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Stable Nitrogen Isotope Ratio and the Anion Concentrations in Cloud-Based Aerosols

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It is important to determine the stable nitrogen isotope ratio for the nitrogenous substances in aerosols and the geochemistry behaviour of stable nitrate ion isotopes in aerosols in order to elucidate the chemical and physical functions of clouds. Hence, aerosol field sampling was conducted in the skies offshore from Malibu Beach and Santa Barbara, California, U.S.A. on 16 and 18 July 2009, using an airplane. The samples were analyzed for nitrate and nitrite ions using ion chromatography and GC-mass spectrometry (GC-MS). The results indicate a higher stable isotopic ratio of δ 15N/14N in the aerosols collected at the cloud top of one cloud than the aerosols collected from the cloud base of a second cloud at the same altitude (30.48 m) on 18 July 2009. NO_2^- nitrite ions were present only in the aerosols sample at the cloud base. At the same altitude, the stable nitrogen isotope ratio in the nitrogenous substances found in the aerosol depended on the aerosol position within the clouds. Furthermore, the altitude effect was small for the isotope ratio. To date, no research has been published that explores the relationship between the electric charge of clouds or the atmosphere and the fate or transformation of aerosols. Present investigation indicated that past models describing the fate or transformation of aerosols within clouds are not based on the actual details of the situation. This study showed that the fates of electrically charged aerosols or ionized aerosols were affected by the electrically charged cloud.

Key Words: Cloud effect, Aerosol, Nitrogen stable isotope ratio, Anion concentration, Electric charge, Cloud base, Cloud top, GC-mass spectrometry, Denitrifier method.

INTRODUCTION

It is very important to examine the stable nitrogen isotope ratio of nitric oxide substances that make up cloud-based aerosols and to understand the geochemistry behaviour of the aerosol to gain knowledge and insights into the atmospheric environment[1,2]. To date, there have been a considerable number of reports and investigations regarding aerosols. Although there have been several studies on nitrogen isotopes and their influence on the fate and transformation of several atmospheric compounds, the chemical and isotopic function of clouds is not well understood[3,4]. Furthermore, the relationship between the phenomena of aerosols and the electric charge of either clouds or the atmosphere has never been considered. It is known that many kinds of clouds and even the atmosphere itself, have electric charges, not just thunderstorm clouds. In this study, aerosol samples were collected from the cloud top and base separately to analyze and investigate the trends in the inorganic anions and the stable nitrogen and oxygen isotope ratios above and below the clouds. In sum, we sought to elucidate how the electric charge of clouds affects aerosols in terms of the stable nitrogen isotopes of nitric-oxide substances and the anion concentration.

EXPERIMENTAL

The aerosol samples (PM 4.5) were taken from the cloud top (Altitude: 182.88 m on 16 July 2009; 30.48 m on 18 July 2009) and the cloud base (Altitude: 30.48 m on July 16, 2010; 30.48 m on 18 July 2010) by a Piper PA-28 Cherokee airplane (Tail number: N777VP). A sampling pump (Model: SP 250, GL science) was run through a small cockpit window for sample extraction and the samples were collected onto polyamide filters (NX047100, Pall Corporation) at a flow rate of 5 L/min. The sampling was conducted on 16 July 2009, from 13:46 to 14:42 pacific daylight saving time (PDT=UTC -7 h) offshore from Malibu beach, California, U.S.A. (Fig. 1) and from 13:51 to 16:07 pacific daylight saving time on 18 July 2009, offshore from Santa Barbara, California, U.S.A. (Fig. 2). These research flights were approved by the U.S. Air Traffic Control Southern California approach and the Santa Barbara approach. The polyamide filters were then transferred into 20 mL of ultra pure water and shaken for approximately 40 min.

The extracts were filtered and analyzed using an ion chromatograph (DX 120/AS, Dianex Inc.). The delta (δ) 15N/14N and delta (δ) 18O/ 16O of NO_3^- were measured using the denitrifier method[5,6]. The NO_3^- was converted into N_2O using a denitrifier (*Pseudomonas aureofaciens*; ATCC 13985) lacking N_2O reductase. The N_2O produced was introduced into a δ XP isotope ratio mass spectrometer coupled with a 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, Tokyo University of Agriculture and Technology (TUAT), Tokyo, Japan. The calibrations for these isotopic analyses were carried out using international standards USGS32, USGS34, USGS35 and IAEA. The stable isotope ratio δ (delta) was calculated with the following equation[7].

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{sample}} \right) \times 1000\ \% \quad (1)$$

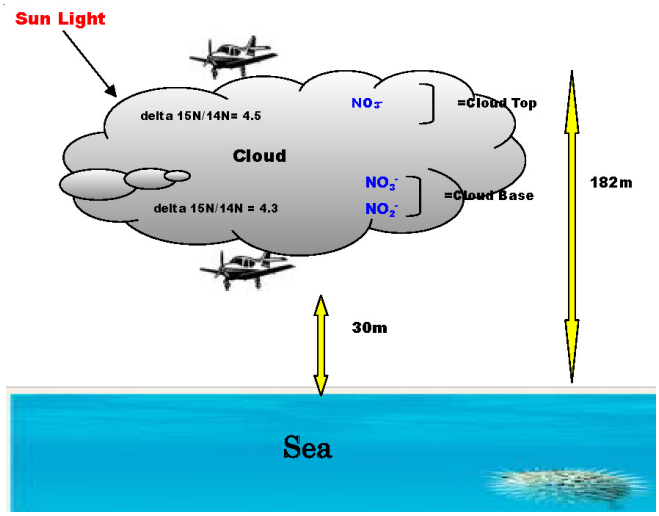

Fig. 1. Sampling on 16 July 2009, at different altitudes

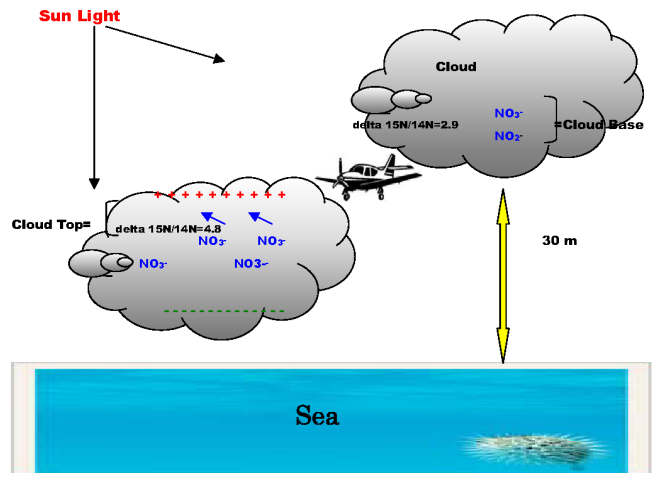

Fig. 2. Sampling on 18 July 2009, at the same altitude

RESULTS AND DISCUSSION

Table-1 shows the inorganic anion concentrations and the stable isotope ratios in the nitric-oxide substances within the aerosols for all of the samples collected during the sampling. Fig. 3 shows the variation in the anion concentrations and the stable isotopic ratio at the cloud top, at the cloud base and in the clear skies on 16 July 2009 and Fig. 4 shows the variations on 18 July 2009. In Fig. 4, it can be observed that at the same altitude, the stable isotope ratio δ (delta) 15N/14N in the aerosol at the top of a cloud is higher than that at the base of a cloud on July 18, 2009 (Fig. 2). Figs. 3 and 4 (sampling on 16 & 18 July 2009) also indicate that aerosols collected from the cloud top did not contain any NO_2^- nitrite ions. However, NO_3^- nitrate ions and other anions, such as chloride ions Cl^- and fluoride ions F^-, are present in both positions within the cloud. In contrast, sulfate ions (SO_4^{2-}) were not present in either position within the cloud on 18 July 2009. Nitrate ions (NO_3^-) were present in higher concentrations at the cloud top than at the cloud base on both 16 and 18 July 2009.

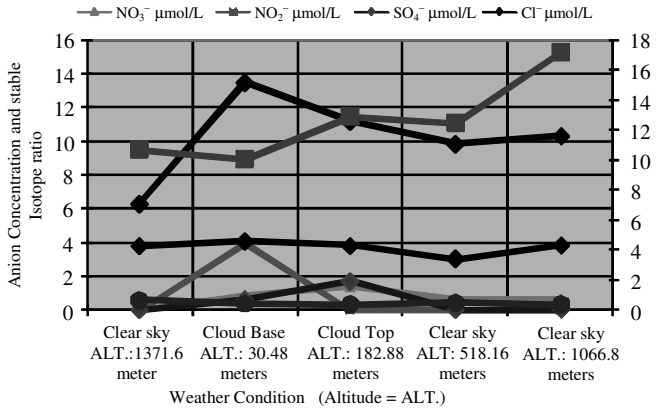

Fig. 3. Weather conditions *vs.* anion concentration and stable isotope ratio on 16 July 2009

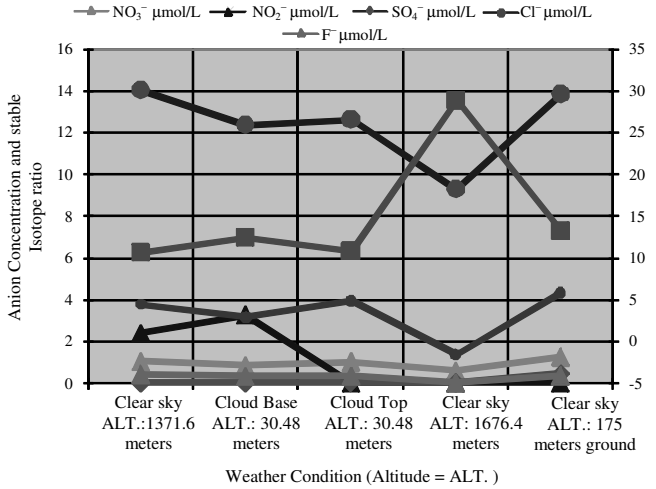

Fig. 4. Weather conditions *vs.* anion concentration and stable isotope ratio on 18 July 2009

The results on both 16 and 18 July 2009, showed that the concentrations of nitrate ions (NO_3^-) at the cloud top were higher than those at the cloud base. At the same altitudes on 18 July 2009, the stable nitrogen isotope ratio in the nitric-oxide substances present in the aerosols at the cloud top of one cloud was higher than that at the cloud base of a second cloud[7]. Furthermore, the altitude effect was small for the isotope ratio of the nitric-oxide substances present in the

TABLE-1
VARIATION IN THE ANION CONCENTRATION AND THE STABLE ISOTOPE RATIOS OF AEROSOL DATA COLLECTED BY FLYING OVER THE SUBURBS OF LOS ANGELES ON 16 AND 18, JULY 2009

Date of sampling	Time of sampling (PDT)	Location	Latitude and longitude	Altitude (m)	Temp. (ºC)	Weather	δ 15N /14N	δ 18O/ 16O	NO_3^- (µmol/L)	NO_2^- (µmol/L)	SO_4^{2-} (µmol/L)	Cl^- (µmol/L)	F^- (µmol /L)
16 JULY 2009	1346-1356	030º from Santa Monica Airport (SMO)	34º05'N 118º42'W	1371.6	33	Clear sky	4.2	10.6	N/A	N/A	N/A	6.27	0.57
16 JULY 2009	1403-1413	Offshore Malibu Beach	34º04.19'N 119º07.56'W	30.48	19	Cloud Base	4.5	10.0	0.85	3.9.	0.58	13.45	0.35
16 JULY 2009	1419-1429	Offshore Malibu Beach	34º05.53'N 119º19.00'W	182.88	19	Cloud Top	4.3	12.9	1.39	N/A	1.68	11.16	0.3
16 JULY 2009	1434-1442	From Offshore Malibu to Camarillo Airport (CMA)	34º04.09'N 119º03.12'W	518.16	26	Clear sky	3.4	12.4	0.64	N/A	N/A	9.82	0.41
16 JULY 2009	1601-1611	From CMA to SMO	34º13.58'N 118º55.48'W	1066.8	25	Clear sky	4.3	17.1	0.59	N/A	N/A	10.3	0.33
18 JULY 2009	1351-1401	From SMO to Santa Barbara (SBA)	34º05.47'N 118º46.63'W	1371.6	33	Clear sky	4.4	10.8	1.01	2.37	N/A	14.03	0.41
18 JULY 2009	1435-1445	Between SBA and Santa Rosa Island	34º03.05'N 120º04.54'W	30.48	18	Cloud Base	2.9	12.4	0.82	3.24	N/A	12.35	0.31
18 JULY 2009	1451-1501	Between SBA and Santa Miguel Island	34º04.34'N 120º21.14'W	30.48	27-20	Cloud Top	4.8	10.8	0.99	N/A	N/A	12.61	0.32
18 JULY 2009	1557-1607	From Santa Cruz Island to SMO	34º03.88'N 120º25.28'W	1676.4	30	Clear sky	-1.7	28.8	0.58	N/A	N/A	9.28	N/A
18 JULY 2009	1646-1656	SMO	34º00.95'N 118º27.08'W	175 Ground	N/A	Clear sky	5.8	13.3	1.23	N/A	0.43	13.85	0.34

aerosols in the cloud on 16 July 2009. In addition to thunderstorm clouds, all other kinds of clouds and the atmosphere itself, have an electric charge[8-10]. Usually, the cloud top has a positive electric charge and the cloud base has a negative electric charge. Hence, the inside of the cloud should function as an electrolyzer or as electrophoretic equipment for the aerosols, especially when dealing with an electrically charged aerosol or an ionized aerosol. In addition, the electric charge should have an effect on the electrically charged and ionized aerosols outside of the cloud. Thus, the positively charged layer of the cloud should have the ability to attract anion aerosols from outside the cloud and the negative electrically charged layer of the cloud should have the ability to attract cation aerosols (Fig. 5).

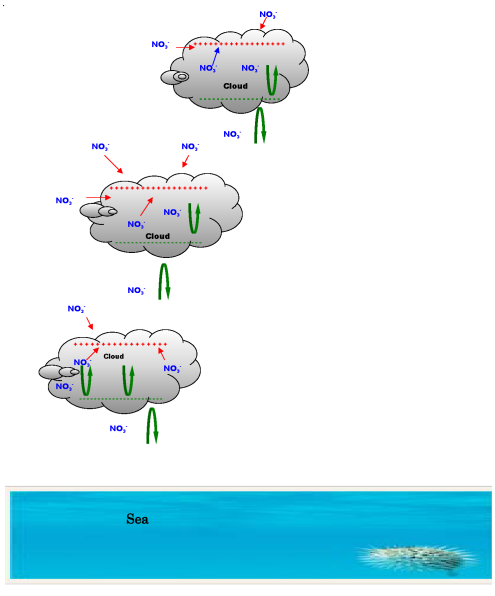

Fig. 5. Image describing the behaviour of NO_3^-

The absolute value of the electric potential or the electric field E_H of the heavier isotopic electrode is higher than that of the electric potential or the electric field E_L of the lighter isotopic electrode[11]. The following relationship between the electric potential or the electric field E and the electrostatic force F is known.

$$\vec{F} = q\vec{E} \quad (2)$$

where, q is the electric charge. Therefore, the electrostatic force F_H of heavier isotopic electrodes is stronger than the electrostatic force F_L of lighter isotopic electrodes. Hence, if the cloud top had a positive electric charge and the cloud base had a negative electric charge, then the cloud top would have a stronger absorption force for heavier isotopes than for lighter isotopes and the cloud base would have a stronger repulsive force for heavier isotopes than for lighter isotopes. These forces had the effect of concentrating a greater number of heavier isotopes in the cloud top of one cloud than in the cloud base of another cloud at the same altitude on 18 July 2009 (Fig. 2). This occurred because the cloud top had a positive electric charge, but the cloud base had a negative electric charge.

The absence of nitrite ions at the cloud top is noteworthy. Because the cloud top was exposed to sunlight during the day, large amounts of hydroxyl free radicals (OH·) were formed in the top layer of the cloud[12]. A chemical reaction produced nitrate ions and these free radicals from the unstable nitrite ions[13]. Hence, the aerosols at the cloud top did not contain nitrite ions.

$$NO_2 + OH \rightarrow HNO_3 \quad (3)$$

Conclusion

To date, the relationship between the electric charge of clouds or the atmosphere and the fate or transformation of

aerosols has not been explored. Present investigation indicated that past models addressing the fate or transformation of cloud aerosols are not based on the actual details of the situation[14,15]. This study showed that the fate of the electrically charged aerosol or ionized aerosol was affected by the electric charge of the cloud. The electric charge of clouds or the atmosphere will vary with the weather conditions. In the future, investigations of cloud aerosols should consider the cloud effect and the variation between the cloud top and base.

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