

Speciation of sulfate in aerosols for the precise estimation of its global cooling effect

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Global cooling effect by aerosol is one of causes which influence earth's climatic change (IPCC, 2013). In particular, sulfate aerosols are known to cool the earth indirectly by forming cloud condensation nuclei (CCN) because of their high hygroscopicity. However, the hygroscopicity can change depending on the sulfate species. For example, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is sulfate having low hygroscopicity. Therefore, determination of sulfate species in aerosols is necessary to interpret the degree of cooling effect by sulfate aerosols in environment.

In this study, aerosol sampling was conducted in Higashi-Hiroshima (34.40 N, 123.71 E), Hiroshima, Japan. In addition, the samples were collected using two methods as to particle size. One method collected non-size-fractionated aerosols for about a year from September 2012 to September 2013. The other method collected size-fractionated aerosol in various periods such as winter when concentrations of anthropogenic aerosols were high (PA sample; collected from January 31 to February 1, 2013), spring (March 4 to 9, 2013), summer (July 22 to August 5, 2013), and fall (November 11 to 25, 2013). For these samples, major ion composition was measured by ion-chromatography, while chemical species of sulfur and calcium in the aerosol samples were determined by X-ray absorption fine structure (XAFS) spectroscopy. Furthermore, to unravel the function of CCN by sulfate aerosols in more detail, samples for single particle analysis were collected on May 31, 2014 during a dust event, which was analyzed individually using scanning transmission X-ray microscopy (STXM).

Atmospheric concentration of each major ion in the atmosphere had seasonal variation. Sulfate ion (SO_4^{2-}) concentration was larger in PA, in which concentration of ammonium ion (NH_4^+) and nitrate ion (NO_3^-) were also larger than those in other seasons. Meanwhile, size distribution of aerosol is important to determine its origin, because it is widely recognized that aerosol larger than $1 \mu\text{m}$ diameter is of natural origin. On the other hand, particles finer than $1 \mu\text{m}$ is of anthropogenic origin. In general, concentrations of SO_4^{2-} and NH_4^+ were larger in finer particles. Therefore, it is strongly suggested that the aerosol sample collected in this period was influenced by human activities. In spring, concentration of calcium ion (Ca^{2+}) increased particularly in the coarse particles, which suggests that its origin was from natural source.

Subsequently, sulfate species in the aerosol samples was determined using XAFS, where it was found that concentration ratio of calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which has low hygroscopicity to total concentration of SO_4^{2-} in the aerosol sample ($[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/[\text{SO}_4^{2-}]_t$) was larger in spring than that in PA. The abundance of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in atmosphere cannot be ignored because of its comparatively high $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/[\text{SO}_4^{2-}]_t$ ratio, especially in spring. It was also found that indirect cooling effect by sulfate will be small in spring due to the larger ratio of $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/[\text{SO}_4^{2-}]_t$. To provide further details of the effect by CCN function, Ca species of single particle samples in the dust period was determined using STXM. It was shown that there was $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at the surface of the particle, which is the site of the chemical reactions with other species in aerosols. In addition, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, which was minor Ca species in the bulk analysis, was also detected in the particles. Individual analysis of single particle is important to determine minor species in aerosol samples, which leads to better understanding of chemical processes in the atmosphere.

In conclusion, it was suggested that the degree of indirect cooling effects of sulfate aerosol can change seasonally because concentrations of low hygroscopicity sulfate species in the atmosphere are variable.

Keywords: aerosol, speciation of sulfate, global cooling effect, X-ray absorption fine structure