

## Oxalate metal complexes in aerosols: implications for the hygroscopicity of oxalate-containing particles

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Some anthropogenic aerosols, such as organic aerosols and sulfate aerosols, have a direct cooling effect by scattering solar radiation, and an indirect cooling effect by acting as cloud condensation nuclei (CCN) because of their hygroscopic properties. The global average contribution of the indirect cooling effect (i.e., the cloud albedo effect) is estimated to be  $-0.3$  to  $-1.8$  W/m<sup>2</sup> [1]. In the report of the Intergovernmental Panel on Climate Change (IPCC), the sum of the direct and indirect cooling effect of aerosols is almost equivalent to the warming effect of carbon dioxide [1]. However, a large uncertainty exists because of the indirect effect discussed in the IPCC report [1], which must be evaluated more precisely for a better understanding of the Earth's climate. Thus, a number of studies have been performed on sulfate aerosols and on 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 organic compounds (WSOCs) in aerosols influence the heat budget at earth surface as they act as CCN activator because of their hygroscopic properties. We can assume that dicarboxylic acids (DCA) contribute to the CCN activity, considering that DCA, which are major constituents of WSOCs, have hygroscopic nature.

Oxalic acid is a major component of DCA and also an important component of identified secondary organic aerosols. In this study, we focused on oxalic acid as a representative component of low molecular weight DCA in the atmosphere, and our results can be extended to other DCA, such as malonic and succinic acids. We expect that oxalic acid can form metal oxalate complexes in aerosols by reacting with metal ions due to several reasons: (i) aerosols contain various metal ions originating from sea salts, desert dusts, continental soils, and anthropogenic sources; (ii) oxalic acid is formed in the aqueous phase at aerosol surfaces in the atmosphere or cloud droplet, where the aqueous phase can be a reaction field for metal complexation; (iii) polyvalent metal ions can form stable complexes with oxalate ion. However, metal oxalate complexes are not detected using conventional methods, such as gas chromatography and ion chromatography (IC). In the latter analysis, a large volume of water sufficient to dissolve metal oxalate complexes in aerosols is usually employed during the water extraction procedure. In this case, metal oxalate complexes can be readily dissolved, despite the low solubility of some metal oxalate complexes, and it is difficult to distinguish between noncomplexed and metal-

complexed oxalate species in aerosols. Hence, only a few studies have suggested that DCA can react with metal ions and mineral aerosols. However, these studies employed indirect methods that cannot show direct evidence of the formation of metal oxalate complexes in aerosols.

In our study [2], we applied X-ray absorption fine structure (XAFS) spectroscopy to show the presence of metal oxalate complexes in aerosols, coupled with IC and inductively coupled plasma atomic emission spectrometry (ICP-AES) analyses to determine the ratio of metal oxalate and noncomplexed oxalate species. In this study, Ca K-edge XANES and Zn K-edge XANES and EXAFS were performed at BL-9A and BL-12C, respectively, which allows us to demonstrate the presence of metal oxalate complexes.

As a result, it was revealed that 10–60% and 20–100% of the total Ca and Zn in the finer particles ( $<2.1$   $\mu\text{m}$ ) were present as Ca and Zn oxalate complexes, respectively. Considering the presence of other metal ions, such as Mg<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup>, the concentration of free oxalic acid can be much lower than that expected. Therefore, the contribution of oxalic acid to hygroscopicity of aerosol particles must have been overestimated. Thus, the present study may claim reevaluation of the contribution of oxalic acid to CCN activity of aerosols, because most of the oxalic acid can exist as non-hygroscopic metal oxalate complexes. Similar to oxalic acid, other WSOCs, such as malonic and succinic acids, can 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.

### References

- [1] IPCC Climate Change 2007, Synthesis Report, the Intergovernmental Panel on Climate Change, Cambridge University Press, UK (2007).
- [2] T. Furukawa and Y. Takahashi, *Atmos. Chem. Phys.*, **11** (2011) 4289.

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