Japan Geoscience Union Meeting 2014
(28 April - 02 May 2014 at Pacifico YOKOHAMA, Kanagawa, Japan)


AAS22-26 Room:511 Time:May 1 15:15-15:30

# Insoluble metal-oxalate complexes in the atmosphere: its stability and global cooling effect

YAMAKAWA, Yoshiaki[1*] ; SAKATA, Kohei[1] ; MIYAHARA, Aya[1] ; MIYAMOTO, Chihiro[2] ; SAKAGUCHI, Aya[1] ; TAKAHASHI, Yoshio[1]

[1]Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University, [2]Department of Science, Hiroshima University

Aerosols have cooling effect on the earth, which is divided into direct and indirect effects. The direct effect is reflection of sunlight directly by aerosols, whereas the indirect effect is the reflection by clouds formed by the aid of aerosols working as cloud condensation nuclei (CCN). Oxalic acid is a main component of secondary organic aerosols and abundant in the atmosphere, which is formed by degradation of organic matters with longer carbon chain such as cyclic olefin. Oxalic acid is hygroscopic, which can work as CCN with indirect cooling effect. It has been estimated that the degree of cooling effect by the aerosols are equal to that of the warming effect of carbon dioxide ($CO_2$). However, there is large uncertainty in the estimation. In addition, it is suggested that oxalic acid may form insoluble metal-oxalate complexes and does not have the indirect cooling effect. Therefore, it is important to re-evaluate the cooling effect of aerosols for precise prediction of global warming. Although dicarboxylic acid including oxalic acid is decomposed into $CO_2$ by photolysis, oxalic acid is more abundant than the other dicarboxylic acids. It is possible that oxalic acid can be stabilized by forming metal-oxalate complexes. This study was aimed (i) to measure the concentration of metal-oxalate complexes in the atmosphere to contribute to precise prediction of global warming and (ii) to measure the half-life time to evaluate the stability of metal-oxalate complexes during photoreaction.

Size-fractionated aerosol samples were collected at Higashi-Hiroshima in winter (Dec., 2012-Jan., 2013), spring (April, 2013), and summer (July-Aug., 2013). The ratio of oxalic acid and total metal-oxalate complexes was estimated based on the X-ray absorption fine structure (XAFS) spectroscopy for zinc (Zn), lead (Pb), and calcium (Ca). Photolysis experiments were conducted by ultraviolet ray for oxalic acid, Zn complex, and magnesium (Mg) complex, while absorption spectra were measured to evaluate photoreactivity.

As a result, metal-oxalate complexes were found in finer particles. There was a positive correlation between the ratio of oxalate/nitrate and ratio of metal-oxalate complexes/total oxalate species. Therefore, it is considered that metal-oxalate complexes are formed by relative increase of oxalate for nitrate. Although concentration of total oxalate species was largest, the ratio of metal-oxalate complexes/total oxalate species was smallest in summer. Concentration of total oxalate species was higher than that of metal ions ($Zn^{2+}$, $Pb^{2+}$, and $Ca^{2+}$). Therefore, it is considered that the ratio of metal-oxalate complexes is smallest in summer.

This ratio was about 30% to 50% for each sample through the year. This result showed that the cooling effect of oxalic acid may be smaller than previous estimation.

As a result of photolysis experiments, half-life time of oxalic acid, Mg complex, and Zn complex is 19 min, 71 min, and 172 min, respectively. This result showed that photoreactivity of oxalic acid was decreased by forming metal-oxalate complexes. Compared to absorption spectra between oxalic acid and metal-oxalate complexes, absorbance was decreased by forming metal-oxalate complexes. Therefore, it is considered that the increase of half-life time may be caused by the decrease of absorbance by forming metal-oxalate complexes.

Keywords: Aerosol, Metal-Oxalate Complex, Global Cooling Effect, Photoreactivity, X-ray Absorption Fine Structure Spectroscopy