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Comparison of concentrations and photoreactivities of oxalic acid and metal-oxalate complexes in aerosols

Yoshiaki Yamakawa[1*], Kohei Sakata[2], Aya Sakaguchi[2], Yoshio Takahashi[2]

[1]Faculty of Science, Hiroshima University, [2]Graduate School of Science, Hiroshima University

Aerosols have cooling effect to 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 (SOA) and abundant in the atmosphere, which is formed by degradation of organic components with longer carbon chain such as malonic acid. Oxalic acid is hygroscopic, which works 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. However, there is large uncertainty in the estimation. In fact, if oxalic acid forms insoluble metal-oxalate complexes in the atmosphere, it is possible that the indirect effect can be smaller than the estimation. In addition, in the presence of metal-complex, it is also important to understand the formation processes. Therefore, this study was aimed (i) to decide the ratio of insoluble metal-oxalate complexes to oxalic acid in the aerosols by X-ray absorption fine structure (XAFS) spectroscopy to contribute to precise prediction of global warming and (ii) to evaluate stabilities of oxalic acid and metal-oxalate complex in the atmosphere during the photoreactions. The latter factor can be related to the dominance of metal-oxalate complexes in the atmosphere, if we can show that the photodegradation reactivity of oxalic acid is much larger than that of metal-oxalate complex by ultraviolet light.

We collected size-fractionated aerosols at Higashi-Hiroshima to determine chemical species of oxalic acid. As a result, (i) zinc (Zn) oxalate complex was found in fine particles ($<$ 2.1 micron) and (ii) calcium (Ca) complex was present in all the particle sizes except for the 4.2 to 10.2 micron particles. Oxalic acid is SOA that is formed by degradation of organic matters, whereas oxalic acid can be distributed to the particle size from 0.5 to 1.0 micron known as droplet mode, where metal-oxalate complexes can be formed.

To estimate the stabilities of oxalic acid and its metal-oxalate complex with Mg^{2+}, their photodegradations by ultraviolet lights in water were determined by measuring their concentrations at various elapsed time using total organic carbon analyzer. As a result, there was no appreciable difference between the two systems up to 8 hours, but the concentration of the complex was kept larger than that of oxalic acid after 8 hours. Therefore, it is possible that oxalic acid actually exists as metal-oxalate complex in the atmosphere possibly by preferential photodegradation of oxalic acid.

We will also analyze chemical species employing XAFS analysis on other metal ions such as lead and copper to measure precisely the ratio of metal-oxalate complex to total oxalate species. We will also conduct photodegradation experiments by ultraviolet light not only for Mg^{2+} complex but also for Zn^{2+} and Ca^{2+} complexes to confirm the difference of photodegradation caused by chemical species.

Keywords: aerosol, metal-oxalate complex, indirect cooling effect, photoreactivity, X-ray absorption fine structure