NO_2 and TMI Oxidations Are Important Mechanisms of Airborne Sulfate Aerosol Formation in Beijing, China during the Haze Event: Evidence by Sulfur Isotope Techniques

Mei-Yi Fan[1,2,3], Yan-Lin Zhang[1,2,3]*, Yu-Chi Lin[1,2,3], Fang Cao[1,2,3]

[1.] Yale-NUIST Center on Atmospheric Environment, International Joint Laboratory on Climate and Environment Change, Nanjing University of Information Science and Technology, Nanjing, 210044, China.

[2.] Key Laboratory Meteorological Disaster; Ministry of Education & Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disaster, Nanjing University of Information Science and Technology, Nanjing, 210044, China.

[3]. Jiangsu Provincial Key Laboratory of Agricultural Meteorology, College of Applied Meteorology, Nanjing University of Information Science & Technology, Nanjing 210044, China.

Sulfate (SO_4^{2-}) is unambiguously an important chemical species, which directly influences climate changes, in the airborne aerosols. To date, its formation mechanism is still debated. To investigate the oxidation pathways of SO_2 to sulfate aerosols, $PM_{2.5}$ aerosol samples were collected in Beijing from November 13 to December 2, 2018. In addition to water-soluble inorganic ions (WSIIs), sulfur isotope in sulfate ($\delta^{34}S\text{-}SO_4^{2-}$) was also determined. During the sampling period, the sulfate concentrations varied from 0.4 to 33.5 μg m^{-3} with a mean value of 11.1 ± 9.3 μg m^{-3}, which accounted for 18 % of WSIIs. Specifically, its concentration in haze days ($PM_{2.5}$ > 150 μg m^{-3}) was 14.8 times higher than that in the clean days ($PM_{2.5}$ < 35 μg m^{-3}), elucidating that sulfate was a pivotal species to induce the haze formation. In terms of $\delta^{34}S\text{-}SO_4^{2-}$, its value ranged from 1.9 to 6.4 ‰ and averaged at 4.4 ± 1.4 ‰. Using Rayleigh distillation model, the isotope fractionation factor between SO_2 and SO_4^{2-} was estimated to be 4.0 ± 1.2 ‰. Considering this fractionation factor, the formation pathways of SO_2 to SO_4^{2-} were quantified through Bayesian isotope mixing model. Our results showed that the contributions of SO_2 to sulfate via OH, H_2O_2/O_3, NO_2 and TMI oxidation were 21 %, 15 %, 29 % and 35 %, respectively. Note that the contributions of sulfate formation by NO_2 and TMI on the haze days exceeded than that on the clean days by factors of 1.4-1.6, highlighting that NO_2 and TMI played important roles of elevated sulfate aerosols in the haze events in Beijing.

Corresponded to Yan-Lin Zhang (zhangyanlin@nuist.edu.cn； dryanlinzhang@outlook.com)