Formation of metal-oxalate complex related to hygroscopicity of oxalic acid and high concentraiton of oxalate species in aerosols

YOSHIO TAKAHASHI AND YOSHIAKI YAMAKAWA

[1]Department of Earth and Planetary Science, The Univ. of Tokyo, Japan, E-mail: ytakaha@eps.s.u-tokyo.ac.jp

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, our previous study showed that oxalic acid forms insoluble metal-oxalate complex [1], which suggested that global cooling effect of oxalic acid is lower than previously estimated, since metal-oxalate complex does not work as cloud condensation nuclei. On the other hand, interaction between oxalic acid and metal ion may affect photoreactivity. In this study, speciation of oxalic acid and measurement of reaction rate constant for photoreaction were also conducted to evaluate the effect of formation of metal-oxalate complex on the hygroscopicity of oxalic acid and stability of oxalate species in aerosols

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 under UV exposure was conducted for oxalic acid and glyoxylic acid. Oxalic and glyoxylic acids were measured by Total Organic Carbon (TOC) Analyzer and redox titration using $KMnO_4$, respectively.

Speciation analyses showed that the ratio of metal-oxalate complexes to total oxalic acid was more than 80%, showing that the cooling effect of oxalic acid can be smaller than previously estimated. As a result of photolysis experiments, half-life time decreased in the order of oxalic acid > Mg complex > Zn complex, showing 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 in the presence of Zn. These results suggested that formation of metal-oxalate complex increase the stability of oxalic acid species in the aerosols due to the decrease of its photolysis reaction rate and also the increase of the formation rate of oxalic acid from gloyxylic acid.

[1] T. Furukawa and Y. Takahashi, *Atmos. Chem. Phys.*, **11** (2011) 4289-4301.