Accounts of the effect of electrically charged clouds on the stable nitrogen isotope ratio and the anion concentration in cloud-based aerosols

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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 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 m) on 18 July 2009. NO₂ 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. 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, isotope, nitrate ions, nitrite ions.

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, 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., 2008; Kundu, 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 AND METHODS

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) (Figure 1) and the cloud base (Altitude: 30.48 m on 16 July, 2010; 30.48 meters on 18 July, 2010) (Figure 2) by a Piper PA-28 Cherokee airplane (Tail number: N777VP) (Figure 3). 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 PDT (Pacific Daylight Saving Time = UTC - 7 h) offshore from Malibu Beach, California, U.S.A. (Figure 6) and from 13:51 to 16:07...
PDT on 18 July, 2009, offshore from Santa Barbara, California, U.S.A. (Figure 7). These research flights were approved by the U.S. Air Traffic Control Southern California Approach and the Santa Barbara Approach (Katsura, 2010). 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, Dionex Inc.). The \( \delta \) (delta) 15N / 14N and \( \delta \) (delta) 18O / 16O of NO\(_3\) were measured using the denitrifier method (Casciotti, 2002; Takebayashi et al., 2010). The NO\(_3\) was converted into N\(_2\)O using a denitrifier (Pseudomonas aureofaciens; ATCC 13985) lacking N\(_2\)O reductase. The N\(_2\)O 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 and Associate Professor KOBA Keisuke), Tokyo University of Agriculture and Technology (TUAT). Building: #2, Room: 328 and 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 \( \delta \) (delta) was calculated with the following equation

\[
\frac{R_{\text{SAMPLE}} - R_{\text{STANDARD}}}{R_{\text{STANDARD}}} \times 1000\% = \delta = \delta
\]

**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. Figure 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 Figure 5 shows the variations on 18 July, 2009. In Figure 5, it can be observed that at the same altitude, the stable isotope ratio (delta) 15N/14N in the
Figure 4. Weather Conditions vs. Anion Concentration and Stable Isotope Ratio on 16 July, 2009.

Figure 5. Weather Conditions vs. Anion Concentration and Stable Isotope Ratio on 18 July, 2009.
Figure 6. Sampling on 16 July, 2009 at different altitudes.

Figure 7. Sampling on 18 July 2009, at the same altitude.
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.

<table>
<thead>
<tr>
<th>Date of sampling</th>
<th>Time of sampling (PDT)</th>
<th>Location</th>
<th>Latitude and longitude</th>
<th>Altitude (m)</th>
<th>Temperature (°C)</th>
<th>Weather</th>
<th>Delta 15N/14N (‰)</th>
<th>Delta 18O/16O (‰)</th>
<th>NO$_2^-$ (μ mol/L)</th>
<th>NO$_3^-$ (μ mol/L)</th>
<th>SO$_2^-$ (μ mol/L)</th>
<th>Cl$^-$(μ mol/L)</th>
<th>F$^-$(μ mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 July, 2009</td>
<td>1346-1356</td>
<td>030º from SMO</td>
<td>34°05'N 118°42'W</td>
<td>1371.6</td>
<td>33</td>
<td>Clear sky</td>
<td>4.2</td>
<td>10.6</td>
<td>N/A</td>
<td>3.9</td>
<td>0.85</td>
<td>3.9</td>
<td>0.08</td>
</tr>
<tr>
<td>16 July, 2009</td>
<td>1403-1413</td>
<td>Offshore Malibu Beach</td>
<td>34°04.19'N 119°07.56'W</td>
<td>30.48</td>
<td>19</td>
<td>Cloud Base</td>
<td>4.5</td>
<td>10.0</td>
<td>0.85</td>
<td>3.9</td>
<td>0.58</td>
<td>3.9</td>
<td>0.08</td>
</tr>
<tr>
<td>16 July, 2009</td>
<td>1419-1429</td>
<td>Offshore Malibu Beach</td>
<td>34°05.53'N 119°19.00'W</td>
<td>182.88</td>
<td>19</td>
<td>Cloud top</td>
<td>4.3</td>
<td>12.9</td>
<td>1.39</td>
<td>N/A</td>
<td>1.68</td>
<td>11.16</td>
<td>0.3</td>
</tr>
<tr>
<td>18 July, 2009</td>
<td>1601-1611</td>
<td>From CMA to SMO</td>
<td>34°04.05'N 119°03.12'W</td>
<td>518.16</td>
<td>26</td>
<td>Clear sky</td>
<td>3.8</td>
<td>12.4</td>
<td>0.64</td>
<td>N/A</td>
<td>9.82</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>18 July, 2009</td>
<td>1434-1442</td>
<td>From Offshore Malibu to Camarillo Airport (CMA)</td>
<td>34°13.58'N 118°55.48'W</td>
<td>1066.8</td>
<td>25</td>
<td>Clear sky</td>
<td>4.3</td>
<td>17.1</td>
<td>0.59</td>
<td>N/A</td>
<td>10.3</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>18 July, 2009</td>
<td>1351-1401</td>
<td>From SMO to Santa Barbara (SBA)</td>
<td>34°05.47'N 118°46.63'W</td>
<td>1371.6</td>
<td>33</td>
<td>Clear sky</td>
<td>4.3</td>
<td>10.8</td>
<td>1.01</td>
<td>2.37</td>
<td>14.03</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>18 July, 2009</td>
<td>1435-1445</td>
<td>Between SBA and Santa Rosa Island</td>
<td>34°03.05'N 120°04.54'W</td>
<td>30.48</td>
<td>18</td>
<td>Cloud Base</td>
<td>2.9</td>
<td>12.4</td>
<td>0.82</td>
<td>3.24</td>
<td>12.35</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>18 July, 2009</td>
<td>1451-1501</td>
<td>Between SBA and Santa Miguel Island</td>
<td>34°04.34'N 120°21.14'W</td>
<td>30.48</td>
<td>27-20</td>
<td>Cloud Top</td>
<td>4.8</td>
<td>10.8</td>
<td>0.99</td>
<td>N/A</td>
<td>12.61</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>18 July, 2009</td>
<td>1557-1607</td>
<td>From Santa Cruz Island to SMO</td>
<td>34°03.98'N 120°25.28'W</td>
<td>1676.4</td>
<td>30</td>
<td>Clear sky</td>
<td>-1.7</td>
<td>28.8</td>
<td>0.58</td>
<td>N/A</td>
<td>9.28</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>18 July, 2009</td>
<td>1646-1656</td>
<td>SMO</td>
<td>34°00.95'N 118°27.08'W</td>
<td>175</td>
<td>Clear sky</td>
<td>5.8</td>
<td>13.3</td>
<td>1.23</td>
<td>N/A</td>
<td>0.43</td>
<td>13.85</td>
<td>0.34</td>
<td></td>
</tr>
</tbody>
</table>

This research 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, 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 (Galemebeck et al., 2010) (Imyanitov, 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 (Figure 10).

The absolute value of the electric potential or the electric field $E$ and the electrostatic force $F$ is known.

$$ F = q E $$

where, $q$ is the electric charge (Coulomb, 1785).

Therefore, the electrostatic force $F_E$ 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 (Figure 7). This occurred because the cloud top had a positive electric charge, but the cloud base had a negative electric charge.
Figure 8. Image describing the existence of NO$_2^-$ in the cloud.

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; Simon et al., 1998). 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 (Figure 8) (Joseph, 1990).

\[
\text{NO}_2^- + \text{OH}^- \rightarrow \text{H}^+ + \text{NO}_3^-
\]  

The clouds on Figures 1 and 2 are St (Stratus) or Sc (Strato cumulus). Imyanitov (1962) unveiled that St and Sc had electric charges. Additionally "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" (Samoilov, 1957). Every nuclide has specific diffusion coefficient and following Fick's law of diffusion is known (Gordon, 1973).

\[
\frac{dw}{dt} = -DA \frac{dc}{dx}
\]  

where \(\frac{dw}{dt}\) is diffusion rate, \(D\) is diffusion coefficient (Negative sign is introduced so that \(D\) will have positive value), \(A\) is the cross-section area and \(\frac{dc}{dx}\) is concentration gradient (c is macromolecule concentration in mass per unit volume of solution). Consider diffusion across a distance interval dx over which the concentration changes from \(c\) to \(c-\text{dc}\). The force that drives the molecules to the more dilute region can be obtained from difference in the molar free energy of the solute at concentration \(c\) and concentration \(c-\text{dc}\). If the corresponding mole fractions of solute are \(x_B\) and \(x_B-\text{dx_B}\) and Henry's law is assumed, the discussion (Gordon, 1973) leads to Gibbs free-energy (\(G\)) difference per molecule of;

\[
G_{c-\text{dc}} - G_c = \frac{RT}{N_A} \ln \frac{x_B-\text{dx_B}}{x_B}
\]  

where \(N_A\) is Avogadro's Number, \(R\) is Gas constant \(8.3143\ \text{J K}^{-1}\ \text{mol}^{-1}\) and \(T\) is absolute Kelvin temperature. Above equation can be written as:

\[
\Delta G = \frac{RT}{N_A} \ln \left(1 - \frac{dc}{c}\right)
\]  

The following equation is well known as

\[
\Delta G = -nF.
\]
where $n$ is number of moles, $F$ is 96500 coulomb (C) and $E$ is electrical potential or voltage.

Therefore specific nuclide has specific electrical potential or voltage, that is, all kinds of isotopes have specific electrical potential or voltage. This principle applied to all of physical and chemical behaviors for at least all kinds of stable isotopes.

**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 (Figures 9 and 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.

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