Nitrogen isotope fractionation during gas-particle conversion of NO_x to NO_3^- in the atmosphere – implications for isotope-based NO_x source apportionment

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Atmospheric fine-particle ($PM_{2.5}$) pollution is frequently associated with the formation of particulate nitrate (pNO_3^-), the end product of the oxidation of NO_x gases (=NO+NO_2) in the upper troposphere. Here we determined the $\delta^{15}N$ values of fresh pNO_3^- ($\delta^{15}N$-pNO_3^-) in $PM_{2.5}$ at a rural site in Northern China, where atmospheric p NO_3^- can be attributed exclusively to biomass burning. The observed δ15N-pNO_3^- (12.17±1.55‰; n=8) was much higher than the N isotopic source signature of NOx from biomass burning (1.04±4.13‰). The large difference between δ15N-pNO_3^- and δ15N-NO_x (Δ(δ15N)) can be reconciled by the net N isotope effect (εN) associated with the gas-particle conversion from NOx to NO3-. For the biomass-burning site, a mean εN (≈ Δ(δ15N)) of 10.99±0.74‰ was assessed through a newly-developed computational quantum chemistry (CQC) module. A second, slightly higher CQC-based mean value for εN (15.33±4.90‰) was estimated for an urban site with intense traffic in Eastern China, and integrated in a Bayesian isotope mixing model to make isotope-based source apportionment estimates for NOx at this site. Based on the δ15N values (10.93±3.32‰, n=43) of ambient pNO_3^- determined for the urban site, and considering the location-specific estimate for εN, our results reveal that the relative contribution of coal combustion and road traffic to urban NO_x are 32±11% and 68±11%, respectively. Our investigations also show that, without the consideration of the N isotope effect during pNO_3^- formation, NOx is derived almost entirely from coal combustion. Similarly, NO_x emissions from coal combustion may be substantively overestimated (by >54% on average) when the N isotope fractionation during atmospheric pNO_3^- formation is neglected.