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Isotopic composition of passively collected nitrogen dioxide emissions: Vehicle, soil and livestock source signatures

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HIGHLIGHTS

- We report the $\delta^{15}N$ and $\delta^{18}O$ values of natural and anthropogenic NO_x emission sources.
- We report the first $\delta^{15}N$ and $\delta^{18}O-NO_2$ values of livestock waste emissions.
- We report the first $\delta^{18}O-NO_2$ values of biogenic soil and vehicle emissions.
- We provide evidence for passive sampler use to collect NO_x for isotope analysis.

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ABSTRACT

Quantifying contributions of local and regional NO_x emission sources is an important initial step towards accurately assessing improvements in NO_x emission reduction efforts. Current global NO_x inventories report large uncertainties in contributions of some NO_x sources, especially diffuse sources (e.g. lightning and soil NO_x). Examining the isotopic composition of NO_x and its oxidation products (NO_y) is one approach to further constrain contributions from these sources. While natural and anthropogenically-derived NO_x emissions are reported to have relatively distinct $\delta^{15}N$ values that could aid NO_x source apportionment studies, existing $\delta^{15}N-NO_x$ source data is limited and variable collection approaches have been employed. To build on existing $\delta^{15}N-NO_x$ source data, inexpensive and easily deployable passive samplers were used to collect nitrogen dioxide (NO_2) emissions and its oxidation product, nitric acid (HNO_3), from multiple emission sources including livestock waste, fertilized soils, and vehicles. The resulting isotope data provides evidence that passive samplers can be used across a range of environmental conditions with widely varying NO_2 concentrations and NO_2 isotopic compositions. Using this approach, we report the first $\delta^{15}N$ and $\delta^{18}O-NO_2$ of livestock waste emissions, as well as the first measurements of $\delta^{18}O-NO_2$ from biogenic soil and vehicle emissions. We observe the highest $\delta^{15}N-NO_2$ values to date of vehicle emissions and investigate potential fractionations associated with oxidation and equilibrium processes. The large differences reported here between $\delta^{15}N-NO_2$ values from fossil fuel-based sources and microbially-produced sources allows for identification and possible quantification of source contributions to ambient NO_x concentrations.

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1. Introduction

Since the Industrial Revolution, anthropogenic NO_x (NO_x = $NO + NO_2$) emissions, primarily from fossil fuel combustion via electricity generating units (EGUs) and vehicles, have surpassed natural NO_x emissions (Galloway et al., 2004). Although natural NO_x sources, including lightning, wildfires, and biogenic soil emissions, account for a portion of global NO_x emissions, the magnitude of these contributions is uncertain (Reis et al., 2009). Quantifying the contributions of various NO_x sources is an important step towards accurate emission inventories and monitoring future emission reductions.

While the primary sources of NO_x in the U.S. have been reduced by regulations set forth in the Clean Air Act and Amendments, other unregulated sources can be locally significant including fertilized soils, biomass burning, lightning, and livestock waste. Microbial denitrification and nitrification in soils can increase NO_x emissions following fertilizer application, resulting in large pulses of biogenic soil NO_x (Veldkamp and Keller, 1997). For example, Hudman et al. (2010) report a 50% increase in soil NO_x over the agricultural

Great Plain in June 2006 due to rainwater-induced pulsing. Jaeglé et al., 2005 suggest that during the summer in the northern mid-latitudes, soil NO_x emissions can reach half that of fossil fuel combustion sources. Microbial denitrification and nitrification occurring in livestock and human waste is also reported to be a significant global source of NO_x (McElroy and Wang, 2005). Another natural source, lightning-produced NO_x, is estimated to contribute up to 70% of the NO_x concentration below 500 mbar over the North Atlantic in July (Levy and Moxim, 1996). The diffuse nature of these non-fossil fuel-based NO_x emission sources makes them difficult to quantify precisely. For instance, Holland et al., 1999 report a global soil NO_x emission range of 4–21 Tg N yr^{-1} and recent studies report a range of lightning-produced NO_x range from 1 to 20 Tg yr^{-1} (Schumann and Huntrieser, 2007). As a consequence of these large uncertainties, investigators are continuously improving upon and developing techniques to quantify contributions of various NO_x sources to atmospheric reactive nitrogen burdens and subsequent removal as nitrogen deposition.

The isotopic composition of NO_x and its oxidation products (NO_y) provide one approach to apportioning precursor NO_x and subsequent contributions to wet and dry NO_y deposition. Natural and anthropogenically-derived NO_x emissions have relatively distinct $\delta^{15}N$ values providing evidence of the contribution of NO_x concentration from multiple emission sources. For example, in the northeastern U.S., significant positive correlations were observed between EGU NO_x emissions and $\delta^{15}N-NO_3^-$ values in wet and dry deposition within a 400 km source region (Elliott et al., 2007, 2009). Also, 20th century fertilizer application was strongly negatively correlated with $\delta^{15}N-NO_3^-$ in a Greenland ice core suggesting transport of fertilizer induced soil NO_x emissions to Greenland (Felix and Elliott, 2013). In a more localized study, $\delta^{15}N-NO_2$ values adjacent to a roadway were significantly higher due to vehicle emissions than those values 400 m away (Redling et al., 2013).

Despite these indications that $\delta^{15}N$ can serve as a robust tracer of NO_x source contributions, isotopic characterization of NO_x sources are limited (Fig. 1). Existing studies employed various collection and analytical approaches and were generally hampered by large mass requirements required for isotopic analysis. While initial measurements of source $\delta^{15}N-NO_x$ values from previous studies allow approximation of relative source contributions, further characterization of $\delta^{15}N-NO_x$ is required to reduce uncertainty, enable quantification of source contributions, and constrain post-emission transformations on isotopic values.

To understand the sources and processes that influence the isotopic compositions of NO_x emissions and subsequent deposition products, we investigated the isotopic composition of primary NO_2 emissions and its oxidation product, HNO_3. Through this work we: 1) provide evidence for the use of inexpensive passive samplers to collect NO_2 emissions for nitrogen and oxygen isotopic analysis; 2) build upon the existing inventory of $\delta^{15}N-NO_2$ source values; and 3) report the first $\delta^{15}N$ and $\delta^{18}O-NO_2$ of livestock waste emissions and $\delta^{18}O-NO_2$ of biogenic soil and vehicle emissions to further constrain the isotopic signatures of NO_x emission sources.

2. Methods

2.1. NO_2 and HNO_3 emission collection methods for concentration and isotope analysis

Passive samplers are ideal for the collection of dry nitrogen deposition as they are less expensive than active samplers, easy to use, and do not require electricity (Elliott et al., 2009; Felix et al., 2013; Golden et al., 2008; Proemse et al., 2013; Puchalski et al., 2011) These advantages enable multiple deployments at a single site and the ability to sample across large spatial scales. Ogawa NO_2
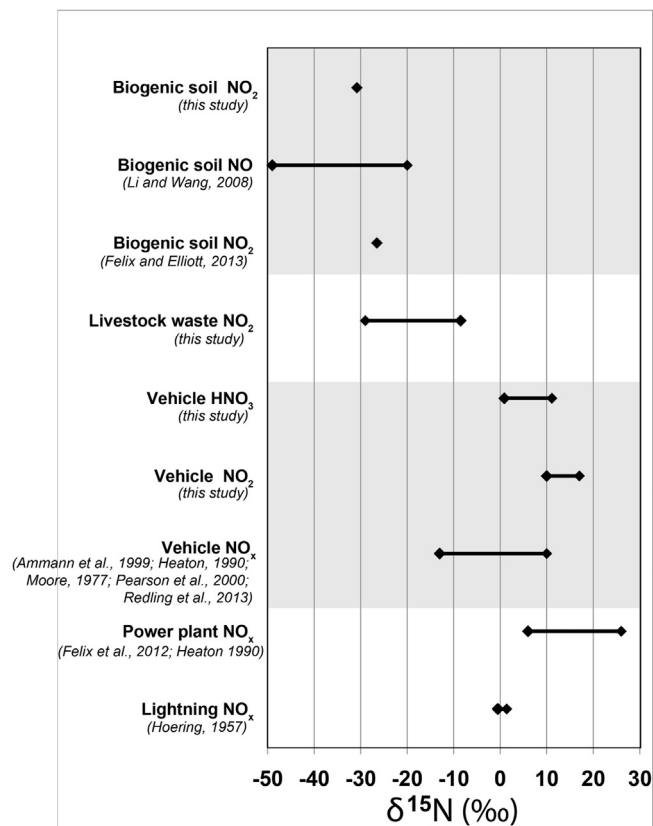

Fig. 1. $\delta^{15}N-NO_x$ of previous literature and $\delta^{15}N-NO_x$ values reported in this study. (Ammann et al., 1999; Felix et al., 2012; Felix and Elliott, 2013; Heaton, 1990; Li and Wang, 2008; Moore, 1977; Pearson et al., 2000; Redling et al., 2013; Hoering, 1957).

passive samplers and HNO_3 passive samplers have been used in previous studies to collect NO_2 and HNO_3 emissions for concentration and isotopic analysis (Bytnerowicz et al., 2005; Elliott et al., 2009; Redling et al., 2013; Smirnoff et al., 2012). The Ogawa sampler used to collect NO_2 in this study consists of a double-sided passive diffusion design equipped with a diffusive end cap, followed by a stainless steel screen, and a 14 mm quartz filter impregnated with triethanolamine. The HNO_3 sampler used in this study was designed by Bytnerowicz et al. (2005) and collects HNO_3 on a 47 mm nylon filter after passing through a 2 μm pore size, 47 mm diameter Zefluor Teflon filter. After sample collection, filters were stored at -20 °C in clean mason jars until they were eluted for concentration and isotope analysis.

To examine variability in field conditions, Ogawa samplers were simultaneously deployed in quadruplicate (4 sample filters, 2 per sampler) at seven sampling sites. The standard deviation for the sample replicates was $\delta^{15}N-NO_2$ and $\delta^{18}O-NO_2$ was 0.7‰ and 1.5‰, respectively. There was no significant correlation between $\delta^{15}N$ or $\delta^{18}O$ and NO_2 ambient concentration and mass of NO_2 collected. Standard deviations for $\delta^{15}N$ and $\delta^{18}O-HNO_3$ could not be calculated, as insufficient sampler availability precluded replicate sample collection. However, a previous study reports the standard deviation among replicate HNO_3 samplers as 0–0.3‰ and 0.3–1.0‰ for $\delta^{15}N$ and $\delta^{18}O$, respectively (Elliott et al., 2009).

2.2. NO_x emission source sampling

2.2.1. Vehicular emissions

Ogawa NO_2 samplers were deployed in the ventilation portion and directly outside a highway tunnel (Squirrel Hill Tunnel,