Decrease of hygroscopicity of oxalic acid by the formation of metal-oxalate complex

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Atmospheric aerosols have both a direct and an indirect cooling effect that influences the radiative balance at the Earth’s surface. It has been estimated that the degree of cooling is large enough to cancel the warming effect of carbon dioxide. Among the cooling factors, secondary organic aerosols (SOA) play a key role in the solar radiation balance in the troposphere as SOA can act as cloud condensation nuclei (CCN) and extend the lifespan of clouds because of their high hygroscopic and water soluble nature. Oxalic acid is one of the major components of SOA, and is produced via several formation pathways in the atmosphere. However, it is not certain whether oxalic acid exists as free oxalic acid or as metal oxalate complexes in aerosols, although there is a marked difference in their solubility in water and their hygroscopicity. We employed X-ray absorption fine structure spectroscopy to characterize the calcium (Ca) and zinc (Zn) in aerosols collected at Tsukuba in Japan with fractionation based on particle size using an impactor aerosol sampler. It was shown that 10%?60% and 20%?100% of the total Ca and Zn in the finer particles (< 2.1 micrometer) were present as Ca- and Zn-oxalate complexes, respectively. Oxalic acid can act as CCN because of its hygroscopic properties, while Ca oxalate (metal oxalate) complexes are not hygroscopic, and so cannot be CCN. Based on the concentration of noncomplexed and metal-complexed oxalate species, we found that most of the oxalic acid is present as metal oxalate complexes in the aerosols, suggesting that oxalic acid does not act as CCN in the atmosphere. Similar results are expected for other dicarboxylic acids, such as malonic and succinic acids. Thus, it is possible that the cooling effect of organic aerosols assumed in various climate modeling studies is overestimated because of the lack of information on metal oxalate complexes in aerosols.

Keywords: oxalic acid, metal complex formation, XAFS, hygroscopicity