Characteristics of Dew in Sakai, Osaka and the Role of Dew on the Atmospheric Chemistry

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[Introduction]
Dew forms very often at remarkably fine and weak wind nights. The formation of dew occurs near the ground surface, and therefore, dew dissolves soluble substances at very high concentrations compared to rain, fog and snow. Dew formed after sunset and dries after sunrise. Substances dissolved in dew at night transform to ions or another chemical forms, and they evaporate into the air or remain as salts.

Sakai-City, Osaka, JAPAN is located south of Osaka-City and an urban area. There are many factories in the west coast of Sakai, and pollutants transport to residential areas by prevailing west wind. There are some heavy traffic roads in Sakai, and the exhaust gas from vehicles is also the main pollution source in Sakai. Therefore, the concentrations of ions in dew are very high. Furthermore, urbanization causes acidification in Sakai, and dew forms only in Autumn season (in Winter, frost forms). This causes decrease in dew water content and as a result it also causes the increase in concentrations in dew.

Here, we summarize the characteristics of dew in Sakai city - dew water content and ion concentrations- and report a potential effect of dew formation - drying on atmospheric chemistry.

[Experiments]
Dew samples were collected on the roof of the A6 building on Osaka Prefecture University. Stainless steel vats (200 mm x 250 mm x 50 mm(H)) coated by PTFE which was put on polystyrene foam (ca. 10 thickness) were used for dew sampling. After sunset, clean vats were placed at the sampling point, and dew samples formed were collected before sunrise. For comparison, the same vat without polystyrene foam was placed at the same sampling point at the same time. In Sakai, dew formed hardly on vats without polystyrene foam.

For drying experiments, an aliquot of the prepared solution or natural dew sample was put on concave hole of PTFE plate and dried with dry Ar flow. The salts remaining on the hole were extracted with pure water (resistivity > 18.2 MΩ cm) and ion concentrations were measured by ion-chromatography. The evaporated gas components in Ar flow were determined by various methods. Nitrogen was measured by an atmospheric pressure mass spectrometry. NO and NO2 were analyzed by a chemiluminescence NOx analyzer. Nitrous acid and ammonia were analyzed by using an annular denuder system / ion-chromatography.

Ozone formation experiments in the semi-laboratory experiments were performed by using natural air and pure water as a surrogate of dew. The natural air is introduced in a Teflon bag through the box containing water thin film. The same sample was also prepared without water film to confirm the role of dew. Both bags (200 - 3000 nm transmission and ca. 90 % of transmittance at 300 nm) were irradiated by natural sun light and changes in ozone concentrations were measured.

[Results and Discussions]
In Sakai-City, dew was obtained only in autumn at no-cloud and weak wind night and formed only on insulated surface. Therefore, no dew formed on the dew sampler without polystyrene foam, and it is easy to compare the effect of dew on absorption of soluble gases. Figure 1 shows the relationship between mol amounts in dew minus those in dry deposition and dew amounts. Ions originated from particles such as Na+ show the vertical value of almost zero and gas origin ions such as HCOO- show linear relationships. This result indicates that deposition of particles is not driven by wet surface under the condition of dew formation and also indicates that uptake of gaseous compounds is strongly related to dew amounts.
Table 1 shows ion concentrations in dew obtained at Osaka Prefecture University in 2003. Concentrations of chloride and sodium ions originated from particles are very high, and those of nitrite and ammonium ions from mainly gas phase are also very high. Surprisingly, nitrite concentration is higher than nitrate.

Table 1 Ion concentrations in dew obtained at Osaka Prefecture University (2003)

<table>
<thead>
<tr>
<th>ion</th>
<th>(ml)</th>
<th>pH</th>
<th>HCOO⁻</th>
<th>ArO⁻</th>
<th>Cl⁻</th>
<th>NO₂⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>SO₃²⁻</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av.</td>
<td>2.99</td>
<td>5.52</td>
<td>31.40</td>
<td>70.19</td>
<td>566.07</td>
<td>103.22</td>
<td>83.69</td>
<td>0.00</td>
<td>67.13</td>
<td>442.19</td>
<td>517.47</td>
<td>19.09</td>
<td>116.20</td>
<td>70.97</td>
</tr>
<tr>
<td>Max.</td>
<td>5.93</td>
<td>6.91</td>
<td>92.74</td>
<td>170.76</td>
<td>3223.80</td>
<td>398.30</td>
<td>195.57</td>
<td>0.00</td>
<td>196.30</td>
<td>2464.70</td>
<td>1147.86</td>
<td>60.16</td>
<td>265.99</td>
<td>388.00</td>
</tr>
<tr>
<td>min.</td>
<td>0.48</td>
<td>3.51</td>
<td>0.00</td>
<td>0.00</td>
<td>41.76</td>
<td>10.90</td>
<td>13.63</td>
<td>0.00</td>
<td>15.63</td>
<td>37.84</td>
<td>351.59</td>
<td>1.39</td>
<td>36.18</td>
<td>7.00</td>
</tr>
</tbody>
</table>

We found that nitrite and ammonium react when dew dries to form N₂ + H₂O, gaseous HONO and nitrite salt + ammonium salt. It is well known that nitrous acid gas, HONO is a main OH radical source in the atmosphere and affects on ozone concentration. If HONO in the gas phase is absorbed in dew and transforms to N₂ and/or nitrite salt when dew dries, total HONO concentration in the atmosphere decreases when dew dries. As a result, ozone buildup is expected to depress when dew forms. The monitoring data show the lower ozone time profile. Furthermore, we investigate the effect of existence of dew (water surface). The results are shown in Figure 2. When the air passed through the water surface, ozone buildup was depressed compared to the case of no water existence. In this case, not only HONO is removed but also other gases of OH radical source such as acetone, form aldehyde. Whatever, existence of water depresses ozone buildup. Recently, many places become arid and aridification could be one reason of increase in ozone concentration. One reason of aridification is warming. The effect of warming is not only rise in sea level but also could be increase in ozone concentration. Therefore, prevention of global warming is important not only for the world but also for our health.

Figure 1 Amounts of Na⁺ and HCOO⁻ in dew as a function of dew volume per unit surface area. Amounts of ions were calculated by subtracting those of dry deposition from those of dew.

Figure 2 Effect of water on ozone buildup
- no water exist
• water exist
For detail exp. condition, see the text.