The Effect of Electrically Charged Clouds on the Stable Nitrogen Isotope Ratio and the Anion Concentrations in Cloud-based Aerosols

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ABSTRACT: It is very important to determine the stable nitrogen isotope ratio for the nitrogenous substances in aerosols and the geochemistry behavior 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 (IC) and GC-mass spectrometry (GC-MS). The results indicate a higher stable isotopic ratio of δ (delta) 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 meters) on 18 July 2009. NO_2^- nitrite ions were present only in the aerosols sampled 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. My 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: Aerosol, Anion, Cloud, Isotope, Nitrogen, Oxygen

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 behavior of the aerosol to gain knowledge and insights into the atmospheric environment (Samuel, *et al.,* 2008; Baechmann *et al.,* 1996) . To date, there have been a considerable number of reports and investigations regarding aerosols. Although there have been several studies 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 (Savarino *et al.,* 2007; Shuvashish *et al.,* 2010). 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.

MATERIALS & METHODS

The aerosol samples (PM 4.5) were taken from the cloud top (Altitude: 182.88 meters on 16 July 2009; 30.48 meters on 18 July 2009) (Fig. 1) and the cloud base (Altitude: 30.48 meters on July 16, 2010; 30.48 meters on 18 July 2010) (Fig. 2) by a Piper PA-28 Cherokee airplane (Tail number: N777VP) (Fig. 3). A sampling pump (Model: SP 250, GL science) was run

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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 liters per minute. The sampling was conducted on 16 July 2009, from 13:46 to 14:42 PDT (Pacific Daylight Saving Time = UTC -7 hours) offshore from Malibu Beach, California, U.S.A. (Fig. 6) and from 13:51 to 16:07 PDT on 18 July 2009, offshore from Santa Barbara, California, U.S.A. (Fig. 7). 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 minutes. The extracts were filtered and analyzed using an ion chromatograph (DX 120/AS, Dianex Inc.). The δ (delta) $15N/14N$ and δ (delta) $18O/16O$ of NO_3^- were measured using the denitrifier method (Casciotti *et al.,* 2002; Takebayashi *et al.,* 2010). 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 Delta 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 (Laboratory of Professor YOH Muneoki & Associate Professor KOBA Keisuke), Tokyo University of Agriculture & Technology (TUAT), Building: #2, Room: 324 & 2N-101, 5-8,Saiwai-Cho 3-Chome, Fuchu-Shi, Tokyo 183-8509, 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 (Richet *et al.,*1977),

$$\left[\frac{RSAMPLE - RSTANDARD}{RSAMPLE} \right] \times 1000 \; °/°° = \delta = delta \quad (1)$$

RESULTS & 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. 4 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. 5 shows the variations on 18 July 2009. In Fig. 5, 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. 7). Figs 4 and 5 (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, SO_4^{2-} sulfate ions were not present in either position within the cloud on 18 July 2009. NO_3^- nitrate ions were present in higher concentrations at the cloud top than at the cloud base on both 16 and 18 July 2009.

My 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 (Richet P. *et al.,*1977). Furthermore, the altitude effect was small for the isotope ratio of the nitric-oxide substances present in the 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 (Galembeck *et al.,* 2010; IMYANITOV *et al.,* 1962; Winn *et al.,* 1978). 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. 10).

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 (HOEFS 2004; KATSURA 1979; Wang 1953). 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 (Coulomb 1785). 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

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Fig. 1. Altitude: 30.48 meters; Position: N:34º04.19', W:119º07.56'; Location: Cloud Base offshore from Malibu Beach; Time: 14:03-14:13 PDT; Date: 16 July 2009; Temperature: +19°C; Climate: Overcast between 30.48 meters and 182.88 meters

Fig. 2. Altitude: 182.88 meters; Position: N:34º05.53', W:119º19.00'; Location: Cloud top offshore from Malibu Beach; Time: 14:19-14:29 PDT; Date: 16 July 2009; Temperature: +19°C; Climate: Overcast between 30.48 meters and 182.88 meters

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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 (meters)	Temperature (°C)	Weather	delta 15N/14N	delta 18O/16O	NO_3^- (µ mol/L)	NO_2^- (µ mol/L)	SO_4^{2-} (µ mol/L)	Cl^- (µ mol/L)	F^- (µ mol /L)
16 JULY 2009	1346-1356	030° from Santa Monica Airport (SMO)	34°05'N 118°42'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	34°04.19'N 119°07.56'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	34°05.53'N 119°19.00'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)	34°04.09'N 119°03.12'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	34°13.58'N 118°55.48'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)	34°05.47'N 118°46.63'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	34°03.05'N 120°04.54'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	34°04.34'N 120°21.14'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	34°03.88'N 120°25.28'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	34°00.95'N 118°27.08'W	175 Ground	N/A	Clear sky	5.8	13.3	1.23	N/A	0.43	13.85	0.34

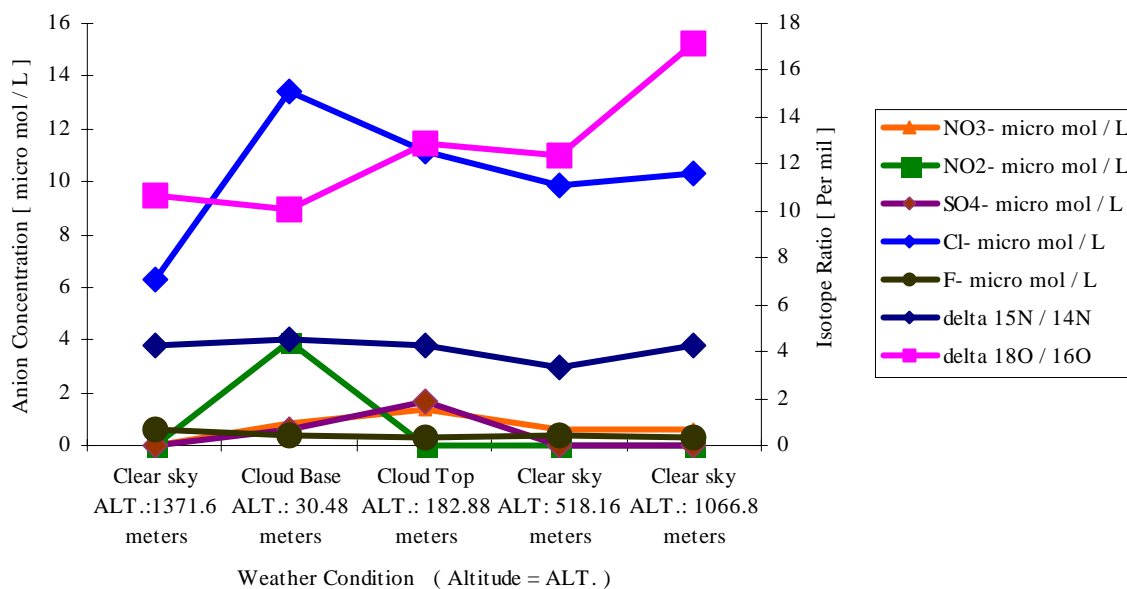**Fig. 3. Piper PA-28 Cherokee (Tail number: N777VP)**

Fig. 4. Weather Conditions vs. Anion Concentration and Stable Isotope Ratio on 16 July 2009
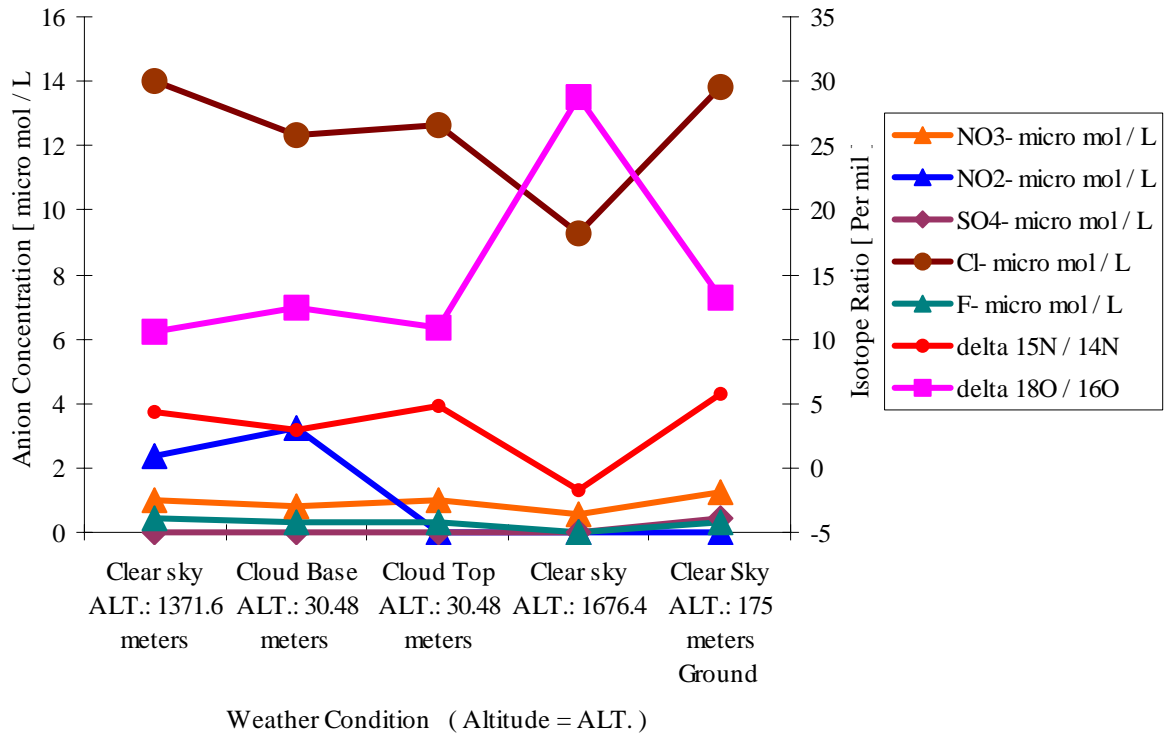
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Fig. 5. Weather Conditions vs. Anion Concentration and Stable Isotope Ratio on 18 July 2009
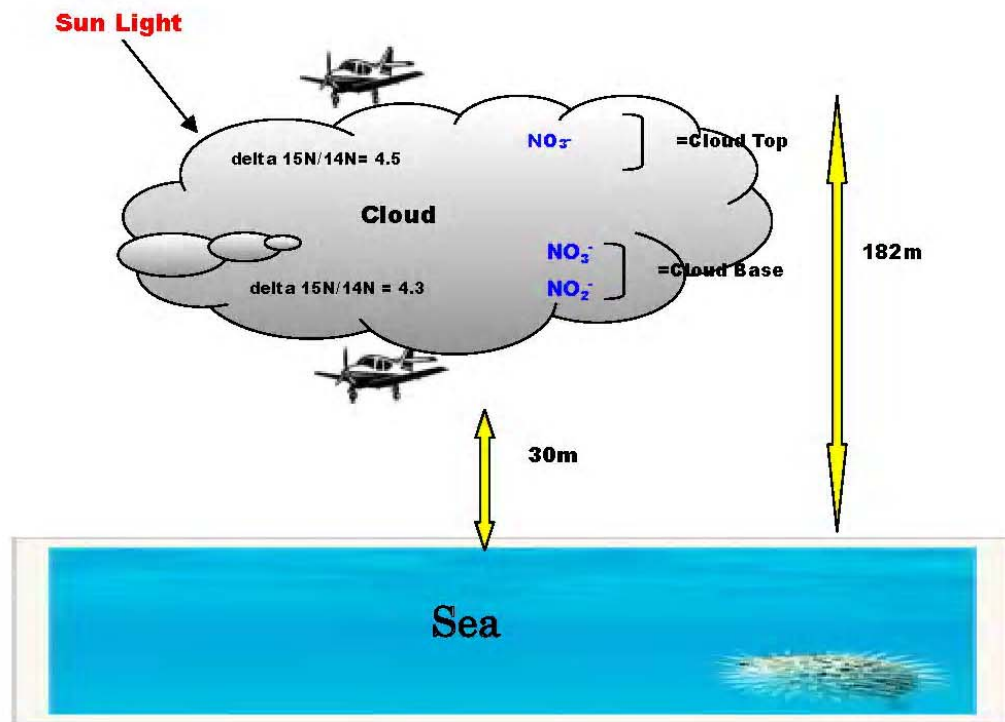

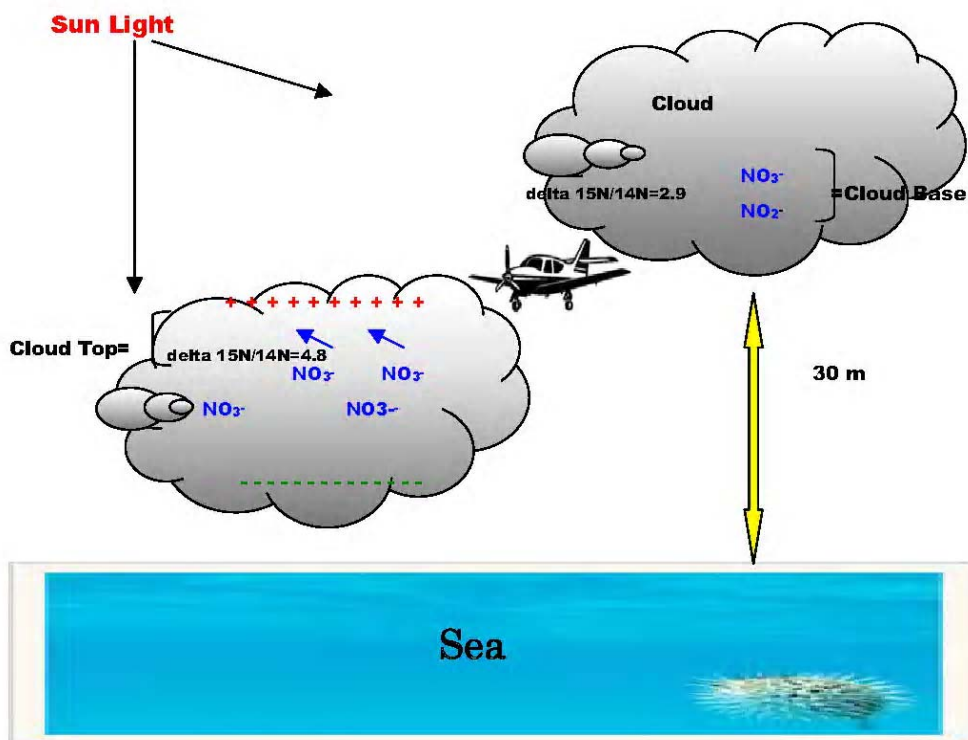**Fig. 6. Sampling on 16 July 2009, at different altitudes**
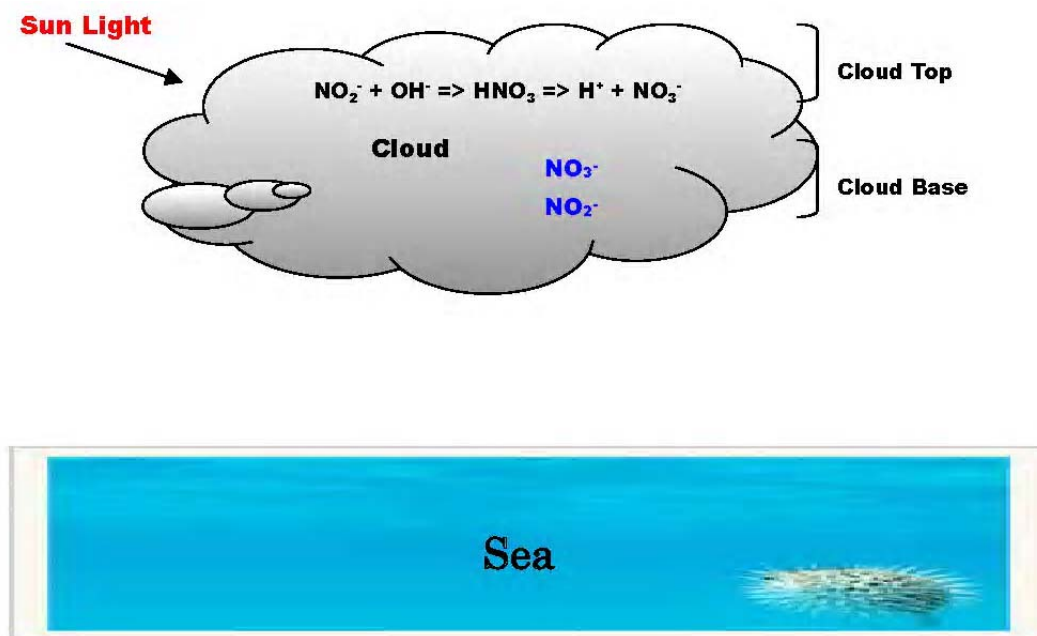
Fig. 7. Sampling on 18 July 2009, at the same altitude
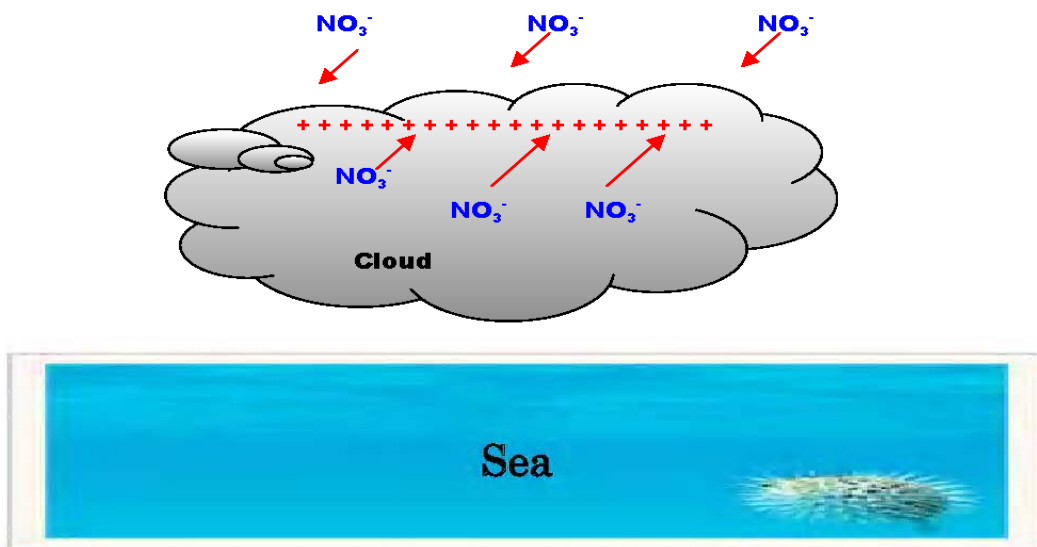
Fig. 8. Image describing the existence of NO_2^- in the cloud

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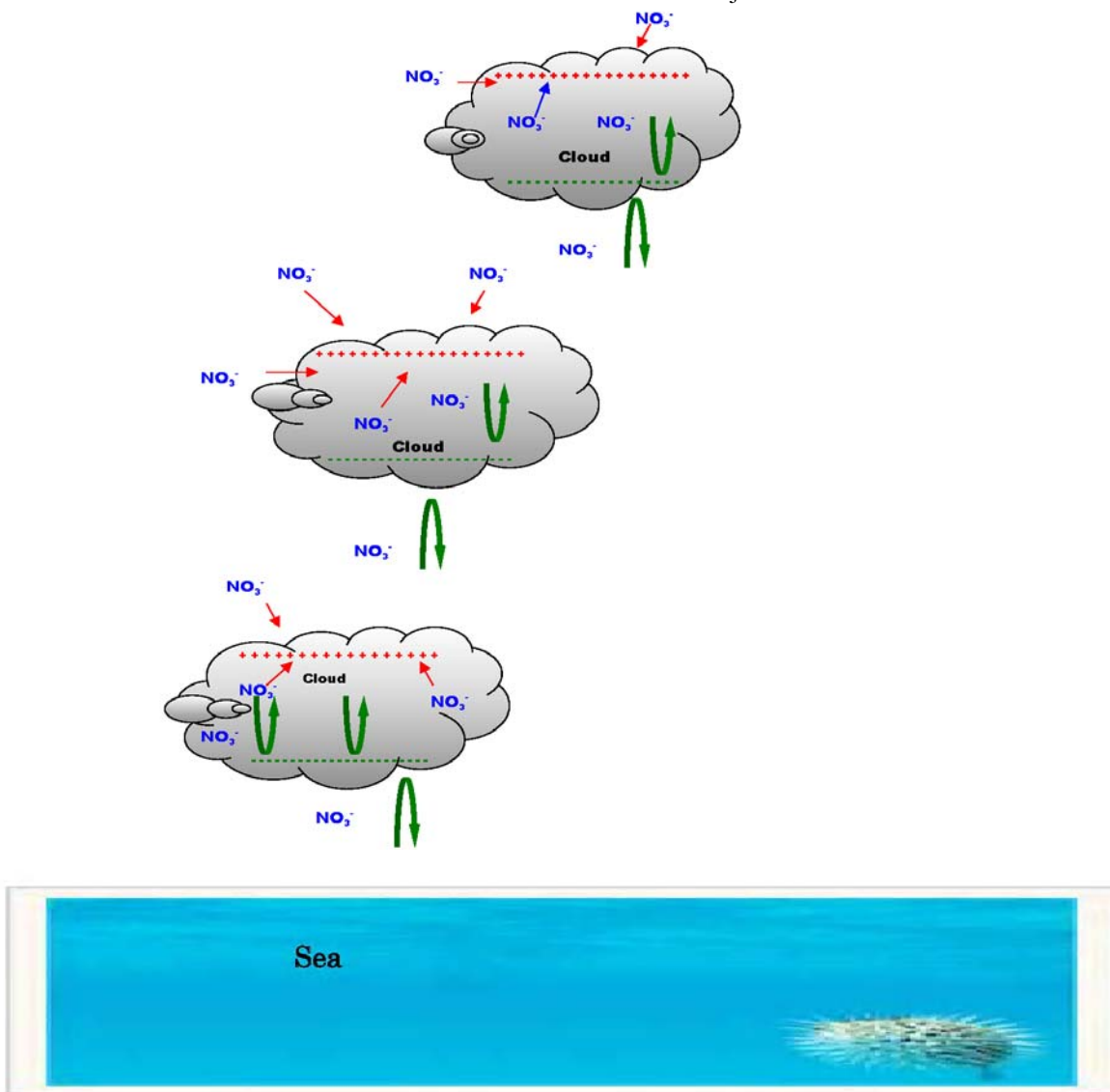**Fig. 9. Image describing the behavior of NO_3^- in the cloud**

Fig. 10. Image describing the behavior of NO_3^-

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. 7). 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 (Watts *et al.,* 1987). A chemical reaction produced nitrate ions and these free radicals from the unstable nitrite ions (Simon *et al.,* 1998) . Hence, the aerosols at the cloud top did not contain nitrite ions (Fig. 8).

$$NO_2^- + OH^- \rightarrow HNO_3 \qquad (3)$$
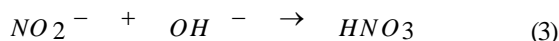
CONCLUSION

To date, the relationship between the electric charge of clouds or the atmosphere and the fate or transformation of aerosols has not been explored. My investigation indicated that past models addressing the fate or transformation of cloud aerosols are not based on the actual details of the situation. This study showed that the fate of the electrically charged aerosol or ionized aerosol was affected by the electric charge of the cloud(Figs. 9 & Fig. 10). 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.

REFERENCES

Baechmann, K., Ebert, P., Haag, I., Prokop, T. and Steigerwald, K. (1996). The chemical content of raindrops as a function of drop radius-I. Field measurement at the cloud base and below the cloud.Atmos. Environ., **30 (7)**, 1019-1033.

Casciotti, K. L., Sigman, D. M., Galanter Hastings, M., Böhlke, J. K. and Hilkert, A. (2002). Measurement of the Oxygen Isotopic Composition of Nitrate in Seawater and Freshwater Using the Denitrifier Method. *Anal. Chem.,* **74 (19)**, 4905–4912.

Coulomb, C. A. (1785). Second Memoire sur l'Electricite et le Magnetisme Simon, C. L. and Brimblecombe, P. (1998). Thermodynamic Model of the System H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O at Tropospheric Temperatures. *J. Phys. Chem. A.,* **102 (12)**, 2137–2154.

Galembeck, F., Bernardes, J. S., Ducati, T., Santos, L. and Burgo, T. (2010). Atmosphere is a reservoir of electric charge, mediated by water ion partition. Abstract, 240th American Chemical Society National Meeting, Boston, MA, Division of Physical Chemistry (PHYS) 501.

Hoefs, J. (2004). Stable Isope Geochemistry, Springer, Verlag, New York.

Imyanitov, I. M. (1962). Present state of research on atmospheric electricity. Soviet Physics Uspekhi, **5 (2)**, 292-322.

Katsura, H. (1979). Electrolytic concentration of D isotope of hydrogen by hydrogen absorbing alloy electrodes. Theses, Tokai University.

Katsura, H. (2010). Study on aerosol in offshore Malibu Beach and Santa Barbara, California by airplane: Relationship between aerosol of top of cloud and aerosol of bottom of cloud regarding nitrogen stable isotope ratio and concentration of nitrate and nitrous. Abstrac, 239th American Chemical Society National Meeting, San Francisco, CA, Division of Geochemistry (GEOC) 204.

Kundu, S., Kimitaka Kawamura, Andreae, T. W., Hoffer, A. and Andreae, M. O. (2010) Diurnal variation in the water-soluble inorganic ions, organic carbon and isotopic compositions of total carbon and nitrogen in biomass burning aerosols from the LBA-SMOCC campaign in Rondônia, Brazil. Journal of Aerosol Science, **41**, 118–133.

Richet, P., Bottinga, Y. and Javoy, M. (1977). A Review of Hydrogen, Carbon, Nitrogen, Oxygen, Sulphur, and Chlorine Stable Isotope Fractionation Among Gaseous Molecules. Annual Review of Earth and Planetary Sciences, **5**, 65-110.

Samuel, M., Savarino, J., Markus, F. M., Yan, N., Bekki, S., Bottenheim, J. W. and Jean, M. F. (2008). Tracing the Origin and Fate of NOx in the Arctic Atmosphere Using Stable Isotopes in Nitrate. Science, **322 (5902)**, 730–732.

Savarino, J., Kaiser, K., Morin, S., Sigman, D. M. and Thiemens, M. H. (2008). Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica. Atmospheric Chemistry and Physics, **7**, 1925–1945.

Takebayashi, Y., Koba, K., Sasaki, Y., Fang, F. and Yoh, M. (2010). The natural abundance of 15N in plant and soil-available N indicates a shift of main plant N resources to NO_3^- from NH_4^+ along the N leaching gradient. Rapid communications in mass spectrometry, **24**, 1001-1008.

Wang, J. H., Robinson, C. V. and Edelman, I. S. (1953). Self-diffusion and Structure of Liquid Water. III.

Measurement of the Self-diffusion of Liquid Water with H^2, H^3 and O^{18} as Tracers *Journal. of American. Chemical. Society*, **75 (2)**, 466–470.

Watts, S. F., Watson, A. and Brimblecombe, P. (1987). Measurements of the aerosol concentrations of methanesulphonic acid, dimethyl sulphoxide and dimethyl sulphone in the marine atmosphere of the British Isles Atmospheric Environment, **21 (12)**, 2667-2672.

Winn, W. P., Moore, C. B., Holmeset, C. R. and Byerley, L. G. (1978). Thunderstorm on July 16, 1975, over Langmuir Laboratory: A case study. Journal of Geophys. Res., **83**, 3079-3092.