



Isotopic constraints on heterogeneous sulfate and nitrate production in Beijing haze

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Stable isotopes ($\Delta^{17}\text{O}(\text{SO}_4^{2-})$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$) were firstly applied to trace the atmospheric chemistry of sulfate and nitrate, to estimate the relative importance of different oxidation mechanisms during the sampling period from October 2014 to January 2015 in Beijing. The observed $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ ranged from 0.1 ‰ to 1.6 ‰ with the mean of (0.9 ± 0.3) ‰. $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ constrained calculations suggest that both in-cloud reactions and the heterogeneous reactions aerosols can dominate sulfate production during Beijing haze, but in most cases, the heterogeneous reaction plays a dominant role. Under the high pH value, $\text{S(IV)} + \text{NO}_2$ may dominate heterogeneous sulfate production, while S(IV) oxidation by O_2 can be the dominant pathway in highly acidic aerosols ($\text{pH} \leq 3$). For nitrate, the observed $\Delta^{17}\text{O}(\text{NO}_3^-)$ ranged from 27.5 ‰ to 33.9 ‰ with a mean of (30.6 ± 1.8) ‰. Calculations based on $\Delta^{17}\text{O}(\text{NO}_3^-)$ indicate that nocturnal reactions ($\text{N}_2\text{O}_5 + \text{H}_2\text{O}/\text{Cl}^-$ and $\text{NO}_3 + \text{HC}$) dominated nitrate formation when $\text{PM}_{2.5} \geq 75 \mu\text{g m}^{-3}$, with possible fractional contribution of 56–97 %. $\Delta^{17}\text{O}(\text{NO}_3^-)$ and chemical kinetic calculations further show that O_3 dominates the NO oxidation during Beijing haze.