Sources of nitrate in precipitation at Hangzhou and Huzhou, East China

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Introduction

The Yangtze River delta region which is one of the most densely populated, most rapidly developing areas in East China, especially Hangzhou City and Huzhou City had become the acid rain area over the last 30 years. The objectives of this study were to investigate the seasonal variations of NO_3^- volume-weighted concentrations in precipitation, characterize the $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^-, explain the variation of $\delta^{15}N$-$_{NO3}$ and $\delta^{18}O$-$_{NO3}$ values and identify NO_3^- sources in precipitation in the East China.

Precipitation samples were collected in two sites from March 2015 to September 2017 using an acid-washed polyethylene bucket (100 cm in diameter). At the end of each month, the samples collected were proportionally mixed according to their precipitation amounts into a large barrel, and thus formed a representative sample of precipitation for the whole month.

Results and Discussion

The variations of SO_4^{2-}, NH_4^+, NO_3^-, $\delta^{15}N$-$_{NO3}$ and $\delta^{18}O$-$_{NO3}$ in precipitation were observed from 2015 to 2017 in Hangzhou and Huzhou, East China. The mean $[NO_3^-]/([NO_3^-]+[SO_4^{2-}])$ molar ratios and NH_4^+/NO_3^- molar ratios indicated that although coal combustion emission was the main NO_3^- sources among NO_x (NO and NO_2) emissions, traffic emission increased significantly with the increase of motor vehicles. It was estimated that the annual inorganic N deposition in Hangzhou (28.1 kg N ha^{-1}) from 2015 to 2017 was higher than that in Huzhou (21.4 kg N ha^{-1}) because of more NO_x from traffic emission. The increased NO_x emission in winter both at Hangzhu and at Huzhou could attribute to the coal burning for winter heating from the North China. In contrast, soil emission from enhanced agricultural activities is thought to be responsible for the decreased NO_x emission in summer. Both $\delta^{15}N$-$_{NO3}$ values (-4.4‰ to 3.7‰) and $\delta^{18}O$-$_{NO3}$ values (27.9‰ to 83.4‰) were in the wide ranges in the study areas. Spatial variation in $\delta^{15}N$-$_{NO3}$ values and $\delta^{18}O$-$_{NO3}$ values between Hangzhou and Huzhou reflects more traffic emissions in Hangzhou. The $\delta^{15}N$-$_{NO3}$ values and $\delta^{18}O$-$_{NO3}$ values were highest in summer and lowest in winter, and were consistent with many previous studies. It is attributed to the changes of contributions from different NO_3^- sources and the different NO_x oxidation pathways in forming HNO_3. The $\delta^{15}N$-$_{NO3}$ values and $\delta^{18}O$-$_{NO3}$ values decreased with the increasing of O_3 concentrations and sunshine hours and decreasing of NO_2/O_3 molar rations, which identified that the NO_x oxidation forming HNO_3 via the OH pathway in summer. Contrary to summer, the oxidation of NO_2 via O_3 forming HNO_3 in the N_2O_5 pathway is preferable in winter. It was demonstrated that combining chemical component with isotopes is useful for determining the main NO_3^- sources including coal fuel consumption, traffic emission and soil emission with the increased soil emission in summer and exotic NO_x from coal consumption in winter at the study areas. The different NO_2 oxidation pathways are particularly important in seasonal variation of NO_3^- stable isotopes.