	0.391 ± 0.011	1.4 ± 0.1	0.079 ± 0.004	0.0139 ± 0.0005	2.26 ± 0.12	0.0143 ± 0.0005	0.044 ± 0.002	0.28 ± 0.01	0.81 ± 0.05	E	2.5	6	27
2011/9/2	0.593 ± 0.006	0.006	0.025 ± 0.003									SE	3.9	10	28
2011/9/21					1.256 ± 0.027	0.1782 ± 0.0056	4.51 ± 0.11	0.1255 ± 0.0013	0.414 ± 0.013	1.76 ± 0.05	0.36 ± 0.09	NE	2.3	11	19
2011/9/22	0.560 ± 0.017	0.105	0.384 ± 0.011	1.7 ± 0.2								ENE	5.4	141	22
2011/10/6	0.671 ± 0.020	0.020	0.087 ± 0.003		2.354 ± 0.051	0.2937 ± 0.0066	3.18 ± 0.07	0.1150 ± 0.0026	0.274 ± 0.008	2.65 ± 0.03	0.12 ± 0.02	NE	2.1	87	18
2011/10/15	4.846 ± 0.017	0.014	0.437 ± 0.020	3.2 ± 0.2	0.142 ± 0.005	0.0210 ± 0.0011	1.79 ± 0.06	0.0184 ± 0.0012	0.097 ± 0.006	1.68 ± 0.05	0.04 ± 0.01	S	1.6	5	19
2011/10/16	2.394 ± 0.019	0.004	0.069 ± 0.006									SSW	3.5	14	22
2011/10/22	0.429 ± 0.010	0.048	0.135 ± 0.005									SSW	2.3	50	21
2011/11/6 †	1.494 ± 0.024	0.049	0.481 ± 0.026	3.8 ± 0.2	1.773 ± 0.043	0.4583 ± 0.0064	585 ± 16	0.4417 ± 0.0086	2.566 ± 0.045	31.13 ± 0.76	7.02 ± 0.23	NE	1.3	5	17
2011/11/7 ‡	1.880 ± 0.008	0.352	4.320 ± 0.097		0.141 ± 0.002	0.0413 ± 0.0018	18.79 ± 1.25	0.2170 ± 0.0092	0.158 ± 0.010	1.64 ± 0.04	0.72 ± 0.03	NE	1.3	5	17
2011/11/8	4.203 ± 0.028	0.060	1.640 ± 0.069		0.473 ± 0.004	0.0676 ± 0.0029	30.01 ± 1.01	0.1647 ± 0.0062	0.211 ± 0.013	2.71 ± 0.06	3.73 ± 0.11	E → NE	1.6	5	14
2011/11/12	1.176 ± 0.021	0.026	0.203 ± 0.006		0.365 ± 0.005	0.0411 ± 0.0019	3.17 ± 0.12	0.0458 ± 0.0029	0.079 ± 0.006	0.62 ± 0.02	0.14 ± 0.01	NW	1.7	14	11
2011/11/15	4.512 ± 0.014	0.153	4.510 ± 0.179		1.637 ± 0.022	0.3170 ± 0.0080	209.8 ± 6.1	0.5094 ± 0.0086	1.118 ± 0.007	17.96 ± 0.54	8.94 ± 0.26	NE	2.0	4	14
2011/11/20	1.469 ± 0.008	0.010	0.097 ± 0.008		0.347 ± 0.007	0.0408 ± 0.0016	2.70 ± 0.18	0.0328 ± 0.0023	0.096 ± 0.006	1.35 ± 0.04	0.34 ± 0.02	W	1.8	51	13
2011/12/2	3.475 ± 0.037	0.269	6.110 ± 0.137	4.5 ± 0.3	1.158 ± 0.017	0.2945 ± 0.0081	138.8 ± 2.6	0.3167 ± 0.0051	1.567 ± 0.021	23.44 ± 0.68	12.73 ± 0.36	NE → NNW	2.6	3	6
2011/12/3	1.009 ± 0.011	0.055	0.364 ± 0.020		0.404 ± 0.004	0.0415 ± 0.0003	1.37 ± 0.03	0.0270 ± 0.0005	0.064 ± 0.001	0.74 ± 0.02	0.16 ± 0.05	NE	2.3	23	11
2011/12/9	2.328 ± 0.018	0.220	3.340 ± 0.077		0.646 ± 0.006	0.1430 ± 0.0039	31.53 ± 0.77	0.0758 ± 0.0014	0.866 ± 0.010	8.31 ± 0.23	11.72 ± 0.30	NNE	2.0	5	5
2012/1/21	1.720 ± 0.012	0.039	0.433 ± 0.013	5.3 ± 0.2	2.669 ± 0.037	0.4206 ± 0.0093	102.4 ± 1.9	0.2221 ± 0.0056	1.272 ± 0.013	6.80 ± 0.16	1.10 ± 0.11	N → NW	3.3	17	3
2012/2/7	1.984 ± 0.015	0.010	0.125 ± 0.006	2.2 ± 0.2								NW → NE	1.7	11	5
2012/2/15	0.285 ± 0.009	0.146	0.271 ± 0.009		0.423 ± 0.006	0.0944 ± 0.0031	31.74 ± 1.11	0.0912 ± 0.0021	1.127 ± 0.023	6.35 ± 0.26	0.66 ± 0.04	NW	2.1	6	5
2012/2/17	2.326 ± 0.014	0.027	0.412 ± 0.010		0.857 ± 0.009	0.2291 ± 0.0061	301.4 ± 7.5	0.1644 ± 0.0037	1.460 ± 0.022	18.85 ± 0.64	17.86 ± 1.18	NE	2.1	2	2
2012/2/24	0.875 ± 0.012	0.021	0.118 ± 0.004		0.382 ± 0.008	0.0477 ± 0.0021	7.83 ± 0.21	0.0304 ± 0.0017	0.135 ± 0.008	1.32 ± 0.02	0.87 ± 0.11	NW	2.1	7	5
2012/2/25	2.182 ± 0.024	0.037	0.520 ± 0.014		0.949 ± 0.025	0.1283 ± 0.0038	20.32 ± 0.09	0.0799 ± 0.0025	0.228 ± 0.009	2.90 ± 0.04	2.26 ± 0.07	NE	2.4	13	4
2012/3/2	0.365 ± 0.012	0.163	0.388 ± 0.010	5.6 ± 0.3	0.261 ± 0.005	0.0418 ± 0.0016	18.82 ± 0.40	0.0270 ± 0.0018	0.320 ± 0.020	2.13 ± 0.07	0.18 ± 0.02	NE	2.2	11	6
2012/3/6					0.149 ± 0.005	0.0179 ± 0.0009	5.72 ± 0.13	0.0174 ± 0.0010	0.104 ± 0.006	0.62 ± 0.02	1.09 ± 0.02	NW → E	2.3	35	8
2012/3/10	0.840 ± 0.006	0.046	0.251 ± 0.009		0.357 ± 0.003	0.0507 ± 0.0025	6.01 ± 0.20	0.0680 ± 0.0057	0.278 ± 0.021	1.21 ± 0.05	0.42 ± 0.08	N	2.5	30	6
2012/3/19	1.503 ± 0.021	0.032	0.317 ± 0.009		0.443 ± 0.006	0.0992 ± 0.0044	33.53 ± 0.81	0.0837 ± 0.0032	0.649 ± 0.027	5.20 ± 0.22	1.24 ± 0.22	WNW → ENE	1.5	22	7
2012/3/25	2.126 ± 0.040	0.088	0.574 ± 0.015		0.437 ± 0.003	0.0930 ± 0.0033	24.38 ± 0.76	0.0637 ± 0.0025	0.457 ± 0.013	6.11 ± 0.21	0.40 ± 0.07	NE → NW	1.7	17	7
2012/4/1	1.687 ± 0.021	0.003	0.031 ± 0.002		7.434 ± 0.098	0.9632 ± 0.0132	2.66 ± 0.08	0.3312 ± 0.0073	1.564 ± 0.019	0.57 ± 0.01	<0.001	SSW	6.3	14	13

Denotes ^{3}H data from Matsumoto et al. (2013).

† and ‡ are data for a single rainfall event. † data were obtained earlier than ‡ data.

 # are meteorological data of Tateno weather station in Tsukuba from Japan Meteorological Agency.

Data shown by shaded area are for the samples of which chemical compositions formed a correlation line between ^{129}I/Na and Fe/Na.

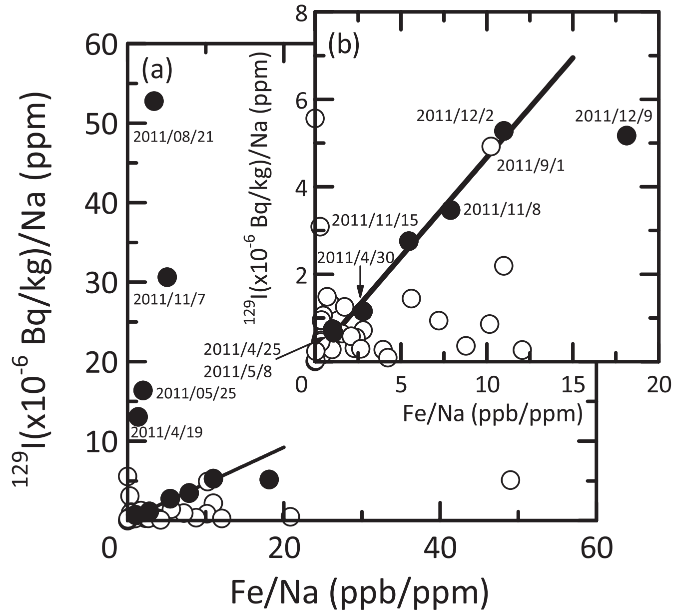

Fig. 5. ^{129}I/Na ratios plotted against Fe/Na ratios. Closed and open circles represent the data for samples with high (>10^{-6} Bq/kg) and low (<10^{-6} Bq/kg) ^{129}I concentrations, respectively. Solid line represent the regressions line determined from 6 data points for samples with high ^{129}I concentrations (R^2 = 0.99). Numbers near data points indicate sampling dates.

the accident; however, several pulses of high ^{129}I concentrations were observed (>10^{-6} Bq/kg: more than two orders of magnitude higher than the minimum concentration for the year) (Fig. 2b). (This threshold value (10^{-6} Bq/kg) was arbitrarily set to distinguish high and low concentrations of ^{129}I.) This means that ^{129}I entered the atmosphere not only at the time of the accident, but also at several times after the accident, even though no evidence of continuous release of radiogenic volatile substances from the reactor was observed. Similar pulses in the concentration of ^{129}I in rainwater collected at Fukushima were reported by Xu *et al.* (2013). Except for these pulses of ^{129}I, the ^{129}I concentrations show a general correlation with those of ^{3}H (Fig. 3); indicating that ^{129}I derived from the FNPP1 accident was washed out of the atmosphere by precipitation, as in the case of ^{3}H.

The composition of cations in the rainwater samples can be explained by mixing at least three end-members (Fig. 4): component A (sea salt), component B (higher Al/Na, Ca/Na, and Mg/Na ratios than component A), and component C (higher Al/Na ratios than component B). In Fig. 4, the end-member compositions of components B and C represent data for precipitation on May 17 and May 13, 2011, respectively. The data points fall along a single line in the Ca/Na vs. Mg/Na (Fig. 4a), K/Na vs. Mg/Na (Fig. 4b), and Mn/Na vs. Mg/Na (Fig. 4c) diagrams, because the mixing lines connecting component A with components B and C are colinear in these diagrams. On the other hand, these three end-members are well resolved in the Al/Na vs. Ca/Na (Fig. 4d), Al/Na vs. Mg/Na (Fig. 4e), and Fe/Na vs. Mg/Na (Fig. 4f) diagrams. In Fig. 4, most data points are located around the point that represents the chemical composition of sea salt, while the data points of the rainwater samples with a high concentration of ^{129}I deviated from the cluster of the sea-salt component. Apparently, the sea salt component has only a very limited influence on the chemical compositions of these high ^{129}I samples.

The correlation between ^{129}I/Na and Fe/Na ratios was observed for some (not all) of the data for the samples with high concentrations of ^{129}I (bold line in Fig. 5). The data point for the rainfall of September 1, 2011, was also located on the regression line, although its ^{129}I concentration (3.91×10^{-7} Bq/kg) is slightly lower than the threshold concentration in this study (i.e., 10^{-6} Bq/kg). It should be noted that a correlation is not expected for the combination of ^{129}I/Na and other elements. Moreover, although one of the three proposed end-members (component C) has a higher Fe/Na ratio than the other two components (A and B) (Fig. 4f), the chemical composition for samples forming the ^{129}I/Na-Fe/Na correlation cannot be explained by a mixture of the Fe-enriched component (C) and others (Fig. 4). Therefore, the additional component supplying iron and ^{129}I is supposed to be independent of the three proposed end-members (A, B, and C).

The "pulse" concentrations of ^{129}I in precipitation were likely related to the dissolution of iron oxide (hematite and/or goethite), which can strongly absorb the iodate ion (IO_3^-) (Couture and Seitz, 1983). Although possible iodine species in soils are iodide (I^-), iodate, and organic iodine (e.g., Yamada *et al.*, 1999), the iodide fraction was the major chemical species of ^{129}I in aerosols collected at Tsukuba (Xu *et al.*, 2015). However, such an iodide component cannot directly produce the observed Fe-^{129}I correlation because iodide ions are not strongly adsorbed by iron oxide (Couture and Seitz, 1983; Kaplan *et al.*, 1999, 2000). Therefore, ^{129}I was likely to be provided (at least partially) as iodate ion from iron oxide. As some types of soils are enriched in iron oxide, the ^{129}I pulses are likely to have been induced by the dissolution of iron oxide in soils. Except for the rainfall of May 8, 2011, the prevailing winds were between East and North East during collection of the samples that had the ^{129}I/Na-Fe/Na correlation (Table 1). Therefore, ^{129}I-bearing iron oxide was likely to have been supplied from an East to North Easterly direction.

CONCLUSIONS

This study analyzed ^3H and ^{129}I concentrations in rainfall at Tsukuba, Japan. Although the concentrations of both the radioactive substrates decreased steadily with time and returned to pre-accident levels, several pulses of high ^{129}I concentration were also observed. Such high concentrations of ^{129}I coincided with high concentrations of iron. Because iron oxides readily absorb iodate ions (IO_3^-) and are generally rich in soils, at least part of ^{129}I in precipitation was likely incorporated into rainwaters by dissolution of iron oxide in soils and could be transported even after other species of ^{129}I were exhausted from the atmosphere.

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REFERENCES

Couture, R. A. and Seitz, M. G. (1983) Sorption of anions of iodine by iron oxides and kaolinite. *Nucl. Chem. Waste Man.* **4**, 301–306.

Doi, T., Masumoto, K., Toyoda, A., Tanaka, A., Shibata, Y. and Hirose, K (2013) Anthropogenic radionuclides in the atmosphere observed at Tsukuba: characteristics of the radionuclides derived from Fukushima. *J. Environm. Radioact.* **122**, 55–62.

Gröning, M., Auer, R., Brummer, D., Jaklitsch, M., Sambandam, C., Tanweer, A. and Tatzber, H. (2009) Increasing the performance of tritium analysis by electrolytic enrichment. *Isotopes Environ. Health Stud.* **45**, 118–125.

Hirose, K. (2012) 2011 Fukushima Dai-ichi Nuclear Power Plant accident: summary of regional radioactive deposition monitoring results. *J. Environm. Radioact.* **111**, 13–17.

Kaplan, D. I., Serne, R. J., Parker, K. E. and Kutnyakov, I. V. (1999) Radioiodide sorption to sediment minerals. *Mat. Res. Soc. Symp. Proc.* **556**, 1059–1065.

Kaplan, D. I., Serne, R. J., Parker, K. E. and Kutnyakov, I. V. (2000) Iodide sorption to subsurface sediments and illitic minerals. *Environ. Sci. Technol.* **34**, 399–405.

Khazov, Yu., Mitropolsky, I. and Rodionov, A. (2006) Nuclear data sheets for A = 131. *Nuclear Data Sheets* **107**, 2715–2930.

Lucas, L. L. and Unterweger, M. P. (2000) Comprehensive review and critical evaluation of the half-life of tritium. *J. Res. Natl. Inst. Stand. Technol.* **105**, 541–549.

Matsumoto, T., Maruoka, T., Shimoda, G., Obata, H., Kagi, H., Suzuki, K, Yamamoto, K., Mitsuguchi, T., Hagino, K., Tomioka, N., Sambandam, C., Brummer, D., Klaus, P. M. and Aggarwal, P. (2013) Tritium in Japanese precipitation following the March 2011 Fukushima Daiichi Nuclear Plant accident. *Sci. Total Environ.* **445**, 365–370.

Matsuzaki, H., Muramatsu, Y., Kato, K., Yasumoto, M. and Nakano, C. (2007) Development of ^{129}I-AMS system at MALT and measurements of ^{129}I concentrations in several Japanese soils. *Nucl. Instrum. Meth. B* **259**, 721–726.

Miyake, Y., Matsuzaki, H., Fujiwara, T., Saito, T., Yamagata, T., Honda, M. and Muramatsu, Y. (2012) Isotopic ratio of radioactive iodine ($^{129}I/^{131}I$) released from Fukushima Daiichi NPP accident. *Geochem. J.* **46**, 327–333.

Muramatsu, Y., Matsuzaki, H., Toyama, C. and Ohno, T. (2015) Analysis of ^{129}I in the soils of Fukushima Prefecture: Preliminary reconstruction of ^{131}I deposition related to the accident at Fukushima Daiichi nuclear power plant. *J. Environm. Radioact.* **139**, 344–350.

Schwantes, J. M., Orton, C. R. and Clark, R. A. (2012) Analysis of a nuclear accident: fission and activation product releases from the Fukushima Daiichi nuclear facility as remote indicators of source identification, extent of release, and state of damaged spent nuclear fuel. *Environ. Sci. Technol.* **46**, 8621–8627.

Steinhauser, G. (2014) Fukushima's forgotten radionuclides: A review of the understudied radioactive emissions. *Environ. Sci. Technol.* **48**, 4649–4663

Timar, J., Elekes, Z. and Singh, B. (2014) Nuclear data sheets for A = 129. *Nuclear Data Sheets* **121**, 143–394.

Xu, S., Freeman, S. P. H. T., Hou, X., Watanabe, A., Yamaguchi, K. and Zhang, L. (2013) Iodine isotopes in precipitation: Temporal responses to ^{129}I emissions from the Fukushima nuclear accident. *Environ. Sci. Technol.* **47**, 10851–10859.

Xu, S., Zhang, L., Freeman, S. P., Hou, X., Shibata, Y., Sanderson, D., Cresswell, A., Doi, T. and Tanaka, A. (2015) Speciation of radiocesium and radioiodine in aerosols from Tsukuba after the Fukushima nuclear accident. *Environ. Sci. Technol.* **49**, 1017–1024.

Yabusaki, S., Tsujimura, M. and Tase, N. (2003) Recent trend of tritium concentration in precipitation in Kanto Plain, Japan. *Bull. Terr. Environ. Res. Cent.* **4**, 119–124.

Yamada, H., Kiriyama, T., Onagawa, Y., Hisamori, I., Miyazaki, C. and Yonebayashi, K. (1999) Speciation of iodine in soils. *Soil Sci. Plant Nutr.* **45**, 563–568.