



# Summertime diurnal variations in the isotopic composition of atmospheric nitrogen dioxide at a small midwestern United States city

Wendell W. Walters<sup>a,\*</sup>, Huan Fang<sup>a</sup>, Greg Michalski<sup>a,b</sup>

<sup>a</sup> Department of Earth, Atmospheric, and Planetary Sciences Purdue University, 550 Stadium Mall Drive, West Lafayette, IN, 47907, United States

<sup>b</sup> Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN, 47907, United States

## ARTICLE INFO

### Keywords:

Nitrogen  
Nitrogen oxides  
Isotopes  
Atmospheric emissions  
Oxidation

## ABSTRACT

The nitrogen and oxygen stable isotopes ( $\delta^{15}\text{N}$  &  $\delta^{18}\text{O}$ ) of nitrogen oxides ( $\text{NO}_x = \text{nitric oxide (NO)} + \text{nitrogen dioxide (NO}_2\text{)}$ ) may be a useful tool for partitioning  $\text{NO}_x$  emission sources and for evaluating  $\text{NO}_x$  photochemical cycling, but few measurements of *in situ*  $\text{NO}_x$  exist. In this study, we have collected and characterized the diurnal variability in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_2$  from ambient air at a small Midwestern city (West Lafayette, IN, USA, 40.426° N, 86.908° W) between July 7 to August 5, 2016, using an active sampling technique. Large variations were observed in both  $\delta^{15}\text{N}(\text{NO}_2)$  and  $\delta^{18}\text{O}(\text{NO}_2)$  that ranged from  $-31.4$  to  $0.4\%$  and  $41.5$ – $112.5\%$ , respectively. Daytime averages were  $-9.2 \pm 5.7\%$  ( $\bar{x} \pm 1\sigma$ ) and  $86.5 \pm 14.1\%$  ( $n = 11$ ), while nighttime averages were  $-13.4 \pm 7.3\%$  and  $56.3 \pm 7.1\%$  ( $n = 12$ ) for  $\delta^{15}\text{N}(\text{NO}_2)$  and  $\delta^{18}\text{O}(\text{NO}_2)$ , respectively. The large variability observed in  $\delta^{15}\text{N}(\text{NO}_2)$  is predicted to be driven by changing contributions of local  $\text{NO}_x$  emission sources, as calculated isotope effects predict a minor impact on  $\delta^{15}\text{N}(\text{NO}_2)$  relative to  $\delta^{15}\text{N}(\text{NO}_x)$  that is generally less than  $2.5\%$  under the sample collection conditions of high ozone concentration ( $[\text{O}_3]$ ) relative to  $[\text{NO}_x]$ . A statistical  $\delta^{15}\text{N}$  mass-balance model suggests that traffic-derived  $\text{NO}_x$  is the main contributor to the sampling site ( $0.52 \pm 0.22$ ) with higher relative contribution during the daytime ( $0.58 \pm 0.19$ ) likely due to higher traffic volume than during the nighttime ( $0.47 \pm 0.22$ ). The diurnal cycle observed in  $\delta^{18}\text{O}(\text{NO}_2)$  is hypothesized to be a result of the photochemical cycling of  $\text{NO}_x$  that elevates  $\delta^{18}\text{O}(\text{NO}_2)$  during the daytime relative to the nighttime. Overall, this data suggests the potential to use  $\delta^{15}\text{N}(\text{NO}_2)$  for  $\text{NO}_x$  source partitioning under environmental conditions of high  $[\text{O}_3]$  relative to  $[\text{NO}_x]$  and  $\delta^{18}\text{O}(\text{NO}_2)$  for evaluating  $\text{VOC-NO}_x\text{-O}_3$  chemistry.

## 1. Introduction

Nitrogen oxides ( $\text{NO}_x = \text{nitric oxide (NO)} + \text{nitrogen dioxide (NO}_2\text{)}$ ) play a key role in controlling the concentrations of atmospheric oxidants that drive tropospheric chemistry (Crutzen, 1973, 1979; Leighton, 1961; Logan, 1983). Photochemical reactions involving  $\text{NO}_x$ , carbon monoxide, and volatile organic compounds (VOC) lead to the formation of tropospheric ozone ( $\text{O}_3$ ), which is a greenhouse gas, an oxidizing pollutant, and influences the lifetimes of other greenhouse gases (Atkinson, 2000; Atkinson and Arey, 2003; Crutzen, 1979). Photochemical cycling involving  $\text{NO}_x$  and reduced hydrogen oxide radicals ( $\text{HO}_x = \text{hydroxyl radical (OH)} + \text{peroxy radicals (HO}_2\text{ and RO}_2\text{)}$ ) is terminated when  $\text{NO}_2$  is further oxidized to nitric acid ( $\text{HNO}_3$ ). Once  $\text{HNO}_3$  is formed, it is primarily removed via wet and/or dry deposition leading to degradation of drinking water, soil acidification, eutrophication, and biodiversity change in terrestrial ecosystems (Galloway et al., 2004). Thus, due to the environmental and human

health consequences of  $\text{NO}_x$  and its oxidation products, it is important to understand the relative contributions of  $\text{NO}_x$  emission sources and the oxidation processes responsible for its removal.

Sources of  $\text{NO}_x$  are both of natural (e.g. lightning, soil nitrification/denitrification, and wildfires) and anthropogenic (e.g. fossil fuel combustion, industry, and agriculture) origins (Galloway et al., 2004; Jaeglé et al., 2005; Reis et al., 2009), but there are uncertainties in the temporal and spatial contributions of various emission sources that might be resolved by nitrogen (N) stable isotope analysis ( $\delta^{15}\text{N}$ ). Numerous studies have quantified the difference in  $\delta^{15}\text{N}$  values of various  $\text{NO}_x$  sources, which indicate relative distinctive values for biogenic  $\text{NO}_x$  (nitrification/denitrification), the transportation sector, and coal-fired power plants (Ammann et al., 1999; Felix et al., 2012; Felix and Elliott, 2013; Fibiger et al., 2014; Heaton, 1987, 1990; Hoering, 1957; Li and Wang, 2008; Miller et al., 2017; Moore, 1977; Snape et al., 2003; Walters et al., 2015a, 2015b). These isotopic “fingerprints” may be a useful tool for constraining the  $\text{NO}_x$  emission budget; however, it is

\* Corresponding author.

E-mail address: [waltersw@purdue.edu](mailto:waltersw@purdue.edu) (W.W. Walters).

<sup>1</sup> Present address: Department of Earth, Environmental, and Planetary Sciences, Brown University, 324 Brook Street, Providence, RI, 02912, United States.

difficult to collect *in situ* NO<sub>x</sub> for isotopic characterization because it is highly reactive and has low mixing ratios. Thus, numerous studies have inferred δ<sup>15</sup>N(NO<sub>x</sub>) values from the δ<sup>15</sup>N of atmospheric nitrate, which is easier to collect and isotopically analyze. However, any attempt to partition NO<sub>x</sub> sources using the δ<sup>15</sup>N values of atmospheric nitrate may be complicated by possible kinetic (Freyer, 1991; Walters and Michalski, 2016a), equilibrium (Walters and Michalski, 2015, 2016b), and photolytic isotope effects that occur during the oxidation of NO<sub>x</sub> to atmospheric nitrate. For example, previous works have suggested isotopic exchange between NO and NO<sub>2</sub> (Freyer et al., 1993; Walters et al., 2016) might alter δ<sup>15</sup>N(NO<sub>2</sub>) values relative to δ<sup>15</sup>N(NO<sub>x</sub>), which may then be propagated into the δ<sup>15</sup>N value of atmospheric nitrate (Riha, 2013; Savarino et al., 2013). Therefore, it is still unclear at locations with multiple significant NO<sub>x</sub> emission sources if δ<sup>15</sup>N(NO<sub>2</sub>) reflects NO<sub>x</sub> emission sources, chemistry effects, or a combination of these processes. It is important to understand drivers of δ<sup>15</sup>N(NO<sub>2</sub>) since NO<sub>2</sub> is precursor to atmospheric nitrate.

The analysis of the oxygen (O) stable isotope composition (δ<sup>18</sup>O) of NO<sub>x</sub> and atmospheric nitrate may trace NO<sub>x</sub> photochemical cycling and be an evaluator of changing daytime and nighttime oxidation chemistry (Michalski et al., 2003, 2014, 2012; Morin et al., 2008). Prior experimental investigations suggest that O isotopic equilibrium is achieved between NO<sub>x</sub> and O<sub>3</sub> (Michalski et al., 2014), erasing the original NO<sub>x</sub> source O isotopic composition. Atmospheric O<sub>3</sub> has a characteristically elevated δ<sup>18</sup>O values of ≈100‰ (Johnston and Thiemens, 1997; Krankowsky et al., 1995; Mauersberger et al., 2001; Thiemens and Heidenreich, 1983; Vicars et al., 2012; Vicars and Savarino, 2014), and the coupling between NO<sub>x</sub> and O<sub>3</sub> in the Leighton Cycle is believed to be the driver of high δ<sup>18</sup>O observed in atmospheric nitrates (Michalski et al., 2003; Morin et al., 2008; Savarino et al., 2008). An experimental study of NO-O<sub>2</sub>-O<sub>3</sub>-NO<sub>2</sub> photochemical equilibrium under tropospheric conditions predicts δ<sup>18</sup>O(NO<sub>x</sub>) of 117 ± 5‰ relative to Vienna Standard Mean Ocean Water (VSMOW) (Michalski et al., 2014), but this appears at odds with recent *in situ* measurements (Dahal and Hastings, 2016; Felix and Elliott, 2014). The δ<sup>18</sup>O values of NO<sub>2</sub> measured using passive diffusion collectors was found to range from 47.3 to 54.6‰ at an urban location (Providence, RI, USA) (Dahal and Hastings, 2016) and from -21.5–37.8‰ at sample sites near NO<sub>x</sub> emission sources (tunnel, fertilized soil emissions, livestock waste facilities) (Felix and Elliott, 2014), which are significantly lower than the model predictions (Michalski et al., 2014). The apparent disagreement between the measured and expected δ<sup>18</sup>O value of *in situ* NO<sub>x</sub> may be attributed to possible O isotopic fractionation associated with the collection of NO<sub>2</sub> (i.e. conversion of NO<sub>2</sub> to nitrite (NO<sub>2</sub><sup>-</sup>)) on passive diffusion pad or O isotopic exchange between NO<sub>2</sub><sup>-</sup> and water during storage (Dahal and Hastings, 2016), influences from O isotopic signatures from NO<sub>x</sub> emissions sources (Felix and Elliott, 2014), or photochemical non-equilibrium with O<sub>3</sub>. Thus, δ<sup>18</sup>O value of *in situ* NO<sub>x</sub> remains uncertain and likely highly variable and what that variations means in terms of photochemical oxidation pathways still requires resolution.

To improve our understanding of the N and O isotopic composition of NO<sub>x</sub>, separate daytime and nighttime isotopic measurements of *in situ* NO<sub>x</sub> are required. In this study, the diurnal variations in δ<sup>15</sup>N and δ<sup>18</sup>O values of *in situ* NO<sub>2</sub> was measured using an active sampling technique, and the data was evaluated in the context of source and chemical isotope effects with the goal of understanding the drivers of δ<sup>15</sup>N and δ<sup>18</sup>O variabilities in NO<sub>2</sub>.

## 2. Methods

### 2.1. Sampling location

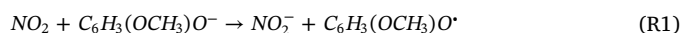
NO<sub>2</sub> was collected from ambient air on the rooftop of a building (Hampton Hall of Civil Engineering) on the campus of Purdue University (West Lafayette, IN, USA, 40.426° N, 86.908° W) (Fig. 1) [Google Earth, 2016]. The surrounding land-use is the urban/sub-urban

sister cities of Lafayette-West Lafayette, IN that have a combined population of roughly 150,000. The sampling location was approximately 12 m above ground and was directly above a loading dock with light daytime diesel truck and gasoline vehicle traffic and approximately 50 m from a regularly traveled road that experiences moderate weekday rush hour traffic at approximately 7–8 a.m. and 5–6 p.m. The 2011 U.S. EPA emission inventory estimates the following yearly NO<sub>x</sub> emission budget for the county of the sampling location (Tippecanoe): Mobile = 59.4%, Fuel Combustion = 35.3%, Biogenic = 4.2%, Industry = 0.7%, Waste = 0.3%, and Fire = 0.1% [Office of Air Quality Planning and Standards (2011)]. To the north and west of the sampling location is mostly roads, a golf course, and agricultural fields (maize and soybean). Approximately 2 km south of the sampling site is a 41.4 MW electrical-heat cogeneration plant that operates 3 natural gas and 1 coal-fired boilers.

### 2.2. *In situ* NO<sub>2</sub> collection

NO<sub>2</sub> was collected using a denuder tube active sampling apparatus (Fig. 2). Briefly, ambient air was drawn through a borosilicate tube (inner diameter = 3 mm and length = 1 m) using an air sampling pump flow controlled to 1 L/min. Based on the Gormley-Kennedy solutions for a cylindrical denuder (Ali et al., 1989), our sample flow rate, and an NO<sub>2</sub> diffusion constant of 1.36 × 10<sup>-5</sup> m<sup>2</sup>/s at 273 K and 1 atm (Massman, 1998), NO<sub>2</sub> should be nearly 100% removed within 50 cm assuming a perfect NO<sub>2</sub> absorber. Our denuder tube should therefore provide roughly 2 times the length required for complete NO<sub>2</sub> absorption. As a quality control check, a second denuder tube was connected in series with the first tube to check for NO<sub>2</sub> breakthrough. The denuder tubes were held vertically to prevent gravitational sedimentation of < 1 μm particulate matter to the tube wall as an extra precaution (Ali et al., 1989). Prior to the denuder tube, a Millipore Fluoropore membrane filter (9 mm diameter) removed fine particulate matter > 1 μm. Particulates were removed before NO<sub>2</sub> because we did not have a denuder transition section to establish laminar flow. Therefore, turbulent flow at the beginning of our denuder tube could collect particulates, such that we opted to remove particles upstream of the denuder. In this set-up, it is possible that NO<sub>2</sub> may have reacted with particulates prior to NO<sub>2</sub> reaching the denuder, but the particulate filter was replaced each sampling period to not allow for excessive particulate buildup to minimize this possibility. All connections between the various components of the sampling apparatus was made using 1/4" Teflon tubing and ultratorr fittings. The sampling inlet (1/4" Teflon tubing) was mounted on the side of a building and sheltered from precipitation and direct sunlight.

The denuder tubes were coated with 0.5 mL of a 2.5 M potassium hydroxide, 25% by weight guaiacol (C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>), and methanol solution and dried with high-purity argon. The denuder tubes were prepared daily and used for NO<sub>2</sub> collection within 24 h. The guaiacol/KOH coating reacts with NO<sub>2</sub> to form NO<sub>2</sub><sup>-</sup> (Ammann et al., 1999; Buttini et al., 1987; Li and Wang, 2008; Williams and Grosjean, 1990). Briefly, NO<sub>2</sub> undergoes an electron transfer reaction with deprotonated guaiacol (C<sub>6</sub>H<sub>3</sub>(OCH<sub>3</sub>)O<sup>-</sup>) (Ammann et al., 2005), which is the preferential guaiacol product (pK<sub>a</sub> = 9.98 (Pearce and Simkins, 1968);) under basic conditions (R1):



Previous studies have found that the guaiacol/KOH coating results in the bound NO<sub>2</sub> as NO<sub>2</sub><sup>-</sup> with a stoichiometric factor of one (Buttini et al., 1987). From a mass-balance perspective, the N and O atoms in the NO<sub>2</sub><sup>-</sup> product derive entirely from the atoms of the bound NO<sub>2</sub>. Thus, the guaiacol/KOH coating provides a promising NO<sub>2</sub> concentration method for conserving both the N and O isotope signatures of atmospheric NO<sub>2</sub>.

Other gaseous oxidized forms of nitrogen might interfere with the collected NO<sub>2</sub>. High oxidized N forms such as N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> should

Download English Version:

<https://daneshyari.com/en/article/8863943>

Download Persian Version:

<https://daneshyari.com/article/8863943>

[Daneshyari.com](https://daneshyari.com)