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Historically Heavy Rainfalls in Singapore on 19 November 2009 and 17 July 2010

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On 19 November 2009 and 17 July 2010, historically heavy rainfalls occurred in Singapore. Aerosol samples (PM 4.5) were collected with a sampling pump at a flow rate of 5 L per min from 16 to 22 November 2009, from 08 to 20 February 2010 and from 16 to 28 July 2010. Rainwater samples were collected every 5 mL of rainfall using an Horiba Raingoround sampler from 17 to 21 November 2009, from 10 to 18 February 2010 and from 16 to 28 July 2010 on a rooftop at the National University of Singapore in Singapore. These samples were analyzed by ion chromatography for anions and by gas chromatography-mass spectrometry for nitrogen and oxygen stable isotope ratios. During periods of historically heavy rainfall, the $\delta^{18}O/^{16}O$ ratios in nitric-oxide substances in aerosols tend to decrease tremendously. The ^{14}N atoms in nitrogen oxide ions in rain drops are converted to ^{14}C through neutron-activated nuclear chemical reactions at higher altitudes. Consequently, $\delta^{15}N/^{14}N$ ratios increase with the production altitudes of rain drops. Therefore, figures displaying the $\delta^{15}N/^{14}N$ ratios of nitrogen oxide ions in different separated rainfall fractions have a characteristic form. This implies that there is some relationship between the chemical characterization of aerosols and the chemical characterization of rainfall.

Key Words: Heavy rainfall, PM 4.5 aerosol samples, Nuclear chemical reactions, Wet deposition.

INTRODUCTION

It is important to examine the stable nitrogen and oxygen isotopic ratios of nitric-oxide substances and the concentrations of anions in aerosols and rainwater (wet deposition) and to understand the geochemical behaviour of the aerosols and anions in rainfall water to gain knowledge and insight into the atmospheric environment[1,2], especially the mechanism of heavy rainfall. To date, there have been a considerable number of reports and investigations studying heavy rainfall[3-6]. Although there have been several studies of stable nitrogen and oxygen isotopes and anion concentrations investigating their influence on heavy rainfalls, the chemical and isotopic characteristics of heavy rainfalls are not well understood[7-10]. Furthermore, the relationships between the phenomena of heavy rainfalls and stable nitrogen and oxygen isotope ratios in aerosols and rainfall have never been considered.

Historically heavy rainfalls occurred in Singapore on 19 November 2009 and on 17 July 2010. On 19 November 2009, between 13:20 Singapore Standard Time (SST) and 13:50 SST alone, 92 mm of rain fell. The total amount of rainfall logged in Singapore that day was 110 mm, or 43 % of the average monthly rainfall for November[11]. On 17 July 2010, between 04:40 SST and 06:40 SST, 179.6 mm of rain fell. The average total monthly rainfall for July is 159 mm[12]. The excess rainfall brought flood damage such as submerged vehicles, submerged land and electric power outages in Singapore.

In this study, aerosol samples (PM 4.5) and rainfall water samples in 5 mL fractions were collected from the beginning of rain events on the rooftop of Building E2 at the National University of Singapore in Singapore (latitude: 1°18' north; longitude: 103°46' east; altitude: 67.0 meter) (NUS) from 16 to 22 November 2009, 08 to 20 February 2010 and 16 to 28 July 2010. These sampling periods include the historically heavy rainfalls discussed above. Anion concentrations in the samples were analyzed by ion chromatography and nitrogen and oxygen stable isotope ratios were analyzed by gas chromatography-mass spectrometry. The objective of this study is to elucidate how historically heavy rainfall affects the chemical and isotopic characteristics of aerosols and rainwater.

EXPERIMENTAL

Aerosol samples (PM 4.5) were taken at the rooftop of Building E2 at the National University of Singapore in Singapore (latitude: 1°18' north; longitude: 103°46' east; altitude: 67.0 meter) from 15:27 SST (Singapore standard time = UTC + 7 h) 16 to 15:27 SST 17 November 2009; from 15:39 SST 17 to 15:39 SST 18 November 2009; from 15:42

SST 18 to 15:42 SST 19 November 2009; from 18:18 SST 19 to 18:18 SST 20 November 2009; from 18:35 SST 20 to 18:35 SST 21 November 2009; from 19:08 SST 21 to 19:08 SST 22 November 2009; from 17:09 SST 08 to 17:09 SST 12 February 2010; from 17:12 SST 12 to 17:12 SST 16 February 2010; from 17:13 SST 16 to 17:13 SST 20 February 2010; from 13:22 SST 16 to 13:22 SST 20 July 2010; from 13:25 SST 20 to 13:25 SST 24 July 2010; and from 13:25 SST 24 to 13:25 SST 28 July 2010. A sampling pump (Model SP 250, GL Science) was operated at the rooftop for sample extraction and the samples were collected onto polyamide filters (NX047100, Pall Corporation) at a flow rate of 5 L per min.

The polyamide filters were then transferred into 20 mL of ultrapure water and shaken for *ca.* 40 min. The extracts were filtered and analyzed using an ion chromatograph (DX 120/AS, Dianex Inc.).

Rainwater (wet deposition) samples were collected at the rooftop using an Horiba Raingoround sampler on 17 November 2009 (Sampling duration: 14:06 SST to 21:46 SST); from 17 to 18 November 2009 (Sampling duration: 22:00 SST 17 to 19:40 SST 18 November 2009); from 18 to 19 November 2009 (Sampling duration: 19:55 SST 18 to 18:00 SST 19 November 2009); from 19 to 20 November 2009 (Sampling duration: 18:30 SST 19 to 18:30 SST 20 November 2009); from 20 to 21 November 2009 (Sampling duration: 18:50 SST 20 to 19:10 SST 21 November 2009); on 10 February 2010 (Sampling duration: 12:00 SST to 14:00 SST); on 11 February 2010 (Sampling duration: 13:11 SST to 14:00 SST); on 18 February 2010; from 16 to 17 July 2010 (Sampling duration: 19:00 SST 16 to 15:00 SST 17 July 2010); from 17 to 19 July 2010 (Sampling duration: 15:00 SST 17 to 07:30 SST 19 July 2010); from 19 to 20 July 2010 (Sampling duration: 08:00 SST 19 to 15:30 SST 20 July 2010); from 20 to 21 July 2010 (Sampling duration: 16:00 SST 20 to 12:45 SST 21 July 2010); from 21 to 22 July 2010 (Sampling duration: 12:55 SST 21 to 18:40 SST 22 July 2010); from 22 to 26 July 2010 (Sampling duration: 18:50 SST 22 to 18:45 SST 26 July 2010); and from 26 to 28 July 2010 (Sampling duration: 18:50 SST 26 to 13:20 SST 28 July 2010). An Horiba Raingoround is a sampling device for the collection of rainfall samples separated every 5 mL from the beginning of a rain event, with automatic rainfall detection. Sampling duration does not refer to the actual duration of rainfall sampling, but rather to the time the Raingoround was set to begin waiting for rainfall and the time that it was set to stop collection.

Rainwater (wet deposition) samples were analyzed using ion chromatography (DX 120/AS, Dianex Inc.). The $\delta^{15}N/^{14}N$ and $\delta^{18}O/^{16}O$ isotope ratios in NO_3^- were measured using the denitrifier method[13,14]. The NO_3^- was converted to N_2O using a denitrifier (*Pseudomonas aureofaciens*; ATCC 13985) lacking N_2O reductase. The N_2O was then introduced into a Delta XP isotope ratio mass spectrometer coupled to an HP6890 gas chromatograph (Hewlett-Packard Co., Palo Alto, CA, U.S.A.) equipped with a Poraplot column and a GC interface III (Thermo Fisher Scientific). The anion concentrations and isotope ratios were measured at the Laboratory of Social Biogeochemistry (Laboratory of Prof. Muneoki Yoh and Assoc. Prof. Keisuke Koba), Tokyo University of Agriculture & Technology (TUAT), Building: #2, Room: 328 & 2N-101, 5-8, Saiwai-Cho 3-Chome, Fuchu-Shi, Tokyo 183-8509, Japan. The calibration curves for these isotopic analyses were constructed using the international standards USGS32, USGS34, USGS35 and IAEA. The stable isotope ratio delta was calculated with the following equation[15].

$$\left[\frac{R_{SAMPLE} - R_{STANDARD}}{R_{STANDARD}}\right] \times 1000 \text{‰} = \delta = \text{delta} \quad (1)$$

RESULTS AND DISCUSSION

Characteriztion of $\delta^{18}O/^{16}O$ of nitrogen oxide ions within aerosol samples during historically heavy rainfall

The $\delta^{18}O/^{16}O$ isotopic ratio observed in nitric-oxide substances in aerosol samples collected from 15:42 SST 18 to 15:42 SST 19 November 2009 was 25.54 and that observed in samples collected from 18:18 SST 19 to 18:18 SST 20 November 2009 was 21.17. These values are less than half the values of the other ratios observed in samples collected during sampling in November 2009 (Table-1). Historically heavy rainfall occurred on 19 November 2009, the date when the samples mentioned were collected. The $\delta^{18}O/^{16}O$ isotopic ratio in observed in nitric-oxide substances in aerosol samples collected from 13:22 SST 16 to 13:22 SST 20 July 2010 was

TABLE-1
STABLE ISOTOPE RATIO AND ANION CONCENTRATION OF AEROSOL (PM 4.5) (5 L/min) AT THE ROOF TOP OF NATIONAL UNIVERSITY OF SINGAPORE IN SINGAPORE FROM 16 TO 22 NOV. 2009 (SINGAPORE STANDARD TIME = UTC + 8 h)

Sampling date and time (Singapore Standard Time = UTC + 8 h)	$\delta^{15}N/^{14}N$ [per mil]	$\delta^{18}O/^{16}O$ [per mil]	NO_3^- [μmol/L]	NO_2^- [μmol/L]	F^- [μmol/L]	Cl^- [μmol/L]	SO_4^{2-} [μmol/L]	PO_4^{3-} [μmol/L]
15:27 16 => 15:27 17 NOV 2009	27.19	56.16	1.18	0.96	0	2.28	1.22	0
15:39 17 => 15:39 18 NOV 2009	9.02	62.37	1.2	0.54	0	2.35	1.75	0
15:42 18 => 15:42 19 NOV 2009	21.36	25.54	0.2	0	0	0.46	0	0
18:18 19 => 18:18 20 NOV 2009	7.78	21.17	0.23	0	0	0.7	0	0
18:35 20 => 18:35 21 NOV 2009	N/A	N/A	0	0	0	0.23	0	0
19:08 21 => 19:08 22 NOV 2009	16.64	41.91	0.62	0.46	0	1.6	0.33	0
Average	16.398	41.43	0.57167	0.326667	0	1.27	0.55	0
Standard deviation	8.213588	18.156587	0.5194	0.396114	0	0.9336	0.75429	0
Variance	67.46302	329.66165	0.26978	0.156907	0	0.8716	0.56896	0
Range	19.41	41.2	1.2	0.96	0	2.12	1.75	0
Minimum value	7.78	21.17	0	0	0	0.23	0	0
Maximum value	27.19	62.37	1.2	0.96	0	2.35	1.75	0
Total	81.99	207.15	3.43	1.96	0	7.62	3.3	0
Number of sample	5	5	6	6	6	6	6	6

TABLE-2
STABLE ISOTOPE RATIO AND ANION CONCENTRATION OF AEROSOL (PM 4.5) (5 L/min) AT THE ROOF TOP (ALTITUDE: 67 meter) OF NATIONAL UNIVERSITY OF SINGAPORE IN SINGAPORE FROM 16 TO 28 JUL 2010 (SINGAPORE STANDARD TIME = UTC + 8 h)

Sampling date and time (Singapore Standard Time = UTC + 8 h)	$\delta^{15}N/^{14}N$ [per mil]	$\delta^{18}O/^{16}O$ [per mil]	NO_3^- [μmol/L]	NO_2^- [μmol/L]	F^- [μmol/L]	Cl^- [μmol/L]	SO_4^{2-} [μmol/L]	PO_4^{3-} [μmol/L]
13:22 16 => 13:22 20 JUL 2010	9.74	34.46	6.23	1.44	0.96	7.84	22.65	N/A
13:25 20 => 13:25 24 JUL 2010	8.03	35.11	9.01	N/A	N/A	13.93	20.46	N/A
13:25 24 => 13:25 28 JUL 2010	5.67	61.12	3.73	N/A	N/A	5.54	10.22	N/A
Average	7.813333333	43.56333333	6.3233333	0.48	0.32	9.10333333	17.77667	0
Standard deviation	2.043632387	15.20799242	2.6412371	0.83138439	0.554256258	4.3353239	6.635242	0
Variance	4.176433333	231.2830333	6.9761333	0.6912	0.3072	18.7950333	44.02643	0
Range	4.07	26.66	5.28	1.44	0.96	8.39	12.43	0
Minimum value	5.67	34.46	3.73	0	0	5.54	10.22	0
Maximum value	9.74	61.12	9.01	1.44	0.96	13.93	22.65	0
Total	23.44	130.69	18.97	1.44	0.96	27.31	53.33	0
Number of sample	3	3	3	3	3	3	3	3

34.46 and that in samples collected from 13:25 SST 20 to 13:25 SST 24 July 2010 was 35.11. These values are almost half the values of other ratios observed during sampling in July 2010 (Table-2). Historically heavy rainfall occurred on 17 July 2010. Thus, during periods of historically heavy rainfall, the $\delta^{18}O/^{16}O$ isotopic ratios in nitric-oxide substances in aerosols tend to decrease tremendously.

Water containing the ^{18}O isotope freezes more rapidly than water containing the ^{16}O isotope[16]. More rain drops are produced rapidly inside cumulonimbus clouds before heavy rainfall than before ordinary rainfall. Hence more of the ^{18}O isotopes present in aerosol are consumed in the production of heavy amounts of raindrops during historically heavy rainfall. Therefore, the $\delta^{18}O/^{16}O$ isotopic ratios in nitric-oxide substances in aerosols decrease during historically heavy rainfall.

Characteriztion of $\delta^{15}N/^{14}N$ in nitrogen oxide ions in rainwater from historically heavy rainfall

Fig. 1 shows the nitrogen and oxygen isotopic ratios in nitrogen oxide ions in water from the historically intense rainfall on 19 November 2009 for each 5 mL fraction collected from the beginning of the rain. Fig. 2 shows the same measurements for 17 July 2010. The patterns of $\delta^{15}N/^{14}N$ as shown in Fig. 1 and 2 are very similar. This implies that the causes of both heavy rainfalls were the same, at least in terms of $\delta^{15}N/^{14}N$. The ratio dropped slightly from fraction 1 to fraction 2. This means that the early raindrops in the first fraction of rain were produced at a slightly higher altitude. The nuclear chemical reaction involving ^{14}N and a neutron (n) that produces the ^{14}C radioisotope is known to occur in the atmosphere, especially at altitudes between 30,000 feet and 50,000 feet (9000-15,000 m) and the neutron is known to be a highly penetrating particle[17-24].

$$ {}^{1}_{0}n + {}^{14}_{7}N \rightarrow {}^{14}_{6}C + {}^{1}_{1}H \quad (2) $$

At higher altitudes, neutron density is higher due to neutrons coming from sources including radiation from the sun. Hence ^{14}N atoms in nitrogen oxide ions in raindrops are more fully converted to ^{14}C by neutrons at higher altitudes. Consequently, $\delta^{15}N/^{14}N$ ratios increase with the production altitudes of raindrops.

The values of $\delta^{15}N/^{14}N$ for the second fractions shown in both Figs. 1 and 2 were at the minimum value. This means

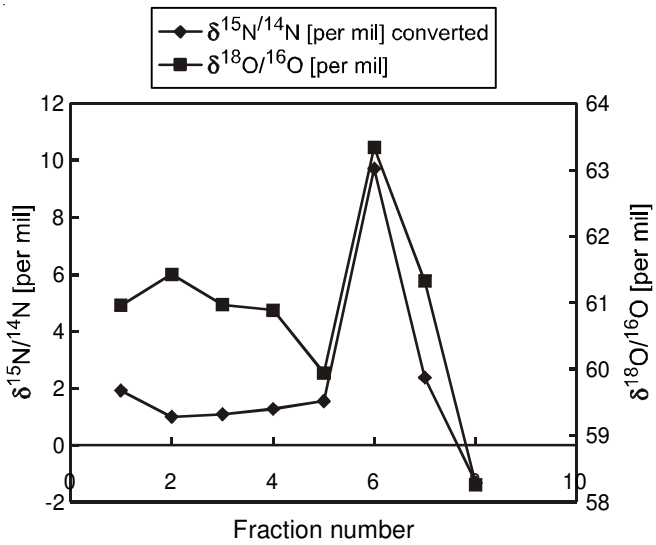

Fig. 1. Isotope ratios in wet deposition from 18 to 19 NOV 2009

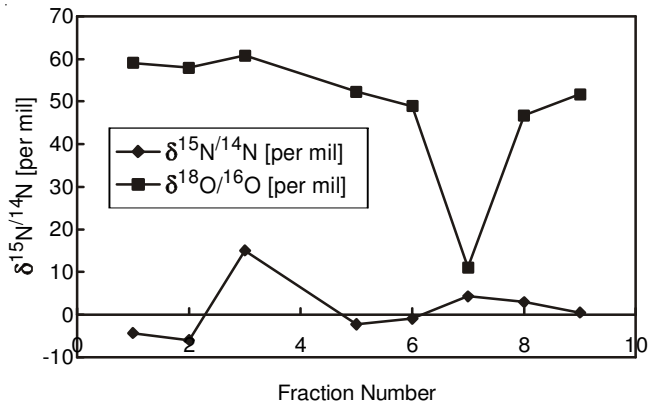

Fig. 2. Isotope ratios in wet deposition from 16 to 17 JUL 2011

that these fractions of raindrops were produced at a lower altitude. The density of neutrons is lower at lower altitudes. Hence ^{14}N atoms in nitrogen oxide ions in raindrops are less fully converted to ^{14}C by neutron-activated nuclear chemical reactions at lower altitudes. Consequently, $\delta^{15}N/^{14}N$ decreases with the production altitudes of raindrops.

After the second fractions, the values of $\delta^{15}N/^{14}N$ increase (Figs. 1 and 2). $\delta^{15}N/^{14}N$ reaches a value of 9.71 per mil at the sixth fraction (Fig. 1) and $\delta^{15}N/^{14}N$ reaches a maximum value of 15.02 per mil at the third fraction (Fig. 2). This indicates

that the altitudes of production of the raindrops was climbing over time. Because neutron density is higher at higher altitudes, this historically heavy rainfall was produced in a cumulonimbus cloud at a higher than normal altitude. Hence ^{14}N atoms in nitrogen oxide ions in raindrops are more fully converted to ^{14}C by neutron-activated nuclear chemical reactions at higher altitudes. Consequently, $\delta^{15}N/^{14}N$ increases with the production altitudes of raindrops.

Characteriztions of anions in rainwater from historically heavy rainfalls

As shown in Table-3, none of the fractions collected during the historically heavy rainfall on 19 November 2009 contained fluoride ions. However, some fractions of other rainwater samples collected, including samples collected on 17 July 2009, contained fluoride ions.

The anion characteriztions of samples collected on 19 November 2009 and 17 July 2010 are not same. This implies that there is some relationship between the characteriztions of aerosols and the characteriztions of rainfall. No fluoride ions were detected in aerosol samples collected in November 2009, thus there was a low level of fluoride ions in the atmosphere as aerosols during this period (Table-1). Therefore, if heavy rainfall scavenged chemicals from the atmosphere, there should be no fluoride ions in rainwater samples collected during this rainfall.

Some fractions of rainwater collected on 17 July 2009 contained fluoride ions (Table-4). However, the fluoride ions

TABLE-3
STABLE ISOTOPE RATIO AND ANION CONCENTRATION OF WET DEPOSITION AT THE ROOF TOP OF NATIONAL UNIVERSITY OF SINGAPORE IN SINGAPORE FROM 18:55 18 to 18:00 19 NOV 2009 (SINGAPORE STANDARD TIME = UTC + 8 h)

Sampling Date and time (Singapore Standard Time = UTC + 8 h)	Fraction number	$\delta^{15}N/^{14}N$ [per mil] converted	$\delta^{18}O/^{16}O$ [per mil]	NO_3^- [μmol/L]	NO_2^- [μmol/L]	F^- [μmol/L]	Cl^- [μmol/L]	SO_4^{2-} [μmol/L]
19:55 18 => 18:00 19 NOV 2009	1	1.91	60.96	26.46	0.74	0	69.07	37.09
19:55 18 => 18:00 19 NOV 2009	2	0.99	61.43	23.16	0.73	0	62.11	33.72
19:55 18 => 18:00 19 NOV 2009	3	1.08	60.97	20.2	0.61	0	58.46	29.13
19:55 18 => 18:00 19 NOV 2009	4	1.27	60.89	20.12	0.75	0	60.05	29.65
19:55 18 => 18:00 19 NOV 2009	5	1.55	59.94	16.9	0.52	0	47.8	25.12
19:55 18 => 18:00 19 NOV 2009	6	9.71	63.34	15.08	15.65	0	31.16	22.37
19:55 18 => 18:00 19 NOV 2009	7	2.37	61.33	23.44	0.69	0	63.26	36.86
19:55 18 => 18:00 19 NOV 2009	8	-1.32	58.26	2.93	60.77	0	134.75	7.69
Average		2.195	60.89	18.53625	10.0575	0	65.8325	27.70375
Standard deviation		3.2273209	1.4302	7.286641	21.1507	0	30.2271	9.633504
Variance		10.4156	2.04549	53.09514	447.35	0	913.675	92.8044
Range		11.03	5.08	23.53	60.25	0	103.59	29.4
Minimum value		-1.32	58.26	2.93	0.52	0	31.16	7.69
Maximum value		9.71	63.34	26.46	60.77	0	134.75	37.09
Total		17.56	487.12	148.29	80.46	0	526.66	221.63
Number of sample		8	8	8	8	8	8	8

TABLE-4
STABLE ISOTOPE RATIO AND ANION CONCENTRATION OF WET DEPOSITION AT THE ROOF TOP (ALTITUDE: 67 meter) OF NATIONAL UNIVERSITY OF SINGAPORE IN SINGAPORE FROM 19:00 16 TO 15:00 17 JUL 2010 (SINGAPORE STANDARD TIME = UTC + 8 h). SAMPLING BY HORIBA RAINGOROUND. IT WAS BEGINNING HEAVY THUNDER SHOWER AT 0400 ON JULY 17 2010. IT BROUGHT FLOOD DAMAGE SUCH LIKE SUBMERGED VEHICLE, SUBMERGED LAND, ELECTRIC POWER OUTAGE, *etc.*, IN SINGAPORE

Sampling Date and time (Singapore Standard Time = UTC + 8 h)	Fraction number	$\delta^{15}N/^{14}N$ [per mil]	$\delta^{18}O/^{16}O$ [per mil]	NO_3^- [μmol/L]	NO_2^- [μmol/L]	F^- [μmol/L]	Cl^- [μmol/L]	SO_4^{2-} [μmol/L]	PO_4^{3-} [μmol/L]
19:00 16 => 15:00 17 JUL 2010	1	-4.28	59.09	1.58	0	0.013	11.9	6.6	0
19:00 16 => 15:00 17 JUL 2010	2	-5.9	57.93	0.79	0	0.055	4.3	2.1	0
19:00 16 => 15:00 17 JUL 2010	3	15.02	60.81	9.62	0	0	45.7	22.4	0
19:00 16 => 15:00 17 JUL 2010	4	N/A	N/A	7.32	0	0	31.1	28	0
19:00 16 => 15:00 17 JUL 2010	5	-2.25	52.24	5.56	1.77	0.012	18	22.5	0
19:00 16 => 15:00 17 JUL 2010	6	-0.92	48.93	3.01	0.72	0	9.1	14.4	0
19:00 16 => 15:00 17 JUL 2010	7	4.26	11.08	4.03	0.57	0	13.8	27	0
19:00 16 => 15:00 17 JUL 2010	8	3	46.72	2.03	0	0	12.1	9.3	0
19:00 16 => 15:00 17 JUL 2010	9	0.49	51.63	1.57	0	0.006	6.1	16.4	0
Average		1.1775	48.55375	3.94555556	0.34	0.00955556	16.9	16.52222	0
Standard deviation		6.556712482	15.94625	2.99877104	0.605784615	0.01786135	13.35187	9.185148	0
Variance		42.99047857	254.28288	8.99262778	0.366975	0.00031903	178.2725	84.36694	0
Range		20.92	49.73	8.83	1.77	0.055	41.4	25.9	0
Minimum value		-5.9	11.08	0.79	0	0	4.3	2.1	0
Maximum value		15.02	60.81	9.62	1.77	0.055	45.7	28	0
Total		9.42	388.43	35.51	3.06	0.086	152.1	148.7	0
Number of sample		8	8	9	9	9	9	9	9

were detected in aerosol samples collected in July 2010 (Table-2). This implies that there was a high enough level of fluoride ions in the atmosphere as aerosols during this period to supply the historically heavy rainfall. After the scavenging of the atmosphere by the rainfall, there should have been fluoride ions in the rainwater collected on 17 July 2010.

Conclusion

The knowledge and insights gained in this study are discussed below.

(1) During periods of historically heavy rainfall, $\delta^{18}O/^{16}O$ isotopic ratios in nitric-oxide substances in aerosols tend to decrease tremendously. This is because the ^{18}O isotope is removed from aerosols for the production of heavy amounts of raindrops.

(2) Cumulonimbus clouds that produce historically heavy rainfall occupy a higher altitude than normal cumulonimbus clouds and the neutron density at that higher altitude is higher due to neutrons coming from the cosmos, including radiation from the sun. Hence ^{14}N atoms in nitrogen oxide ions in raindrops are more fully converted to ^{14}C radioisotopes by neutron-activated nuclear chemical reactions at higher altitudes. Consequently, $\delta^{15}N/^{14}N$ ratios increase with the production altitudes of raindrops. Therefore, figures displaying the $\delta^{15}N/^{14}N$ ratios of nitrogen oxide ions in different separated rainfall fractions have a characteristic form.

(3) This implies that there is some relationship between the chemical characteriztions of aerosols and the chemical characterizations of rainfall.

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