

Metal complexation inhibits the effect of oxalic acid in aerosols as cloud condensation nuclei (CCN)

Some anthropogenic aerosols, such as organic and sulfate aerosols, have a direct cooling effect by scattering solar radiation and an indirect cooling effect (cloud albedo effect) by acting as cloud condensation nuclei (CCN) because of their hygroscopic properties [1] (Fig. 1). In the report of the Intergovernmental Panel on Climate Change (IPCC) [2], the sum of the direct and indirect cooling effects of aerosols is almost equivalent to the warming effect of carbon dioxide (Fig. 1). However, a large uncertainty exists because of the indirect effect discussed in the IPCC report [2], which must be evaluated more precisely for a better understanding of the Earth's climate. Thus, many studies have been performed on sulfate and organic aerosols because of their complex nature in terms of composition and chemical transformation in the atmosphere, and also because of their importance in the global CCN budget. Among the various organic aerosols studied, water-soluble dicarboxylic acids (DCAs) contribute to the CCN activity, considering that DCAs, which are major constituents of organic aerosols, are hygroscopic [2,3]. Oxalic acid is a major component of DCA and also an important component of identified secondary organic aerosols [3]. In this study, we focused on oxalic acid as a representative component of low-molecular-weight DCAs in the atmosphere. It is possible that oxalic acid can form metal oxalate complexes in aerosols, since polyvalent metal ions can form stable complexes with oxalate ions. However, if the metal oxalate complexes are insoluble, it is possible that the role of oxalic acid as

the CCN with the cooling effect can be discounted. Nevertheless, there have been few studies identifying the oxalic acid species, whether noncomplexed oxalic acid or metal oxalate complex, in the atmosphere. Thus, we applied X-ray absorption fine structure (XAFS) spectroscopy, a powerful tool for the speciation of various elements in aerosols [4], to show the presence of metal oxalate complexes in aerosols. In this study, XAFS was employed for calcium (Ca) and zinc (Zn) to demonstrate the presence of their oxalate complexes [5]. Coupled with ion chromatography (IC) and inductively coupled plasma atomic emission spectrometry (ICP-AES) analyses, it was possible to determine the ratio of metal oxalate to noncomplexed oxalate species. The ratio determined can contribute to the precise evaluation of the effects of oxalic acid and other DCAs on the hygroscopicity and CCN activity of aerosol particles.

We measured the Ca and Zn *K*-edge XAFS spectra to characterize Ca and Zn species in aerosols collected at Tsukuba. For Ca, X-ray absorption near-edge structure (XANES) spectra were mainly used for the speciation of Ca in aerosols [4]. For Zn, both XANES and extended X-ray absorption fine structure (EXAFS) spectra were measured at **BL01B1** beamline in SPring-8. Size-fractionated aerosol samples were collected in summer (July-Aug. 2002) and winter (Jan.-Feb. 2003) for this purpose using an impactor aerosol sampler. For example, Zn *K*-edge EXAFS spectra in *k*-space for Zn in aerosols at various particle sizes in summer and winter are shown in Fig. 2. The spectra

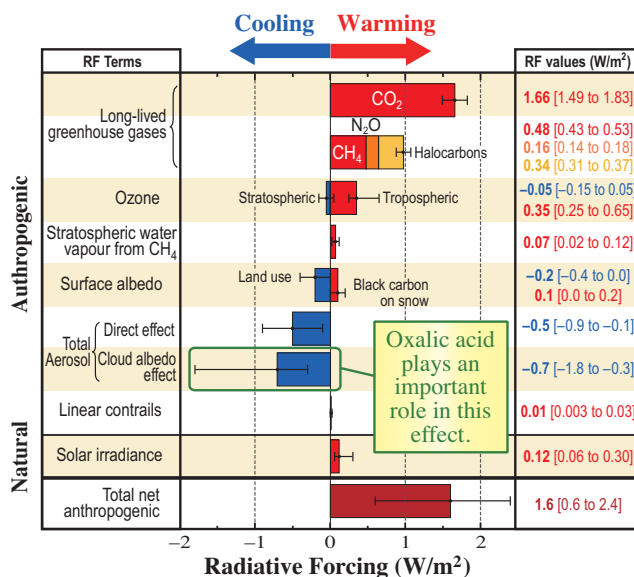


Fig. 1. Radiative forcing (RF) showing the degree of each factor that causes global warming/cooling after 1750 estimated by IPCC (2007).

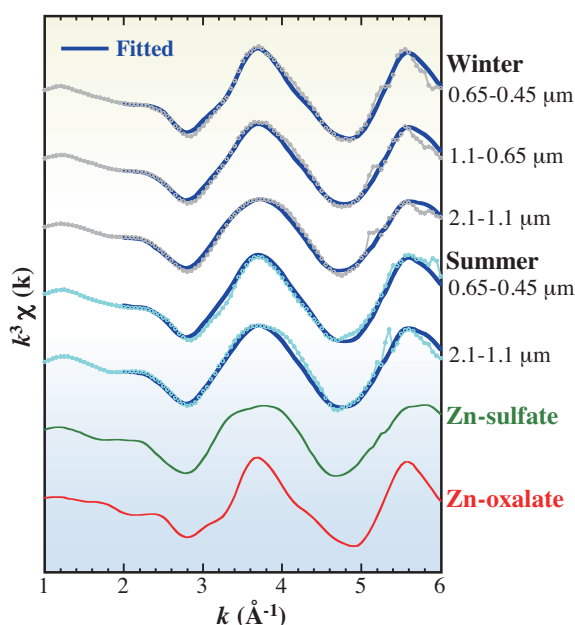


Fig. 2. *K*-edge EXAFS spectra of Zn in aerosols at various particle sizes in summer (July-Aug. 2002) and winter (Jan.-Feb. 2003), Zn sulfate, and Zn oxalate.

can be well fitted by those of Zn sulfate and Zn oxalate, which are possible species for these particle sizes, considering the relatively large amounts of total Zn, sulfate, and oxalate species compared with those in larger particle size fractions. The successful fitting

provides us the ratio of metal oxalate to noncomplexed oxalate species. Based on the calculation considering the total amounts of oxalate, Ca, and Zn determined by IC and ICP-AES coupled with the Ca- and Zn-oxalate fractions determined by XAFS, it was found that 10–60% and 20–100% of the total Ca and Zn in the finer particles (<2.1 μm) were present as Ca- and Zn-oxalate complexes, respectively (Fig. 3). Considering other metal ions abundant in aerosols that can form stable oxalate complexes such as Cu²⁺ and Pb²⁺, it is likely that almost all oxalate species are in the form of insoluble metal complexes.

Oxalic acid is hygroscopic and can thus increase the CCN activity of aerosol particles, while complexes with various polyvalent metal ions such as Ca and Zn are not hygroscopic; thus, they cannot contribute to the increase in the CCN activity of aerosols (Fig. 3). Therefore, the contribution of oxalic acid to the hygroscopicity of aerosol particles must have been overestimated. Thus, the present study suggests the reevaluation of the contribution of oxalic acid to the CCN activity of aerosols. Similar to oxalic acid, other dicarboxylic acids in the atmosphere, such as malonic and succinic acids, can also transform to metal complexes in aerosols. Therefore, in discussing the hygroscopicity and related effects of organic aerosols, it is necessary to evaluate the contribution of the complexation of dicarboxylic acids with metal ions.

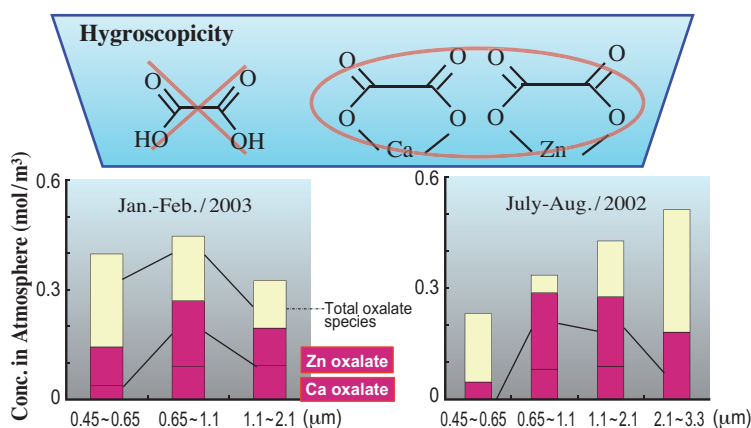


Fig. 3. Ca- and Zn-oxalate fractions relative to total oxalate species in aerosols with schematics of hygroscopicities of various oxalate species.

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