

Triple O isotopes of atmospheric nitrates simultaneously collected using sector-based samplers distant from anthropogenic sources

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Abstract

This study presents the first triple oxygen isotopic results ($\delta^{17}\text{O}$ and $\delta^{18}\text{O}$) obtained for atmospheric nitric acid (HNO_3) simultaneously collected with particulate nitrate (p- NO_3). The system used for sampling these nitrates allowed exclusively collecting plumes from targeted anthropogenic sources. Our findings imply that understanding nitrate distribution requires characterizing nitrate forms individually, and assuming isotopic values of the nitrate phases are interchangeable is not always adequate.

Introduction

The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of atmospheric N-species are regarded as helpful for understanding transformation pathways of oxidized N emissions. Therefore, numerous research studies have mostly characterized wet (precipitation) and particulate (aerosols) nitrates separately, or bulk nitrates prior to determining their $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values. Regular nitrate collection mostly used open sampling cumulating nitrates incoming from various directions and potentially several sources. Here we simultaneously sampled nitrates, including nitric acid, the much less studied gaseous form. Sector-based multi-stage filter system allowed maximizing collection of nitrates specifically from five anthropogenic sources in Alberta, Canada (Savard et al., 2017).

Sample Collection and Isotopic Analysis

The ‘conditional sampling’ method restricted collection of nitrogen compounds from the sources of interest by sampling only when the wind direction was from those sources. The CAPMoN sampling set-up was consecutively installed at the different sites, each at varying distances from the targeted point (<1 to 25 km), and diffuse sources (3 to >125 km). The anthropogenic emissions are from four sites in central Alberta: coal-fired power plants (CFPP) at Genesee, 55 km southwest of Edmonton; traffic-dominated emissions at Terrace Heights, a residential area near downtown Edmonton; and an industrial area, at Fort Saskatchewan, northwest of Edmonton, where two sectors were identified to separate different industries to the degree possible. Sampling in the northwest sector targeted emissions from a mixture of sources of which the largest were a chemical plant and metal refinery (referred to as chemical plus metal industries), while the north sector point emissions were dominated by a fertilizer plant and an oil refinery (referred to as fertilizers plus oil). In addition, the rural Vauxhall area was selected for collecting nitrates emitted from multiple small gas compressor stations scattered throughout the southern Alberta region (and reduced N forms from cattle and swine feedlots, see Savard et al., 2017). We have treated all samples through chemical protocols (transformation to N_2O) and performed the isotopic analyses using state-of-the-art gold-furnace pre-concentrator online with an isotope ratio mass spectrometer (N_2 and O_2 ; see Smirnov et al., 2012).

Results

We find that the $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of HNO_3 and particulate NO_3 from all sources show similar trends, confirming that triple O isotopes cannot be used for fingerprinting sources, but can help understanding regional conditions and oxidation pathways of NO_x . Overall, the w- and p- NO_3 $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values show the expected higher values during cold periods relative to values obtained for warm months, but only the $\Delta^{17}\text{O}$ values of HNO_3 is following this pattern. Two important points are that: (1) the HNO_3 $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ ranges are distinct from the w- and p- NO_3 ones; and (2) the $\Delta^{17}\text{O}$ differences between p- NO_3 and HNO_3 shifts from positive during cold

sampling periods to negative during warm ones, with very low p-NO₃ $\Delta^{17}\text{O}$ values observed during warm months.

Interpretation

The observed trends likely reflect nitrates derived from NO_x at isotopic disequilibrium with O₃ (and RO₂). Most studies have assumed that since photochemical steady state takes place within a few minutes after emission of NO_x from a combustion source, isotopic steady state is also reached quickly. However, recent modeling suggests that isotopic equilibrium of NO_x with O₃ could take up to a few hours at relatively low NO_x and O₃ concentrations (Michalski et al., 2014). Given the short distances and average wind speed in some of the studied sites in rural Alberta, the first nitrates formed in the plumes shortly after emission from the NO_x sources have low $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values since NO_x has not yet reached isotopic equilibrium with O₃ and peroxy and organo-peroxy radicals (RO₂). These nitrates that are in the form of p-NO₃, or that attach to particles, remain in the plume, while HNO₃ deposits upon contact with vegetation or other surfaces. As the plume travels, the NO_x becomes more enriched, and the newly formed nitrates take on higher $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values. However, p-NO₃ collected downwind will be a mixture of the low- $\delta^{18}\text{O}$ and - $\Delta^{17}\text{O}$ nitrate formed earlier and the high- $\delta^{18}\text{O}$ and - $\Delta^{17}\text{O}$ nitrate formed more recently, while HNO₃ will have less of the low- $\delta^{18}\text{O}$ and - $\Delta^{17}\text{O}$ nitrate. Additionally, we infer that the N₂O₅ oxidation pathway chiefly produces p-NO₃ during cold months, whereas the OH and N₂O₅ paths both contribute to producing p-NO₃ and HNO₃ of warm months. The implications of these research results will be discussed at the symposium.

References

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