

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



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## ABSTRACT

The nitrogen and oxygen stable isotopes ( $\delta^{15}\text{N}$  &  $\delta^{18}\text{O}$ ) of nitrogen oxides ( $\text{NO}_x$  = nitric oxide (NO) + nitrogen dioxide ( $\text{NO}_2$ )) 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 VOC- $\text{NO}_x$ - $\text{O}_3$  chemistry.

## 1. Introduction

Nitrogen oxides ( $\text{NO}_x$  = nitric oxide (NO) + nitrogen dioxide ( $\text{NO}_2$ )) 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 ( $\text{HO}_x$  = hydroxyl radical (OH) + peroxy radicals ( $\text{HO}_2$  and  $\text{RO}_2$ )) 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

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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

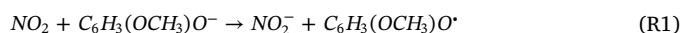
NO<sub>2</sub> was collected from ambient air on the rooftop of a building (Hampton Hall of Civil Engineering) on the campus of Purdue University (West Lafayette, IN, USA, 40.426° N, 86.908° W) (Fig. 1) [Google Earth, 2016]. The surrounding land-use is the urban/sub-urban

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

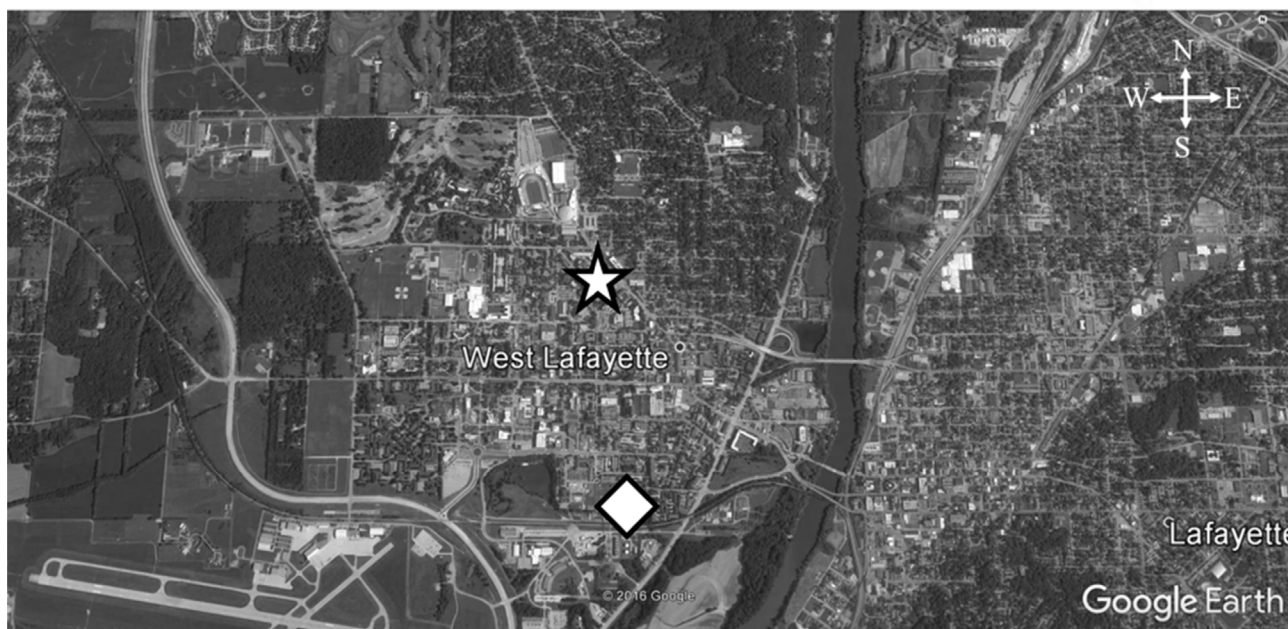


Fig. 1. Aerial view of the area near the sampling site. The location of sampling site is indicated by the star and the location of the nearby utility plant (3 natural gas boilers and one coal-fired boiler) is indicated by the diamond. Image from Google Earth.

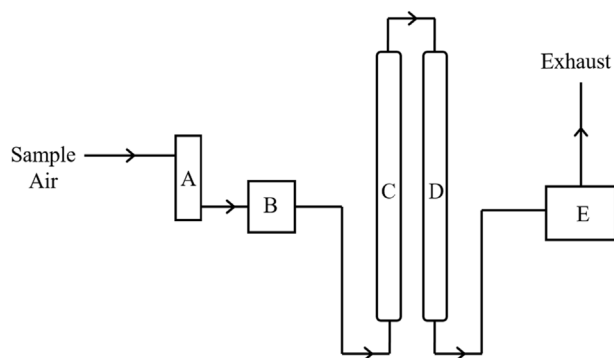


Fig. 2. Sampling apparatus schematic for collection of atmospheric  $\text{NO}_2$ , where A is the flow meter (1 L/min), B is aerosol filter, C is the  $\text{NO}_2$  binding denuder tube, D is the  $\text{NO}_2$  breakthrough denuder tube, and E is the air sampling pump.

not have a major impact on our collected  $\text{NO}_2$  since presumably these molecules will bind as  $\text{NO}_3^-$ , while our analysis is selective towards  $\text{NO}_2^-$  (see section 2.3). Other N oxidized forms that include peroxyacetyl nitrate (PAN) and nitrous acid (HONO) may, however, bind as  $\text{NO}_2^-$  (Buttini et al., 1987). PAN should not be an interference because it usually has very low concentrations at ambient temperature and previously found not to bind with the guaiacol/KOH coating (Buttini et al., 1987). HONO has been found to bind with the guaiacol/KOH coating as  $\text{NO}_2^-$  (Buttini et al., 1987), but interference is expected to be small because [HONO] is generally much lower than  $[\text{NO}_2]$  by a factor of 10–20 (Harris et al., 1982). Thus, we did not remove HONO before collection of  $\text{NO}_2$ , because coatings designed for HONO collection (i.e. sodium carbonate (Febo et al., 1993);) can also bind  $\text{NO}_2$  with an efficiency as high as 28% (Williams and Grosjean, 1990), which may interfere with our results more than not removing the present HONO.

Ambient air was sampled separately during the daytime (~6 h) and nighttime (~8 h) during weekdays from July 7 to August 4, 2016. Daytime and nighttime collections typically occurred between 8:30 a.m. to 4:00 p.m. and 9:30 p.m. to 5:30 a.m., respectively (Table S1).  $\text{NO}$ - $\text{NO}_2$ - $\text{NO}_x$  concentrations were measured using a Thermo Scientific  $\text{NO}_x$  43C analyzer. After collection, the denuder tubes were separately rinsed with 3 mL of 18.2 M $\Omega$  Millipore Water.  $\text{NO}_2^-$  test strips

(AquaChek<sup>®</sup>) were used as a semi-quantitative check for  $[\text{NO}_2^-]$  and was found to always test positive for the capture denuder and negative for the breakthrough denuder. Thus, the eluent from the second denuder tube was discarded and the eluent from the first denuder tube was immediately placed in a freezer until isotopic analysis. As a quality control check of our data, we estimate collection yield for each sample based on peak yields from isotopic analysis (see below) compared to the expected amount that was determined from the integrated  $[\text{NO}_2]$  measured using the Thermo Scientific  $\text{NO}_x$  43C analyzer. This was the chosen method rather than  $[\text{NO}_2^-]$  quantification using Ion Chromatography or colorimetric analysis because (1) we were generally sample-limited and needed all collected sample for isotopic analysis and (2) we found the denuder extraction matrix to impede with the colorimetric determination of  $[\text{NO}_2^-]$  (e.g. US EPA Method 353.2), such that it was difficult to analyze low  $[\text{NO}_2^-]$  samples because of relatively low precision ( $\pm 5 \mu\text{M}$ ).

### 2.3. Isotopic analysis of $\text{NO}_2$

Isotopic analysis ( $\delta^{18}\text{O}$  &  $\delta^{15}\text{N}$ ) was performed on the product  $\text{NO}_2^-$  in the frozen eluent extracted from the first denuder tube. Samples were left out at room temperature to thaw approximately 2 h before the analysis. The entire eluent of approximately 3 mL from each sample was converted into nitrous oxide ( $\text{N}_2\text{O}$ ) using sodium azide in an acetic acid buffer (McIlvin and Altabet, 2005). The product  $\text{N}_2\text{O}$  was extracted and purified using an automated headspace gas chromatography system and analyzed by a Thermo Delta V Continuous Flow Isotope Ratio Mass Spectrometer for  $m/z$  44, 45, and 46 at the Purdue Stable Isotopes Lab. Measured  $\delta^{15}\text{N}$  (relative to air  $\text{N}_2$ ) and  $\delta^{18}\text{O}$  (relative to VSMOW) was calibrated to  $\text{KNO}_3$  salts that included RSIL-N7373, RSIL-N23, RSIL-10219 assuming the following respective ( $\delta^{15}\text{N}(\text{‰})$ ,  $\delta^{18}\text{O}(\text{‰})$ ) values: (-79.6, 4.5), (3.7, 11.4), and (2.8, 88.5) (Böhlke et al., 2007). Direct calibration of our  $\text{NO}_2^-$  samples to  $\text{NO}_2^-$  standards, and the direct conversion of  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$  using the sodium azide method (McIlvin and Altabet, 2005), allows us to ignore the uncertainty in correcting for isotopic fractionation of  $\delta^{18}\text{O}$  using typical nitrate isotopic reference materials (Casciotti et al., 2007).

The  $\text{NO}_2^-$  samples typically contained between 30 and 125 nmoles of  $\text{NO}_2^-$  based on the product  $\text{N}_2\text{O}$  yield. Linearity effects were

corrected by using variable  $\text{NO}_2^-$  amounts of the standards that ranged between 20 and 250 nmoles. The isotopic precision was found to be highly dependent on the amount of  $\text{NO}_2^-$  analyzed. Near our sample sizes of 30–125 nmoles, the average standard deviation between the residual values of the calibrated standards for  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  was 1.1‰ and 0.6‰, respectively. This uncertainty is slightly higher than our usual isotopic precision for  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of 0.6‰, and 0.4‰ that is found at  $\text{NO}_2^-$  amounts greater than 200 nmoles. Thus, we report  $\delta^{15}\text{N}(\text{NO}_2)$  and  $\delta^{18}\text{O}(\text{NO}_2)$  “raw measurement” errors of  $\pm 1.1‰$  and  $\pm 0.6‰$ . Additionally, since our  $\text{NO}_2$  samples are of atmospheric origin,  $\delta^{15}\text{N}$  was also approximately corrected for  $\text{N}_2\text{O}$  isobaric influences from  $\Delta^{17}\text{O}$  (Hastings et al., 2003). Unfortunately, we did not have enough sample for  $\Delta^{17}\text{O}$  analysis, such that we estimated this value based on the measured  $\delta^{18}\text{O}(\text{NO}_2)$  and assuming a mixing line between  $\text{RO}_2$  ( $\delta^{18}\text{O} = 23‰$ ,  $\Delta^{17}\text{O} = 0‰$ ; (Michalski et al., 2012)) and terminal O atom of  $\text{O}_3$  ( $\delta^{18}\text{O} = 126.3‰$  and  $\Delta^{17}\text{O} = 39.3‰$ ; (Vicars and Savarino, 2014), which are the oxidants responsible for oxidizing NO. This typically resulted in a small  $\delta^{15}\text{N}$  correction of  $-3‰$  during the daytime and  $-1.5‰$  during the nighttime.

#### 2.4. Control tests

Previous control tests demonstrated the robustness for characterizing  $\delta^{15}\text{N}(\text{NO}_2)$  using the same denuder tubes employed in this study, with an isotopic precision of approximately  $\pm 0.7‰$  (near our analytical precision) (Walters et al., 2016). Additionally, it was found that NO is not removed by the guaiacol/KOH denuder coating (Walters et al., 2016). To assess the precision of our sampling technique for  $\delta^{18}\text{O}(\text{NO}_2)$ , further control tests were conducted by flowing an aliquot of air from an  $\text{NO}_2$  bulb through our sampling apparatus (Fig. 2). Isotopic analysis of the product  $\text{NO}_2^-$  resulted in  $\delta^{18}\text{O}$  of  $-1.8 \pm 1.2‰$  ( $n = 7$ ), which indicates excellent precision; however, the  $\delta^{18}\text{O}$  value of the  $\text{NO}_2$  bulb is unknown. Since nearly 100% of  $\text{NO}_2$  appears to bind on the denuder tube,  $\delta^{18}\text{O}$  fractionation due to incomplete  $\text{NO}_2$  collection should not be of concern. Assuming  $\delta^{18}\text{O}(\text{NO}_2)$  is conserved as it is bound as  $\text{NO}_2^-$ , the major concern with preserving the  $\delta^{18}\text{O}$  composition during sample storage is the possible O isotopic exchange of  $\text{NO}_2^-$  with water once eluted from the denuder tube. The elutant has a  $\text{pH} > 10$ , so that  $\delta^{18}\text{O}$  exchange with water should be minimal (Casciotti et al., 2007). This was tested by periodically injecting 20–50 nmoles of a standard  $\text{KNO}_2^-$  salt (RISL-N10219) into the eluted guaiacol/KOH mixture over a period of one month. The controls were immediately placed in a freezer until isotopic analysis as performed in our collection of *in situ*  $\text{NO}_2$ . Our control tests indicate that O isotopic exchange between  $\text{NO}_2^-$  and  $\text{H}_2\text{O}$  does occur in our samples, reaching approximately 3.5% within the first three days, based on a laboratory water  $\delta^{18}\text{O}$  of  $-8‰$  (Fig. 3). After this initial exchange, no further exchange in  $\delta^{18}\text{O}$  was observed, as all control samples that were kept in solution between 3 and 31 days prior to isotopic analysis indicated an average O exchange with water of  $2.7 \pm 2\%$  (Fig. 3). This consistent fraction of O exchange between  $\text{NO}_2^-$  and  $\text{H}_2\text{O}$  is hypothesized to be the result of the time it took for the samples to freeze and thereby slowing the exchange to a negligible rate and/or exchange that might have occurred when samples thawed.

Our samples were analyzed between 3 and 20 days of collection and were corrected assuming an O isotopic exchange of  $2.7 \pm 2\%$  with water. The degree of uncertainty in the amount of  $\delta^{18}\text{O}$  exchange ( $\pm 2\%$ ) adds an uncertainty in our reported  $\delta^{18}\text{O}(\text{NO}_2)$  of about 1.5‰. Therefore, the uncertainty in our  $\delta^{18}\text{O}(\text{NO}_2)$  measurements is reported as  $\pm 2.1‰$ , which is the propagated error of our raw  $\delta^{18}\text{O}(\text{NO}_2^-)$  measurement uncertainty and the uncertainty in  $\delta^{18}\text{O}$  resulting from  $\text{NO}_2^-$  exchange with water.

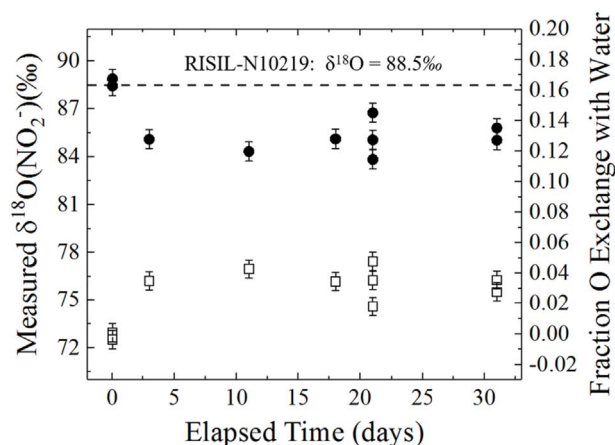


Fig. 3. Impacts of  $\delta^{18}\text{O}$  exchange between  $\text{NO}_2^-$  and  $\text{H}_2\text{O}$  ( $\delta^{18}\text{O} = -8‰$ ) contained within the KOH/guaiacol elutant as a function of time contained within solution before isotopic analysis. The black circles represent the measured  $\delta^{18}\text{O}(\text{NO}_2^-)$  (primary y-axis) and the open squares represent the estimated fraction of O exchange between  $\text{NO}_2^-$  and water (secondary y-axis).

### 3. Results

#### 3.1. Measured $[\text{NO}_x]$ and $f(\text{NO}_2)$

Daytime  $[\text{NO}_x]$  exhibited an early morning increase between 6 and 10 a.m. that reached an average high of  $7.1 \pm 4.1$  ppb<sub>v</sub> around 8:00 a.m. (Fig. 4). After this morning peak,  $[\text{NO}_x]$  steadily decreased throughout the day to a baseline  $[\text{NO}_x]$  of approximately  $2.5 \pm 0.4$  ppb<sub>v</sub> (Fig. 4). A smaller  $\text{NO}_x$  peak near 5 p.m. is observed on some of the collection days during the workdays (Monday through Friday); however, this afternoon peak is not obvious in the 1 h averaged  $[\text{NO}_x]$  measurements that spans the entire collection period from July 7 to August 4, 2016. It is important to note that the volume of traffic is much lower during the summertime than during the school year (September–May). A diurnal cycle in  $f(\text{NO}_2)$ , i.e.  $\text{NO}_2/\text{NO}_x$ , is also observed with daytime values averaging  $0.82 \pm 0.04$  and nighttime values averaging  $0.91 \pm 0.004$  (Fig. 4). Additionally,  $f(\text{NO}_2)$  values were observed to be lowest when  $[\text{NO}_x]$  concentrations were the highest.

#### 3.2. $\text{NO}_2$ isotope composition

A summary of the collected  $\text{NO}_2$  samples is reported in the Supporting Information (Table S1) that includes the sampling start and end times, the average  $[\text{NO}_x]$  and  $f(\text{NO}_2)$  during each collection period measured from the Thermo 42C  $\text{NO}_x$  analyzer, meteorology data including temperature, relative humidity and any meteorological events that occurred (e.g. fog and rain) (assessed via wunderground.com), collection yields, and measured  $\delta^{18}\text{O}$ , and  $\delta^{15}\text{N}$ . As a quality control of the data, we only use collected samples in which collection yields were within 15% of quantitative collection. This cutoff point is chosen based on the propagated error of quantitative collection of approximately 15% that includes the analytical error in flow rate,  $[\text{NO}_2^-]$  determination, and the Thermo 42C  $\text{NO}_x$  analyzer. Out of 32 samples 23 were found to be within the propagated error limits of quantitative collection. The data that was found to result in incomplete collection occurred mostly during fog events, rain, and/or under high relative humidity conditions and probably represents a collection artifact resulting from  $\text{NO}_2$  reactions on the wetted filter,  $\text{NO}_2$  loss on the tubing inlet, or incomplete capture of  $\text{NO}_2$  using the denuder under high relative humidity conditions. Interestingly, the fog and rain events that resulted in a lower than expected collection yield, had relatively elevated  $\delta^{15}\text{N}(\text{NO}_2)$  values ranging from  $-4.2$ – $7.8‰$  and averaging  $(-0.1 \pm 4.2‰)$  (Table S1), and while we cannot rule out the possibility of collection artifacts during these sampling periods, these  $\delta^{15}\text{N}(\text{NO}_2)$  values may

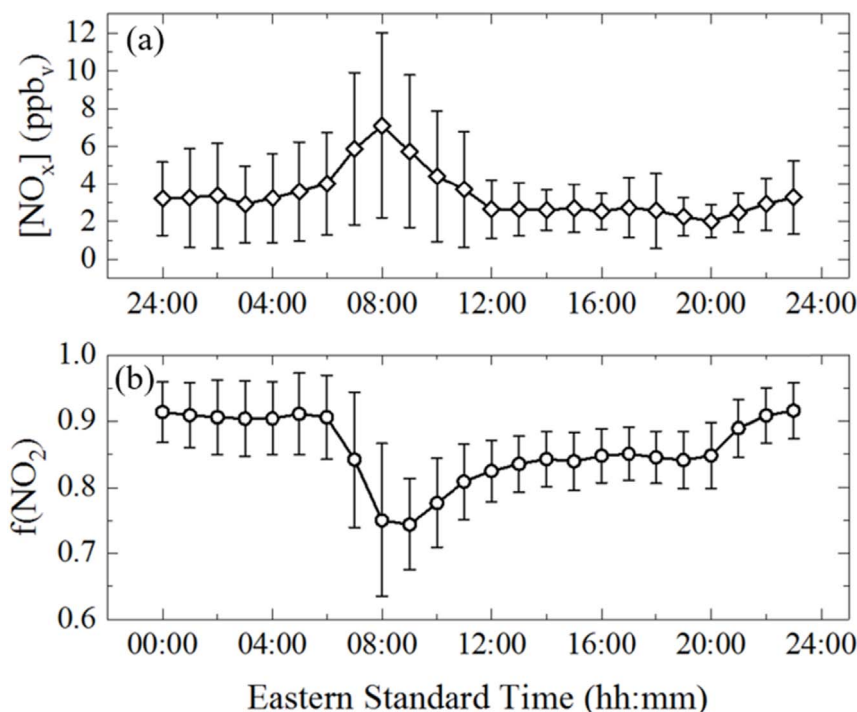


Fig. 4. Averaged diurnal variations in  $[\text{NO}_x]$  (a) and  $f(\text{NO}_2)$  (b) at our sampling location during the collection period of July 7 to August 4, 2016. Diamonds represent averages for each hour taken from measurements at 30 s intervals each day and the gray lines represent  $\pm 1\sigma$  for each hour.

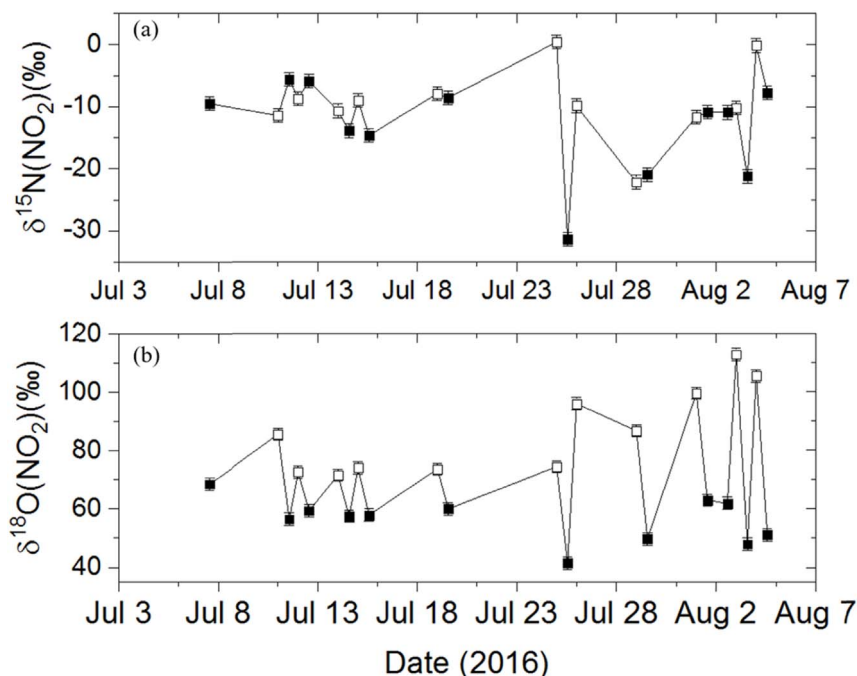


Fig. 5. Measured (a)  $\delta^{15}\text{N}(\text{NO}_2)$  and (b)  $\delta^{18}\text{O}(\text{NO}_2)$  of *in situ*  $\text{NO}_x$  collected from July 7, 2016 to August 5, 2016 during the daytime (open squares) and nighttime (black squares).

also be influenced by wet scavenging of  $\text{NO}_2$  (e.g. Yoo et al., 2014), which may preferentially remove  $^{14}\text{NO}_2$  leaving the collected  $\text{NO}_2$  with higher  $\delta^{15}\text{N}$  values. The measured  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of the quality controlled data ( $\pm 15\%$  within quantitative  $\text{NO}_2$  collection) are displayed in Fig. 5.

### 3.2.1. Diurnal changes in $\delta^{15}\text{N}(\text{NO}_2)$ values

The measured  $\delta^{15}\text{N}(\text{NO}_2)$  values (Fig. 5) had large variations that ranged from  $-31.4$  to  $0.4\text{‰}$  and averaged  $-11.4 \pm 6.9\text{‰}$  ( $n = 23$ ). This  $\delta^{15}\text{N}(\text{NO}_2)$  range is wider than the  $-9.0$  to  $-3.6\text{‰}$  range

previously reported in an urban location (Dahal and Hastings, 2016), but near the reported range of  $-24.6\text{‰}$  to  $7.3\text{‰}$  measured from a roadside transect (Redling et al., 2013). The average  $\delta^{15}\text{N}(\text{NO}_2)$  value is close to the  $\delta^{15}\text{N}(\text{NO}_x)$  value of approximately  $-9\text{‰}$  predicted by isotope mass-balance for the West Lafayette region during the July to August period (Walters et al., 2015b). Samples collected during the daytime and nighttime had an average  $\delta^{15}\text{N}(\text{NO}_2)$  of  $-9.2 \pm 5.7\text{‰}$  ( $n = 11$ ) and  $-13.4 \pm 7.3\text{‰}$  ( $n = 12$ ), respectively, indicating that on average  $\delta^{15}\text{N}(\text{NO}_2)$  is slightly higher during the daytime than during the nighttime. However, the difference in the daytime and nighttime

**Table 1**  
Nighttime measured  $\delta^{15}\text{N}(\text{NO}_2)$ , calculated  $\delta^{15}\text{N}(\text{NO}_2)$  shift, and estimated  $\delta^{15}\text{N}(\text{NO}_x)$ .

Collection Start	Collection End	Average $f(\text{NO}_2)$	$\delta^{15}\text{N}(\text{NO}_2)$ (‰) (Measured)	Calculated $\delta^{15}\text{N}(\text{NO}_2)$ Shift (‰) <sup>a</sup>	$\delta^{15}\text{N}(\text{NO}_x)$ (‰) <sup>b</sup>
7/7/2016 21:30	7/8/2016 5:30	0.901	-9.5	2.1	-11.6
7/11/2016 21:30	7/12/2016 5:30	0.939	-5.6	1.3	-6.9
7/12/2016 21:30	7/13/2016 5:30	0.935	-5.9	1.4	-7.2
7/14/2016 21:30	7/15/2016 5:30	0.881	-13.9	2.5	-16.4
7/15/2016 21:30	7/16/2016 5:30	0.894	-14.6	2.2	-16.8
7/19/2016 21:30	7/20/2016 5:30	0.932	-8.6	1.4	-10.0
7/25/2016 21:30	7/26/2016 5:30	0.891	-31.4	2.3	-33.8
7/29/2016 21:30	7/30/2016 5:30	0.929	-21.0	1.5	-22.5
8/1/2016 21:30	8/2/2016 5:30	0.917	-10.9	1.7	-12.6
8/2/2016 21:30	8/3/2016 5:30	0.938	-10.9	1.3	-12.2
8/3/2016 21:30	8/4/2016 5:30	0.909	-21.3	1.9	-23.2
8/4/2016 21:30	8/5/2016 5:30	0.891	-7.8	2.3	-10.1

<sup>a</sup>  $\delta^{15}\text{N}(\text{NO}_2)$  shift was calculated according to Eq. (1).

<sup>b</sup>  $\delta^{15}\text{N}(\text{NO}_x) = [\delta^{15}\text{N}(\text{NO}_2) \text{ (Measured)}] - [\delta^{15}\text{N}(\text{NO}_2) \text{ Shift}]$ .

means are not statistically significant (two-sided  $t$ -test  $p > 0.05$ ).

### 3.2.2. Diurnal changes in $\delta^{18}\text{O}(\text{NO}_2)$ values

Large variations were also observed in  $\delta^{18}\text{O}(\text{NO}_2)$  values (Fig. 5) that ranged from 41.5 to 112.7‰ and averaged  $70.7 \pm 18.7\%$  ( $n = 23$ ). The standard deviation in  $\delta^{18}\text{O}(\text{NO}_2)$  is significantly reduced when comparing daytime to nighttime collections. During the daytime,  $\delta^{18}\text{O}(\text{NO}_2)$  averaged  $86.5 \pm 14.1\%$  ( $n = 11$ ), while during the nighttime,  $\delta^{18}\text{O}(\text{NO}_2)$  averaged  $56.3 \pm 7.1\%$  ( $n = 12$ ). The daytime and nighttime means are statistically significantly different (two-side  $t$ -test  $p < 0.05$ ). These  $\delta^{18}\text{O}(\text{NO}_2)$  values are both larger and more variable than recently reported  $\delta^{18}\text{O}(\text{NO}_2)$  values of  $50.5 \pm 3.2\%$  and  $47.4 \pm 1.2\%$  for  $\text{NO}_2$  collected using Ogawa diffusion samplers at an urban location during the summer and winter, respectively (Dahal and Hastings, 2016). Additionally, our  $\delta^{18}\text{O}(\text{NO}_2)$  values are much larger than reported values of  $-12.6 \pm 3.1\%$  and  $-2.0 \pm 5.0\%$  of  $\text{NO}_2$  collected using Ogawa diffusion samplers placed inside and outside of a road tunnel (Felix and Elliott, 2014).

## 4. Discussion

### 4.1. Measured $[\text{NO}_x]$ and $f(\text{NO}_2)$

The large influence of traffic  $\text{NO}_x$  emission is observable in the early morning rush-hour  $[\text{NO}_x]$  peak that averaged  $7.1 \pm 4.1$  ppb<sub>v</sub> around 8:00 a.m. (Fig. 4). This early morning  $\text{NO}_x$  emission spike is typical of urban areas (Boersma et al., 2009; Gao, 2007; Murphy et al., 2006). An afternoon rush-hour peak in  $[\text{NO}_x]$  is not observed in Fig. 4. This is likely an atmospheric dilution effect caused by an increased boundary layer height and the breakdown of the early morning nocturnal inversion layer (Gaur et al., 2014). Higher afternoon oxidant concentrations that quickly converts  $\text{NO}_x$  to atmospheric nitrate may also be a factor in keeping afternoon  $\text{NO}_x$  concentrations low relative to the morning (Boersma et al., 2009). During the nighttime,  $[\text{NO}_x]$  concentrations remain relatively steady, between 3 and 5 ppb<sub>v</sub> (Fig. 4), due to the decreased boundary layer height and the titration of  $\text{O}_3$  by  $\text{NO}$  (Nishanth et al., 2012).

The emission of  $\text{NO}_x$  and its photochemical cycling plays a significant role on the observed diurnal cycle in  $f(\text{NO}_2)$  (Fig. 4). Mobile emission of  $\text{NO}_x$  is primarily in the form of  $\text{NO}$  resulting in a decrease in  $f(\text{NO}_2)$  during the early morning rush-hour  $\text{NO}_x$  spike (Fig. 4). In addition, the photolysis of  $\text{NO}_2$  results in a lower  $f(\text{NO}_2)$  value during the daytime relative to the nighttime when photolysis of  $\text{NO}_2$  ceases and nighttime oxidation of  $\text{NO}$  by  $\text{O}_3$  pushes nighttime  $\text{NO}_x$  towards  $\text{NO}_2$ , which is evident by the nighttime  $f(\text{NO}_2)$  close to 1 (Fig. 4).

### 4.2. $\delta^{15}\text{N}(\text{NO}_2)$

The observed  $\delta^{15}\text{N}(\text{NO}_2)$  may reflect  $\text{NO}_x$  emission sources with characteristic  $\delta^{15}\text{N}$  values (e.g. Felix et al., 2012; Fibiger et al., 2014; Miller et al., 2017; Walters et al., 2015a, 2015b), isotope effects associated with the partitioning of  $\delta^{15}\text{N}$  between  $\text{NO}$  and  $\text{NO}_2$  (Walters et al., 2016; Walters and Michalski, 2015), post  $\text{NO}_2$  oxidation reactions (Freyer, 1991; Walters and Michalski, 2015), and/or a combination of these effects. Therefore, to understand the drivers behind the observed variability in  $\delta^{15}\text{N}(\text{NO}_2)$  we need to systematically evaluate these effects.

#### 4.2.1. $\delta^{15}\text{N}(\text{NO}_2)$ isotope effect influence

During the nighttime, nearly all  $\text{NO}_x$  exists as  $\text{NO}_2$  (Fig. 4), as we found nighttime  $f(\text{NO}_2)$  to average 0.913 for the collected samples. Therefore,  $\delta^{15}\text{N}(\text{NO}_2)$  values should be close to  $\delta^{15}\text{N}(\text{NO}_x)$ , but not exactly equal to one another since  $f(\text{NO}_2) \neq 1$ ; Walters et al., 2016). We estimate the possible  $\delta^{15}\text{N}$  effect on  $\text{NO}_2$  relative to  $\text{NO}_x$  assuming  $\text{NO}_x$  isotope exchange is the primary driver of  $\delta^{15}\text{N}$  partitioning between  $\text{NO}$  and  $\text{NO}_2$  during the nighttime (Freyer et al., 1993; Walters et al., 2016) using Eq. (1):

$$\delta^{15}\text{N}(\text{NO}_2)(\text{‰}) = 1000 \left[ \frac{(\alpha_{\text{NO}_2/\text{NO}} - 1)(1 - f_{\text{NO}_2})}{(1 - f_{\text{NO}_2}) + (\alpha_{\text{NO}_2/\text{NO}} f_{\text{NO}_2})} \right] \quad (1)$$

Where  $\alpha_{\text{NO}_2/\text{NO}}$  is the N isotopic fractionation factor between  $\text{NO}_2$  and  $\text{NO}$  during the nighttime, which was previously reported to be 1.0216 based on field measurements (Freyer et al., 1993). Using Eq. (1), we have estimated the possible  $\delta^{15}\text{N}$  shift in  $\text{NO}_2$  relative to  $\text{NO}_x$  to range between 1.3 and 2.5‰, indicating that  $\delta^{15}\text{N}(\text{NO}_2)$  may be slightly higher relative to the total  $\delta^{15}\text{N}(\text{NO}_x)$  during the nighttime under our sampling conditions (Table 1). Future  $\text{NO}_x$  speciated  $\delta^{15}\text{N}$  measurements are necessary to confirm the predicted  $\delta^{15}\text{N}$  increase in  $\text{NO}_2$  relative to  $\text{NO}$  under nighttime conditions, and this will be the focus for future research.

Nighttime post- $\text{NO}_2$  oxidation reactions would likely occur via nighttime  $\text{NO}_2$ ,  $\text{NO}_3$ , and  $\text{N}_2\text{O}_5$  equilibration and subsequent hydrolysis of  $\text{N}_2\text{O}_5$  to form  $\text{HNO}_3$  (Calvert et al., 1985). The nighttime lifetime of  $\text{NO}_2$  can be approximated based on its reaction with  $\text{O}_3$  to form  $\text{NO}_3$ . We estimate an approximate chemical lifetime ( $\tau$ ) of 21.0 h assuming nighttime  $[\text{O}_3]$  of 15 ppb<sub>v</sub> (taken from nighttime measured  $[\text{O}_3]$  during July 2016 at Flora, IN, which is approximately 40 km east of the sampling site; <http://www.in.gov/idem/airquality>) and a reaction rate at 298 K, of  $3.52 \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  ( $k_{\text{NO}_2+\text{O}_3}$ ; Atkinson et al., 2004) and calculated according to Eq. (2):

$$\tau = \frac{1}{k_{\text{NO}_2+\text{O}_3} [\text{O}_3]} \quad (2)$$

This nighttime NO<sub>2</sub> lifetime is relatively long especially considering the lifetime of NO<sub>3</sub> resulting in the back formation of NO<sub>2</sub>, which may occur through NO<sub>3</sub> reaction with NO. We estimate a nighttime NO<sub>3</sub> lifetime of 5.1 s, which is calculated assuming an observed average night NO concentration of approximately 0.3 ppb<sub>v</sub> and a reaction rate at 298 K of  $2.60 \times 10^{-11} \text{ cm}^3 \cdot \text{molecules}^{-1} \text{ s}^{-1}$  (Atkinson et al., 2004) (Eq. (3)):

$$\tau = \frac{1}{k_{\text{NO}_3+\text{NO}}[\text{NO}]} \quad (3)$$

Therefore, it is approximately assumed that nighttime  $\delta^{15}\text{N}(\text{NO}_2)$  should reflect a mixture of local NO<sub>x</sub> sources and possibly NO<sub>x</sub> isotope exchange, as post-NO<sub>2</sub> oxidation reactions should have a minimal influence on the NO<sub>2</sub> loss under ambient nighttime conditions.

Daytime  $\delta^{15}\text{N}(\text{NO}_2)$  is more complicated to predict than nighttime  $\delta^{15}\text{N}(\text{NO}_2)$  because the photochemical reactions involving NO<sub>x</sub> may lead to significant  $\delta^{15}\text{N}$  partitioning between NO and NO<sub>2</sub> (Freyer et al., 1993; Walters et al., 2016). The average of  $f(\text{NO}_2)$  during our daytime collection periods was 0.745, indicating that partitioning of  $\delta^{15}\text{N}$  between NO and NO<sub>2</sub> could be significant; however, under summertime conditions at our sampling site, (i.e.  $[\text{NO}_x] \ll [\text{O}_3]$ ) the photochemical reactions should destroy NO<sub>x</sub> isotopic equilibrium (Freyer et al., 1993). We estimate NO<sub>x</sub> photochemical cycling on  $\delta^{15}\text{N}(\text{NO}_2)$  assuming the partitioning of  $^{15}\text{N}$  between NO and NO<sub>2</sub> to be influenced by NO oxidation, NO<sub>2</sub> photolysis, and NO $\leftrightarrow$ NO<sub>2</sub> isotopic exchange (Walters et al., 2016). Currently, we know the experimental fractionation factor for NO $\leftrightarrow$ NO<sub>2</sub> isotopic exchange ( $^{15}\alpha_{\text{NO}_2/\text{NO}} = 1.0356 \pm 0.0015$  at 297 K; Walters et al., 2016) and an estimated fractionation factor for NO oxidation by O<sub>3</sub> from *ab initio* methods ( $^{15}\alpha_{\text{NO}_2/\text{NO}} = 0.993$  at 298 K (Walters and Michalski, 2016b));, but the NO<sub>2</sub> photolysis isotope effect is unknown. For our model, we assume no isotopic fractionation associated with NO<sub>2</sub> photolysis. Utilizing these isotopic fractionation factors and reaction rates (Atkinson et al., 2004; Sharma et al., 1970), we have constructed a simple box model to estimate the photochemical isotope effect on  $\delta^{15}\text{N}(\text{NO}_2)$  for each of our daytime sampling conditions (Table 2).

The NO<sub>x</sub> photochemical inputs included NO<sub>x</sub> concentrations based on the measured average NO<sub>x</sub> for each sampling period and O<sub>3</sub> concentrations estimated from reported average daily measurements from Flora, IN (taken from <http://www.in.gov/idem/airquality>) and to simplify the model, it was assumed the average O<sub>3</sub> represents a steady-state O<sub>3</sub> concentration. NO<sub>2</sub> photolysis rates were optimized to achieve a modeled  $f(\text{NO}_2)$  that was close to the average measured value. The results of this simple box model are displayed in Table 3. Overall, we see that the competing NO<sub>x</sub> photochemical isotope effects tend to cancel out resulting in a small  $\delta^{15}\text{N}(\text{NO}_2)$  shift relative to  $\delta^{15}\text{N}(\text{NO}_x)$  of 0.1–2.4%. Thus, this simple model suggests that daytime NO<sub>x</sub>

**Table 2**

Summary of the NO<sub>x</sub> photochemical nitrogen isotope box model including reaction specific fractionation factors ( $\alpha$ ), reaction rates at 298 K ( $k(298 \text{ K})$ ) and NO<sub>2</sub> photolysis rate ( $j$ ).

Reaction	$\alpha$	$k(298 \text{ K})^a$	$j(\text{NO}_2)^b$
<b>NO Oxidation</b>			
$^{14}\text{NO} + \text{O}_3 \rightarrow ^{14}\text{NO}_2 + \text{O}_2$	1	1.73	–
$^{15}\text{NO} + \text{O}_3 \rightarrow ^{15}\text{NO}_2 + \text{O}_2$	0.993	1.72	–
<b>NO<sub>x</sub> Isotope Exchange</b>			
$^{14}\text{NO} + ^{15}\text{NO}_2 \rightarrow ^{15}\text{NO} + ^{14}\text{NO}_2$	1	8.14	–
$^{15}\text{NO} + ^{14}\text{NO}_2 \rightarrow ^{14}\text{NO} + ^{15}\text{NO}_2$	1.0356	8.43	–
<b>NO<sub>2</sub> Photolysis</b>			
$^{14}\text{NO}_2 + h\nu \rightarrow ^{14}\text{NO} + \text{O}$	1	–	optimized
$^{15}\text{NO}_2 + h\nu \rightarrow ^{15}\text{NO} + \text{O}$	1	–	optimized

<sup>a</sup> ( $10^{-14} \text{ cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$ ) from (Atkinson et al., 2004; Sharma et al., 1970).

<sup>b</sup>  $j(\text{NO}_2)$  was optimized such that model  $f(\text{NO}_2) \approx$  measured average  $f(\text{NO}_2)$  for each collection period.

**Table 3** Summary of daytime NO<sub>x</sub> photochemical  $\delta^{15}\text{N}$  box model. Model inputs include average measured NO<sub>x</sub> (Avg [NO]<sub>M</sub>), O<sub>3</sub> concentrations (Avg [O<sub>3</sub>]), and  $j(\text{NO}_2)$  (optimized to achieve a model  $f(\text{NO}_2)$  that is approximately equal to the averaged measured  $f(\text{NO}_2)$ ) (Avg  $f(\text{NO}_2)_M$ ). Model outputs include the estimated  $\delta^{15}\text{N}(\text{NO}_2)$  shift relative to  $\delta^{15}\text{N}(\text{NO}_x)$ .

Collection Start	Collection End	Avg [NO <sub>x</sub> ] <sub>M</sub> (ppb <sub>v</sub> )	Avg [O <sub>3</sub> ] (ppb <sub>v</sub> ) <sup>a</sup>	NO <sub>x</sub> /O <sub>3</sub>	Model $j(\text{NO}_2)^b$	Model $f(\text{NO}_2)$	Estimated $\delta^{15}\text{N}(\text{NO}_2)$ Shift (‰)	Estimated $\delta^{15}\text{N}(\text{NO}_2)$ (‰) <sup>c</sup>
7/11/2016 8:30	7/11/2016 16:00	3.8	47	0.08	3.8	0.84	0.5	–11.9
7/12/2016 8:30	7/12/2016 16:00	3.4	33.6	0.10	3.4	0.80	0.9	–9.6
7/14/2016 8:40	7/14/2016 15:50	1.9	35.3	0.05	3.4	0.80	0.1	–10.8
7/15/2016 8:40	7/15/2016 15:40	2.1	31.9	0.07	4.5	0.75	0.3	–9.2
7/19/2016 9:10	7/19/2016 15:30	2.9	39.4	0.07	3.5	0.83	0.4	–8.3
7/25/2016 9:05	7/25/2016 15:40	2.3	38.8	0.06	4.2	0.80	0.2	0.2
7/26/2016 8:40	7/26/2016 15:40	5.8	35.8	0.16	7.3	0.68	2.4	–12.2
7/29/2016 8:45	7/29/2016 15:50	4.2	41	0.10	7.6	0.70	1.1	–23.3
8/1/2016 8:30	8/1/2016 15:50	5.3	37.4	0.14	10.5	0.61	2	–13.6
8/3/2016 8:50	8/3/2016 15:30	5.5	54.2	0.10	10.5	0.69	1.1	–11.3
8/4/2016 8:50	8/4/2016 15:05	7.9	51.1	0.15	10.5	0.69	2.3	–2.5

<sup>a</sup> Average measured O<sub>3</sub> at Flora, IN (<http://www.in.gov/idem/airquality>) for each collection period.

<sup>b</sup> ( $10^{-3} \text{ s}^{-1}$ ).

<sup>c</sup>  $\delta^{15}\text{N}(\text{NO}_2) = [\delta^{15}\text{N}(\text{NO}_2) (\text{Measured})] - [\delta^{15}\text{N}(\text{NO}_2) \text{ Shift}]$ .

photochemical isotope effects at our sampling location should be small. We note the uncertainty in the  $\text{NO}_2$  photolysis isotope effect and future work will need to determine this value. However, varying the  $\text{NO}_2$  photolysis fractionation factor from 0.995 to 1.005 in our model resulted in a shift in the calculated  $\delta^{15}\text{N}(\text{NO}_2)$  of approximately 1‰, indicating this effect to be small. We emphasize that this simple box model roughly approximates the  $\delta^{15}\text{N}(\text{NO}_2)$  daytime isotope effect and future chemical kinetic modeling will need to be done to better predict this isotope effect. Additionally, future  $\text{NO}_x$  speciation and  $\delta^{15}\text{N}$  measurements will be helpful in determining the conditions that may influence daytime  $\delta^{15}\text{N}$  partitioning between  $\text{NO}$  and  $\text{NO}_2$  and its temporal variability.

In addition to photochemical cycling, post- $\text{NO}_2$  oxidation reactions must be taken into consideration. During the daytime,  $\text{NO}_2$  is primarily oxidized by  $\text{OH}$  leading to the formation of  $\text{HNO}_3$ , resulting in an  $\text{NO}_2$  chemical lifetime on the order of a few hours (Valin et al., 2013). While this is a relatively short lifetime, the reaction between  $\text{NO}_2$  and  $\text{OH}$  is expected to have a small kinetic isotope effect of  $^{15}\alpha = 0.9971$  (Freyer, 1991). Thus, we expect this reaction to have a minimal influence on  $\delta^{15}\text{N}(\text{NO}_2)$ , but future work should investigate post daytime  $\text{NO}_2$  oxidation on  $\delta^{15}\text{N}(\text{NO}_x)$ , which will likely require experimental chamber studies and detailed chemical kinetic models.

#### 4.2.2. $\delta^{15}\text{N}(\text{NO}_2)$ source effect

Based off our  $\text{NO}_x$  isotope predictions, isotope effects associated with  $\text{NO}_x$  atmospheric processing are expected to have a relatively minor impact on  $\delta^{15}\text{N}(\text{NO}_2)$  under our sampling conditions. Therefore, the wide variability observed in  $\delta^{15}\text{N}(\text{NO}_2)$  is likely driven by changing contributions from  $\text{NO}_x$  source emissions to the measured background  $\text{NO}_2$ . Important local  $\text{NO}_x$  emission sources near our sampling site include: biogenic  $\text{NO}_x$ , fuel combustion, and traffic with  $\delta^{15}\text{N}(\text{‰})$  ranges of  $-59.8$  to  $-19.9$ ,  $-19.7$  to  $-13.7$ , and  $-9$  to  $-2$ , respectively (Felix and Elliott, 2014; Li and Wang, 2008; Miller et al., 2017; Walters et al., 2015b; Yu and Elliott, 2017). Our measured  $\delta^{15}\text{N}(\text{NO}_2)$  and predicted  $\delta^{15}\text{N}(\text{NO}_x)$  (Tables 1 and 3) are generally within the range of these emission sources; therefore, the variability observed in  $\delta^{15}\text{N}(\text{NO}_2)$  is likely driven by changing relative contributions from these emission sources rather than chemical processing.

To gain a better understanding of the influence of changing contributions from  $\text{NO}_x$  sources at our site and their diurnal variability, we have modeled the  $\text{NO}_x$  source contribution of our calculated  $\delta^{15}\text{N}(\text{NO}_x)$  using the EPA IsoSource Model that calculates all possible unique source proportions at a source increment of 1% based of isotopic mass balance (Phillips and Gregg, 2003). We use a value of  $-2\text{‰}$  for traffic-derived  $\text{NO}_x$ , which is based on on-road mobile measurements near urban areas (Miller et al., 2017). Local fossil-fuel combustion was assumed to have a value of  $-17.9\text{‰}$ , which is the average value ( $1\sigma = \pm 1\text{‰}$ ) previously measured from one of the natural gas boilers (Walters et al., 2015b) and is the main contributor to  $\text{NO}_x$  emission at the utility plant. Biogenic emitted  $\text{NO}_x$  has a large variability in  $\delta^{15}\text{N}(\text{NO}_x)$  ranging from  $-59.8$  to  $-19.9\text{‰}$  (Felix and Elliott, 2014; Li and Wang, 2008; Yu and Elliott, 2017). For the purpose of evaluating approximate relative source contribution determination we use a soil value of  $-53.6\text{‰}$ , which was the average value found for 12 h of post-wetting soils in a previous laboratory study (Yu and Elliott, 2017). We note that the large variability in biogenic  $\delta^{15}\text{N}(\text{NO}_x)$  makes it difficult to exactly quantitatively determine  $\text{NO}_x$  source contributions, but using a set  $\delta^{15}\text{N}(\text{NO}_x)$  value will help us determine approximate relative changes in  $\text{NO}_x$  source emissions at our sampling site. We have restricted our mass-balance model to these three sources since they likely play the most influential role on the local  $\text{NO}_x$  emission budget and enable an approximate evaluation of relative source contributions from these sources.

Fig. 6 displays a statistical distribution of all possible combination of solutions utilizing local  $\text{NO}_x$  sources with specified  $\delta^{15}\text{N}$  that match the estimated  $\delta^{15}\text{N}(\text{NO}_x)$  based off mass-balance separated for both

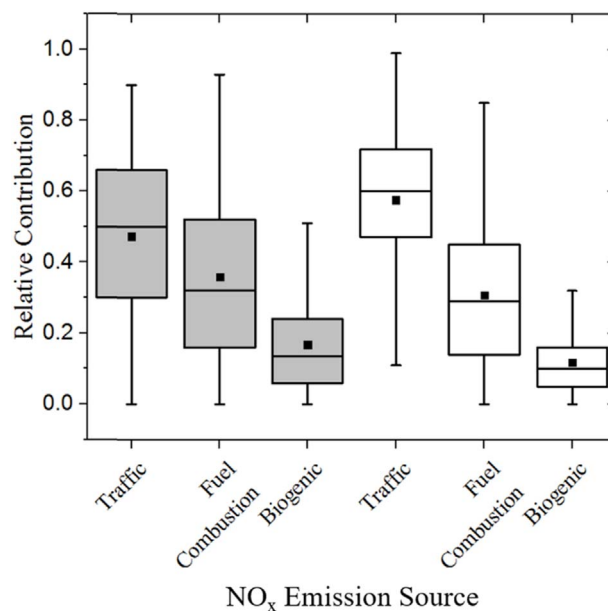


Fig. 6. Statistical distribution indicating the minimum, 25th percentile, 50th percentile, 75th percentile, maximum, and average (black square) of all feasible solutions that satisfy mass-balance between the assumed major local  $\text{NO}_x$  emission sources and estimated  $\delta^{15}\text{N}(\text{NO}_x)$  based on our  $\delta^{15}\text{N}(\text{NO}_2)$  measurements and accounting for possible isotope effects. The gray shading corresponds to nighttime while no shading corresponds to the daytime.

daytime and nighttime collection periods. This mass-balance analysis was conducted for each sampling period except for one daytime sample (7/25/2016; Table 3), in which the estimated  $\delta^{15}\text{N}(\text{NO}_x)$  value of  $0.2\text{‰}$  was higher than any of the  $\text{NO}_x$  emission sources and no feasible solution could be generated. However, we note that this value is nearly within analytical measurement precision of the traffic  $\delta^{15}\text{N}(\text{NO}_x)$  signature. Samples collected during the night had an average solution distribution for traffic, natural gas-fired power plant, and biogenic emissions of  $0.47 \pm 0.22$ ,  $0.36 \pm 0.24$ , and  $0.17 \pm 0.14$ , while samples collected during the daytime had an average solution distribution for traffic, natural gas-fired power plants, and biogenic emissions of  $0.58 \pm 0.19$ ,  $0.30 \pm 0.20$ , and  $0.11 \pm 0.09$ . This simple mass-balance model indicates that there may be interesting temporal variability in  $\text{NO}_x$  emission sources, as the distribution of possible feasible solutions suggest that traffic  $\text{NO}_x$  contributes more to the overall daytime  $\text{NO}_x$  emission budget, which is expected due to higher daytime traffic. Combining both day and night samples yield an average solution distribution for traffic, natural gas-fired power plant, and biogenic emissions of  $0.52 \pm 0.22$ ,  $0.34 \pm 0.22$ , and  $0.15 \pm 0.13$ . These estimates compare reasonably well with the estimation of these sources based on the 2011 U.S. EPA national emission inventory (NEI) for the sampling location county (Tippecanoe) of Traffic = 0.594, Fuel Combustion = 0.353, Biogenic = 0.042 [Office of Air Quality Planning and Standards (2011)]. Our slightly higher predicted biogenic contribution compared to the NEI is likely explained due to the NEI data representing yearlong  $\text{NO}_x$  emission estimates, while our estimated source contribution is based on  $\text{NO}_x$  emitted during the summer, in which biogenic emissions likely play a more influential role to the local  $\text{NO}_x$  emission budget. However, we note that our mixing system is extremely simplified, and there may be other contributing  $\text{NO}_x$  emission sources at our sampling site that are not taken into account in our model.

It is important to point out that this mass-balance model is an approximation with the goal to understand the drivers of  $\delta^{15}\text{N}(\text{NO}_2)$  variability in ambient/background air and not to exactly pinpoint the  $\text{NO}_x$  source proportions at our sampling location. However, this model does highlight the potential to use  $\delta^{15}\text{N}(\text{NO}_x)$  to evaluate  $\text{NO}_x$  source contributions in a well-mixed area to evaluate spatial and temporal



changes. To quantitatively use this tool, we need to have a better characterization of environmental  $\delta^{15}\text{N}(\text{NO}_x)$  source values and will also need to collect  $\delta^{15}\text{N}(\text{NO}_x)$  from ambient air as opposed to  $\delta^{15}\text{N}(\text{NO}_2)$  as conducted in this study. This is because we are still somewhat uncertain as to how  $\text{NO}_x$  processing may impact  $\delta^{15}\text{N}(\text{NO}_2)$  relative to  $\delta^{15}\text{N}(\text{NO}_x)$ , although our calculations indicate it to be relatively small at our sampling site. Now that we have a model that may be useful to predict the  $\delta^{15}\text{N}$  partitioning between  $\text{NO}$  and  $\text{NO}_2$ , we need to validate it using simultaneous  $\text{NO}$  and  $\text{NO}_2$  collection for  $\delta^{15}\text{N}$  analysis, which will be the subject for future research.

### 4.3. $\delta^{18}\text{O}(\text{NO}_2)$

#### 4.3.1. Daytime $\delta^{18}\text{O}(\text{NO}_2)$

Daytime  $\text{NO}_2$  was highly enriched in  $^{18}\text{O}$ , with an average  $\delta^{18}\text{O}(\text{NO}_2)$  value of  $86.5 \pm 14.1\text{‰}$  ( $n = 11$ ) (Fig. 5). During the daytime,  $\delta^{18}\text{O}(\text{NO}_2)$  values are expected to reflect the oxidants responsible for the conversion of  $\text{NO}$  to  $\text{NO}_2$ , as the photochemical cycling of  $\text{NO}_x$  is rapid and should quickly erase any  $\delta^{18}\text{O}(\text{NO}_x)$  source signatures. For an urban area,  $\text{O}_3$  should dominate the conversion of  $\text{NO}$  to  $\text{NO}_2$  (R1). Thus,  $\delta^{18}\text{O}(\text{NO}_2)$  values should reflect  $\text{NO}_x$  photochemical equilibrium with  $\text{O}_3$  that has a high  $\delta^{18}\text{O}$  value (Alexander et al., 2009; Michalski et al., 2003; Vicars and Savarino, 2014). Previously, tropospheric  $\text{O}_3$  has been reported to have elevated  $\delta^{18}\text{O}(\text{O}_3)$  values ranging from 95 to 130‰ (Johnston and Thiemens, 1997; Krankowsky et al., 1995; Vicars and Savarino, 2014), and a prior experimental investigation found that the photochemical cycling of  $\text{NO-O}_2\text{-O}_3\text{-NO}_2$  to result in  $\delta^{18}\text{O}(\text{NO}_2)$  of 117‰ (Michalski et al., 2014). This experimental value is near our highest measured daytime  $\delta^{18}\text{O}(\text{NO}_2)$  value of 112.7‰ (Fig. 7). However, there was large variability observed in daytime  $\delta^{18}\text{O}(\text{NO}_2)$  that spanned 41.2‰ across the collection periods with values as low as 71.5‰, which may not be explained by  $\text{NO}_x$  isotopic photochemical equilibrium with tropospheric  $\text{O}_3$ .

$\text{NO}$  may also be oxidized by peroxy radicals and this may be reflected in the  $\delta^{18}\text{O}(\text{NO}_2)$ . Peroxy radicals are estimated to have an oxygen isotopic composition that reflects tropospheric  $\text{O}_2$  (Michalski et al., 2012) that is approximately 23‰ (Kroopnick and Craig, 1972). Assuming no isotope effect during the  $\text{NO} + \text{RO}_2$  (or  $\text{HO}_2$ ) reaction, the  $\text{O}$  transferred from  $\text{RO}_2$  (or  $\text{HO}_2$ ) to  $\text{NO}_2$  can be approximated to be the  $\delta^{18}\text{O}(\text{RO}_2\text{(or HO}_2)) \approx 23\text{‰}$ . Thus, the lower daytime  $\delta^{18}\text{O}(\text{NO}_2)$  values may be the result of  $\text{NO}$  oxidation by peroxy radicals. An isotope mass-balance model can be used to estimate the  $\text{NO}$  oxidation branching ratio ( $x$ ):

$$\delta^{18}\text{O}(\text{NO}_2) = x \times (\delta^{18}\text{O}(\text{O}_3)) + (1 - x) \times (\delta^{18}\text{O}(\text{ROO}\cdot\text{orHOO}\cdot)) \quad (4)$$

Where  $\delta^{18}\text{O}(\text{NO}_2)$  is the observed  $\text{NO}_2$   $\delta^{18}\text{O}$  values that is produced by fractions of oxygen derived from  $\text{O}_3$  (117‰) and peroxy radicals (23‰). Using these oxidant end-member  $\delta^{18}\text{O}$  values, we estimate the daytime branching ratio of  $\text{NO}$  oxidation by  $\text{O}_3$  to be  $0.68 \pm 0.15$ , signifying that  $\text{O}_3$  was generally the dominate daytime oxidant at our sampling location as expected. However,  $\text{NO}$  oxidation through peroxy radicals seems to have played a significant role and reached a branching ratio as high as 0.48 during our sampling periods (Fig. 7). This is important since  $\text{NO}$  oxidation through peroxy radicals occurs without the loss of  $\text{O}_3$  providing a pathway for the buildup of tropospheric  $\text{O}_3$ . Thus, the isotopic composition of daytime  $\text{NO}_2$  may provide a useful way to assess  $\text{VOC-NO}_x\text{-O}_3$  chemistry, which is a fundamental underpinning of atmospheric chemistry modeling.

To assess whether the estimated  $\text{NO}$  branching ratio based on  $\delta^{18}\text{O}\text{-NO}_2$  is reasonable, we have compared our results to a simulation from the RACM model (Stockwell et al., 1997) that included photolysis parameters at our sampling site in July (Madronich, 1987). We chose to run the RACM model with initial conditions corresponding to rural summer surface case 8 and 9 as described in (Stockwell et al., 1997). Briefly,  $[\text{NO}_x]$  is set to 5 ppb<sub>v</sub>, which is relatively close to the observed daytime  $[\text{NO}_x]$  (Fig. 4), and the concentration of nonmethane organic carbon (NMOC) is set to 33 ppb<sub>v</sub> and 100 ppb<sub>v</sub> for case 8 and case 9, respectively. While these conditions are not the exact conditions of our sampling site, it should provide an approximate expectation of the  $\text{NO}$  oxidation branching ratio for comparison to the branching ratio derived from our  $\delta^{18}\text{O}$  results. A two-day simulation was run and the branching ratio of  $\text{NO}$  oxidation by  $\text{O}_3$  was calculated to be of  $0.8516 \pm 0.019$  ( $\bar{X} \pm \sigma$ ) and  $0.7599 \pm 0.020$ , under the initial condition of low and high concentrations of organic compound, respectively. These branching ratios compare well with our estimated value of  $0.68 \pm 0.15$  based on daytime  $\delta^{18}\text{O}(\text{NO}_2)$  measurements. The modeling results support our hypothesis that the oxidants responsible for the oxidation of  $\text{NO}$  can be roughly approximated using  $\delta^{18}\text{O}(\text{NO}_2)$ , which has important implications for evaluating the impact of  $\text{NO}_x$  emissions on oxidation chemistry.

#### 4.3.2. Nighttime $\delta^{18}\text{O}(\text{NO}_2)$

Nighttime  $\text{NO}_2$  was found to have low  $\delta^{18}\text{O}$  values relative to the daytime, averaging  $56.3 \pm 7.1\text{‰}$ . This is likely the result of the absence of  $\text{NO}_x$  photochemical cycling during the night, limiting isotopic equilibrium between  $\text{NO}_x$  and its oxidants. We hypothesize that  $\text{NO}_2$  produced during the night should reflect the mass-balance between  $\delta^{18}\text{O}$  of the emitted nighttime  $\text{NO}$  and the  $\delta^{18}\text{O}$  of the  $\text{O}$  atom transferred from the responsible oxidant ( $\delta^{18}\text{O}(\text{O}_{\text{trans}})$ ):

$$\delta^{18}\text{O}(\text{NO}_{2\text{night}}) = \frac{1}{2}(\delta^{18}\text{O}(\text{NO}_{\text{source}})) + \frac{1}{2}(\delta^{18}\text{O}(\text{O}_{\text{trans}})) \quad (5)$$

Thus, a portion of the oxygen in nighttime  $\text{NO}_2$  should be from the  $\text{NO}$  source that likely has a relatively lower  $\delta^{18}\text{O}$  than does the main  $\text{NO}$  oxidant,  $\text{O}_3$ , resulting in a lower nighttime  $\delta^{18}\text{O}(\text{NO}_2)$  during the night relative to the day. It is important to note that  $\text{NO}_2$  collected during the nighttime will not entirely reflect the mass-balance between  $\delta^{18}\text{O}(\text{NO})$  and  $\delta^{18}\text{O}(\text{O}_{\text{trans}})$  (Eq. (5)). This is because there is residual daytime  $\text{NO}_2$ , which reached photochemical equilibrium with atmospheric oxidants, that is also collected during the nighttime. The daytime lifetime of  $\text{NO}_2$  can be estimated to be approximately 6.8 h assuming that  $\text{OH}$  is the main sink ( $k(\text{NO}_2 + \cdot\text{OH})_{298\text{K}} = 4.1 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  (Atkinson et al., 2004);  $[\text{OH}] = 1 \times 10^{-6} \text{ molecules cm}^{-3}$ ). Thus, there will still be photochemically cycled  $\text{NO}_2$  present during our nighttime collection. Due to this interference, it is difficult to estimate the  $\delta^{18}\text{O}(\text{NO}_{\text{source}})$  values using back-calculation of Eq. (5). However, our results indicate that  $\delta^{18}\text{O}(\text{NO}_{\text{source}})$  should have a relatively lower  $\delta^{18}\text{O}$  value compared to the  $\text{NO}$  oxidants. Additionally, future work should aim to quantify  $\delta^{18}\text{O}(\text{NO}_x)$  of emission sources since this likely plays a role in

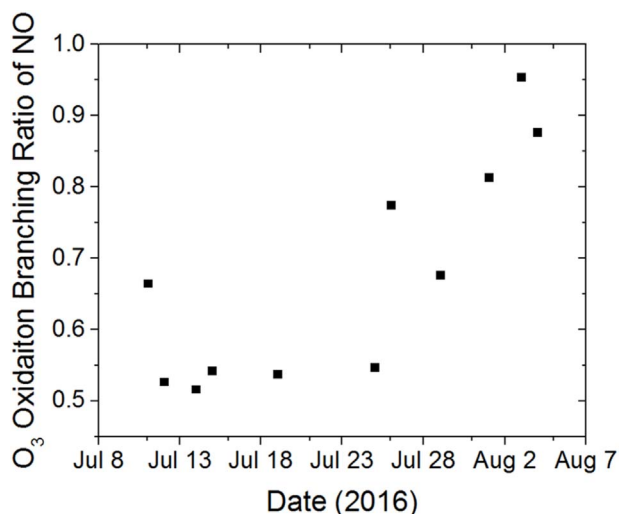


Fig. 7. Estimated  $\text{NO}$  oxidation branching ratio between  $\text{O}_3$  (red) and  $\text{ROO}\cdot$  (black) calculated from Eq. (4).

observed  $\delta^{18}\text{O}(\text{NO}_2)$  values during the nighttime.

## 5. Conclusion

Diurnal variability in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of ambient  $\text{NO}_2$  was assessed at a small Midwestern city. Overall, we predict that variability in  $\delta^{15}\text{N}$  ( $\text{NO}_2$ ) is largely driven by changing contributions from local  $\text{NO}_x$  source emissions as predicted isotope effects under the sampling conditions are expected to be small  $< 2.5\%$ . A statistical mass-balance model indicates that there may be interesting temporal variabilities in  $\text{NO}_x$  emission sources with higher traffic contribution during the daytime. Results also indicate that biogenic emissions during the summer might be a significant contributor to local  $\text{NO}_x$  emission budgets estimated to represent  $15 \pm 13\%$  at the sampling site. The relatively minor partitioning between  $\text{NO}$  and  $\text{NO}_2$  predicted at our sampling site indicates that during the summer under conditions of  $[\text{NO}_x] \ll [\text{O}_3]$ ,  $\delta^{15}\text{N}$  should be approximately conserved as  $\text{NO}_x$  is transformed into atmospheric nitrate, but future chamber studies are necessary to evaluate isotope effects associated with post  $\text{NO}_2$  oxidation. Variability in  $\delta^{18}\text{O}(\text{NO}_2)$  is driven by the photochemical cycling of  $\text{NO}_x$ , in which  $\text{NO}$  reactions with  $\text{O}_3$  produce an elevated  $\delta^{18}\text{O}$  value. During the nighttime,  $\delta^{18}\text{O}$  ( $\text{NO}_2$ ) values are lower due to  $\delta^{18}\text{O}$  contributions from  $\text{NO}_x$  emission sources with hypothesized lower  $\delta^{18}\text{O}$  values than atmospheric oxidants and due to the absence of  $\text{NO}_x$  photochemical cycling.

Future work should aim toward fine-tuning our method to develop collection techniques that can be used to characterize  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$  of  $\text{NO}_2$  under optimized conditions and at higher time resolution. This could be achieved using a more sophisticated denuder setup utilizing annular or honeycomb denuder geometries. Future speciated  $\text{NO}_x$   $\delta^{15}\text{N}$  measurements are needed to fully understand the atmospheric processes that dictate the  $\delta^{15}\text{N}$  partitioning between  $\text{NO}$  and  $\text{NO}_2$  under environmental conditions, and this will be the subject for future research. Additionally, the results suggest the potential to use  $\delta^{15}\text{N}(\text{NO}_x)$  to evaluate  $\text{NO}_x$  source contributions under ambient conditions, but in order to quantitatively use this tool, future work must better characterize environmental  $\delta^{15}\text{N}(\text{NO}_x)$  source signatures, as well to better quantify the isotope effects during  $\text{NO}_x$  photochemical cycling after its emission.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2018.01.047>.

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