

Interaction between oxalate aerosol and metal: stability and global cooling effect of aerosol

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Photoreaction contributes to the formation and removal processes of oxalic acid that is a major component of organic aerosols. Oxalic acid is formed by photooxidation of high molecular weight organic aerosols via glyoxylic acid, and decomposed into carbon dioxide. In addition, previous study showed that oxalic acid forms insoluble metal-oxalate complex, which suggested that global cooling effect of oxalic acid is lower than previous estimation because metal-oxalate complex does not work as cloud condensation nuclei. Interaction between oxalic acid and metal might affect photoreactivity like hygroscopicity. In this study, speciation of oxalic acid and measurement of reaction rate constant for photoreaction were conducted to evaluate the effect of metal for global cooling effect and photoreaction.

Size fractionated aerosol samples were collected at Higashi-Hiroshima in winter, spring, and summer. Speciation analysis of oxalic acid was conducted by X-ray absorption fine structure (XAFS) spectroscopy for zinc (Zn), lead (Pb), and Calcium (Ca). Photoreaction experiments were conducted by ultraviolet ray about oxalic acid and glyoxylic acid. Oxalic acid and glyoxylic acid were measured by Total Organic Carbon (TOC) Analyzer and colorimeter using Schiff base, respectively.

As a result of speciation, Ca and Zn oxalate complexes were found in fine particles ($<1.7 \mu\text{m}$), but Pb complex was hardly found. The ratio of metal-oxalate complexes to total oxalic acid was about 30% to 50% about each sample. This result showed that the cooling effect of oxalic acid might be smaller than previous estimation.

As a result of photolysis experiments, half-life time of oxalic acid, Mg complex, and Zn complex is 19 minutes, 71 minutes, and 172 minutes, respectively. This result showed that photoreactivity of oxalic acid was decreased due to the decrease of quantum yield by forming metal-oxalate complexes. In contrast, photoreactivity of glyoxylic acid was increased by coexisting with Zn. Photoreaction of glyoxylic acid to oxalic acid is addition reaction of oxygen, which differs that of oxalic acid to carbon dioxide by cutting carbon bond. It is thought that the reason why photoreactivity was improved is what Zn worked as catalyst.

Keywords: organic aerosol, oxalic acid, metal complex, photo reactivity, indirect effect