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PI2) Ionic Compositions of $PM_{2.5}$ in Summer and Winter at Jeju City

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1. Introduction

Jeju City is now facing dramatic changes due to the population growth, the increase in tourists and subsequent increase of a number of motor vehicles. So the status of air quality in Jeju City are presumed to be worse since a few years ago. Therefore, understanding the composition, sources and the formation of secondary ionic species can help steer the air quality management policy in Jeju City.

In these days, We are trying to investigate the contributions of various pathways of sulfate and nitrate formation to $PM_{2.5}$ mass in the urban environment of Jeju City, Korea. However, in Jeju City, data on fine particle mass concentrations and chemical compositions are limited, particularly for urban areas. In this study, we assessed the composition and contents of water-soluble ionic species in $PM_{2.5}$ and tried to understand implications for the aerosol chemistry in the downtown area of Jeju City.

2. Experiment and Methods

The intensive samplings of $PM_{2.5}$ were performed for 24 hr or 48~72 hr starting at 10 a.m. (local time) during the periods of Dec. 2013~Feb. 2014, Dec. 2014~Feb. 2015, and Jun.~ Aug. 2015 at the downtown area in Jeju City, Jeju Island.

A sequential air sampler was operating at a total flow rate of 16.7 L/min. The $PM_{2.5}$ samples were collected on pre-weighed Teflon filters (Zeflour^{TM}, 2 ㎛ pore size and 47 mm diameter, Pall Co.). The filters were extracted with 20 mL of ultra-pure water in an ultrasonic bath for 60 minutes. The water extracts were filtered through a 0.45 ㎛-pore size 13 mm filter (Whatman^{TM}, Syring Filter) and then stored in a bottle. The 20 μL extracts were injected into an ion chromatography (IC) system for quantifying eight major inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}).

3. Results and Discussion

The sum of water-soluble ionic species, including Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+-}, Cl^-, NO_3^- and SO_4^{2-}, accounted for 39% of $PM_{2.5}$ mass concentration in the summer and about 51% in the winter. Sulfate, ammonium and nitrate contributed to about 92% (93% in summer and 91% in winter) of the total mass of the water-soluble ionic species, and other cations and anions contributed to a minor fraction (2~17%) of the water-soluble ions (6.6% for summer and 7.9% for winter), at the downtown area in Jeju City.

The nss-SO_4^{2-} accounted for 99% of the total sulfate in $PM_{2.5}$ during this sampling period. Nss-SO_4^{2-}, NO_3^- and NH_4^+ were the dominant ionic species in $PM_{2.5}$, which accounted for 36.2% (6.39±3.47 μg/m^3) of $PM_{2.5}$ mass in the summer and 47.5% (8.39±5.34 μg/m^3) in the winter. Nss-SO_4^{2-}, NO_3^- and NH_4^+ were the main secondary inorganic aerosol (SIA) components in particulate matters mainly occurring as ammonium sulfate and ammonium nitrate, which were originated by the neutralization of sulfuric acid and nitric acid with ammonia. Other cations and anions (sum of Na^+, K^+, Mg^{2+}, Ca^{2+-}, and Cl^-) generally contributed to less than 3.3% (2.6% for summer and 3.7% for winter) of $PM_{2.5}$ mass.

In the summer, the $[NO_3^-]/[SO_4^{2-}]$ molar ratios were very low and relatively constant (~0.02) and also scattered at the $[NH_4^+]/[SO_4^{2-}]$ below 1.5 (so called, ammonium-poor). The large number of summertime samples were ammonium-poor (more than 65% of samples). In the samples with the $[NH_4^+]/[SO_4^{2-}]<1.5$, the nitrate formation is independent of ammonium. This suggests that nitrate formation is not important in the ammonium-poor samples. The small amount of nitrate observed in these samples may be associated with crustal species in $PM_{2.5}$. In the winter time, the $[NO_3^-]/[SO_4^{2-}]$ molar ratios increased sharply as the $[NH_4^+]/[SO_4^{2-}]$ molar ratios increased above 1.5. Therefore, most of wintertime samples were ammonium-rich. The nitrate from these samples showed a strong association with ammonium.