Technical considerations for the use of passive samplers to quantify the isotopic composition of NO_x and NO₂ using the denitrifier method

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HIGHLIGHTS:

- Passive sampling is not isotopically representative of emission sources directly.
- Nitrogen isotopes reflect mix of local and distant NO_x sources and possibly chemistry.
- Oxygen isotopes of NO_x captured as nitrite must be corrected for fractionation that occurs during denitrifier method.
- Lower than expected $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ for NO_x and NO₂ are a result of passive collection effects.

ABSTRACT

The isotopic composition of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) hold potential to trace emissions sources, as well as chemistry in the atmosphere. Passive samplers that collect NO_x and NO_2 as nitrite could provide a simple and inexpensive means by which to collect samples in a variety of environments, and we report here on several methodological considerations when using Ogawa passive collectors of NO_x and NO_2 for concentration analysis via colorimetric methods and isotopic analysis via the denitrifier method. Using Ogawa samplers, NO_x and NO_2 were collected in Providence, RI, USA (41.8°N, 71.4°W) with exposure times of seven, fourteen, twenty-one, and twenty-eight days during summer and winter in an area dominated by vehicle emissions, particularly diesel delivery trucks. Average values were -9.7 ± 0.7 ‰ for $\delta^{15}\text{N}$ - NO_x and -8.3 ± 0.9 ‰ for $\delta^{15}\text{N}$ - NO_2 based on duplicate seven, fourteen, twenty-one, and twenty-eight day exposures ($n=8$) in summertime, and -11.9 ± 0.7 ‰ for $\delta^{15}\text{N}$ - NO_x and -6.4 ± 1.4 ‰ for $\delta^{15}\text{N}$ - NO_2 based on seven, fourteen, twenty-one, and twenty-eight day exposures ($n=7$) in wintertime. The oxygen isotopic composition ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) was also determined with averages of: 36.3 ± 2.4 ‰ for $\delta^{18}\text{O}$ - NO_x ($n=8$), 50.5 ± 3.2 ‰ for $\delta^{18}\text{O}$ - NO_2 ($n=8$), 6.2 ± 0.8 ‰ for $\Delta^{17}\text{O}$ - NO_x and 10.8 ± 0.6 ‰ for $\Delta^{17}\text{O}$ - NO_2 ($n=4$) in summer; and 38.7 ± 2.9 ‰ for $\delta^{18}\text{O}$ - NO_x and 47.4 ± 1.2 ‰ for $\delta^{18}\text{O}$ - NO_2 ($n=7$), 7.7 ± 1.5 ‰ for $\Delta^{17}\text{O}$ - NO_2 ($n=4$) and 5.3 ± 1.2 ‰ for $\Delta^{17}\text{O}$ - NO_x ($n=5$), in winter. Our isotopic results differ from previous studies that utilized passive samplers and suggest specific nitrogen and oxygen isotopic signatures associated with vehicular emissions. To collect sufficient sample for multiple isotopic analyses (e.g., 10 nmol N for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$; 50 nmol N for $\Delta^{17}\text{O}$) the exposure time for the samplers, even in urban areas, is at least days. This necessarily results in collection of a mixture of local emissions sources, as well as background air that can represent multiple NO_x sources. Thus, passive samplers cannot be used to diagnose isotopic signatures unless only exposed to a single emissions source. The oxygen isotopic composition of nitrite (the collection analyte) results determined via the denitrifier method must be corrected in comparison to nitrate isotopic reference materials, resulting in an increase of ~ 25 ‰. Even with this correction, the oxygen isotopic results are lower than what would be expected for ozone-dominated atmospheric chemistry in an urban area, and the oxygen isotopic results for NO_x were consistently lower than that found for NO_2 . We suggest that the oxygen isotopic composition of NO and NO_2 were modified upon capture and conversion to nitrite on the passive sampler pads, and does not directly reflect abundances in the atmosphere.

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60 **1. INTRODUCTION**

61 Nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) play a key role in global atmospheric chemistry
 62 (e.g., Levy et al., 1999). In the troposphere, NO_x contributes to the formation of ozone,
 63 and ultimately forms nitric acid that is lost from the atmosphere via wet and dry
 64 deposition. During the day, the primary oxidation reactions include:

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70 During the night, R2 is limited and products such as NO_3 and N_2O_5 , which are
 71 photosensitive, play an important role in NO_x loss from the atmosphere:

75 Sources of NO_x emissions into the atmosphere can be of both natural and
 76 anthropogenic origin, including biogenic soil emissions, biomass burning, lightning, and
 77 fossil fuel and biofuel combustion (e.g., Hastings et al., 2013). There has been keen
 78 interest in the potential of the stable isotopic composition of NO_x to allow for tracing the
 79 emission sources, chemical influences, and environmental impacts of NO_x (e.g., see
 80 Kendall et al., 2007 for a review).

81 Passive samplers, which rely upon molecular diffusion of the atmospheric gases
 82 along a diffusive path onto the adsorbent of the analytical device, have been used to
 83 measure atmospheric NO_x concentrations (see Yu et al., 2008 for a review). These
 84 have great potential to allow for a wide range of atmospheric sampling and isotopic
 85 measurements, especially given their portability and low cost. Felix and Elliott (2014)
 86 used Ogawa passive samplers to collect NO_2 and quantified the isotopic composition (δ
 87 ^{15}N - NO_2) inside and outside a vehicular tunnel in Pittsburgh, PA. They found $\delta^{15}\text{N}$ - NO_2
 88 in a range of +14.4 to +17.0 ‰ and +10.2 to +16.9 ‰ inside and outside the tunnel,
 89 respectively. These ranges are very different than found based on actively collected
 90 NO_x related to vehicles. Actively collected NO_x emissions directly from vehicle tailpipes

¹ δ is defined as the relative isotopic enrichment of a sample with respect to a reference material. Its unit is per mil (‰) and is calculated by using formula, $[\delta = ((R_{\text{sample}}/R_{\text{reference}}) - 1) \times 1000 \text{ ‰}]$, where $R = ^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$, $^{17}\text{O}/^{16}\text{O}$ for $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$, respectively. δ values for Nitrogen are referenced to atmospheric nitrogen (N_2) and oxygen isotopic values are referenced to Vienna Standard Mean Ocean Water (VSMOW).

in South Africa had $\delta^{15}\text{N}$ in a range of -13 to -2 ‰ (Heaton, 1990), and a recent similar study in the U.S. found a range of $\delta^{15}\text{N}$ from -19.1 to 9.8 ‰ (Walters et al., 2015a). Other actively collected NO_x emissions influenced heavily by vehicle emissions include next to a highway in Norway (mean of $\delta^{15}\text{N}\text{-NO}_2 = +5.7 \pm 2.8$ ‰ and $\delta^{15}\text{N}\text{-NO} = +3.1 \pm 5.4$ ‰; Ammann et al., 1998); and in an urban U.S. city next to a highway with a $\delta^{15}\text{N}$ range of -0.6 to -7.7 ‰ (Fibiger et al., 2014). In these studies, some have captured NO_2 alone, while some have collected NO_x (i.e. $\text{NO} + \text{NO}_2$). These different $\delta^{15}\text{N}$ values warrant the necessity of more studies to understand the discrete isotopic composition of NO_x and NO_2 associated with urban air or vehicular emissions so that the rationale behind discrepancies among various techniques can be understood and constrained.

In this study, we report on the use of Ogawa NO_x and NO_2 pads to quantify the nitrogen and oxygen isotopic compositions of atmospheric NO_x and NO_2 in Providence, Rhode Island, USA. Using colorimetric analysis and the denitrifier method to quantify the concentration and isotopes, respectively, we report on important methodological considerations for the determination of the isotopes ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$) of NO_x and NO_2 using passive samplers.

2. METHODS

Ogawa passive samplers were deployed in Providence, RI, USA at Brown University (41.8°N, 71.4°W). The samplers were mounted on the side of a building, sheltered from precipitation and direct sunlight, at a height of approximately 3 m above the ground. The location was chosen for its proximity next to a loading dock that sees regular vehicular traffic, particularly diesel delivery trucks. The sampling location is also less than 1.5 km from regularly traveled interstate highways (I-95, I-195).

The Ogawa passive samplers consist of two chambers on each side and can concurrently capture NO , NO_2 , and NO_x concentrations. Each chamber consists of a diffusive end cap followed by a cellulose fiber filter pad coated with specific adsorbent(s) and placed between two stainless screens. For analyzing NO_x and NO_2 concentrations, NO_2 and NO_x collection filter pads are mounted, with one on each side of the sampler. The NO_2 filter pad is impregnated with triethanolamine (TEA) that, in the presence of water, will produce nitrite ions and TEA N-Oxide (Hamilton et al., 2004). In this reaction, triethanolamine acts as a reductant and water molecules are derived from ambient air:

This 100% conversion of NO_2 to nitrite (NO_2^-) can be achieved only if sufficient triethanolamine is coated onto the sampling pad and sufficient water vapor is present in the air (Hamilton and Heal, 2004; Glausius et al., 1999). For collection of NO_x , the NO_x pad contains triethanolamine and 2-phenyl-4, 4, 5, 5-tetramethylimidazoline-1-oxyl 3-oxide (PTIO). PTIO converts NO to NO_2 in a (1:1) stoichiometric manner (Akaike et al., 1996) and NO_2 is converted to NO_2^- by TEA as above (R8). Adsorbed analytes are extracted from the pads with water and can be analyzed for concentrations by analytical techniques such as FIA or IC or colorimetry.

2.1 Sample Collection

Sampling was conducted during summer and winter months. In July 2014, eight Ogawa passive samplers were deployed in parallel. Duplicate samples were taken over four different sampling periods: 1 week, 2 weeks, 3 weeks and 4 weeks. In other words, two samplers were removed from the sampling site every week. In a similar fashion, seven samplers were deployed in December 2014-January 2015 (only one sampler was deployed in week one). The passive samplers, NO_x pads, and NO_2 pads were handled based upon the method protocols provided by Ogawa, with minor modifications (Ogawa and Co., 2006). The filter pads were kept refrigerated until use, and two types of blanks were tested. Filter blanks were measured by placing pads directly into 8 mL of ultrapure ($18 \text{ M}\Omega$) water, to confirm absence of nitrate and nitrite. Field blanks were also tested by loading the pads into the samplers and then immediately removing them. After exposure, the sample NO_x and NO_2 filter pads were immersed into 8mL of ultrapure water in pre-cleaned amber HDPE plastic bottles, and stored at room temperature. Samples collected in summer were analyzed ~3 weeks after immersion in water; samples collected in winter were analyzed within 1 week. Meteorological conditions were monitored via a weather station located 1.1 km away (College Hill station, 25 m above ground, hourly data accessed via wunderground.com), and pressure, temperature and humidity values were obtained to convert concentration units of collected samples from μM to ppbv following the Ogawa protocol (Ogawa and Co., 2006).

2.2 Colorimetric determination of sample concentration

Samples were analyzed for nitrate (NO_3^-) and nitrite (NO_2^-) concentrations photometrically via typical colorimetric absorbance techniques using a Westco Scientific SmartChem 200 discrete chemistry analyzer (based on USEPA Method 354.1 for nitrite; USEPA Method 353.2 (Revision 2.0) and Standards Methods Method 4500 for nitrate). Nitrite is the primary analyte of interest. Nitrate concentrations were determined because the isotopic method will resolve both nitrate and nitrite (see below) and can therefore interfere with nitrite results. The detection limit was $0.05 \mu\text{M}$ for NO_2^- , calculated by adding the mean of water blank concentrations ($n=6$) to 3 times the standard deviation of the mean. Reproducibility of quality controls run multiple times with each sample run was $\pm 0.05 \mu\text{M}$ ($\pm 1 \text{ S.D.}$; $n=9$). The NO_2 filter blanks were consistently below detection limit for NO_2^- ; the NO_x filter blanks occasionally showed concentrations of $\sim 0.5 \mu\text{M}$.

The NO_x pads with PTIO are blue in color, which produces interference for colorimetric analysis of ion concentrations. To resolve this, 3 mL of organic solvent (diethyl ether) were added to extract PTIO/PTI from the aqueous phase. Immersing NO_x pads in 8mL of solutions containing known concentrations of nitrite and nitrate prepared in the lab, then adding the organic solvent tested the efficacy of this method. Consistent results were obtained for expected concentrations (between 5 – 20 μM) of solution with nitrite alone, nitrate alone, and nitrate and nitrite together. (Though we note that there

was a nitrate blank associated with the ether that had to be accounted for.) Consequently, aliquots (~2 mL) of each NO_x sample were treated with ether prior to colorimetric analysis. The rest of the sample volumes (~6 mL) were left untreated as the PTIO color did not interfere with the isotopic analysis described below. We also note that for the longest sampling exposures (twenty-eight days) the blue color on the pads was diminished significantly (i.e. the blue color faded with longer exposure times).

Following the protocol by Ogawa, ambient gas phase NO₂ concentrations in ppbv are calculated as $C = (Q_{NO_2} \cdot \alpha_{NO_2}) / t$ where C = concentration in ppbv, Q_{NO₂} = NO₂ mass in ng, α_{NO₂} = sampling rate, and t = sampling time in mins. The NO₂ mass is determined assuming 1:1 with the NO₂⁻ concentration. Sampling rate (α) values are dependent on ambient pressure, temperature and humidity, and are determined based upon lookup tables provided by Ogawa. Similarly, the ambient NO concentration is calculated as $C = ((Q_{NO_x} - Q_{NO_2}) \cdot \alpha_{NO}) / t$ where Q_{NO_x} is the mass of NO_x in ng. Finally, the NO_x concentration (in ppbv) is calculated as the sum of the concentration of NO and NO₂.

For verification purposes, the passively collected NO_x and NO₂ concentrations were compared with the relevant exposure-period average of hourly measurements from nearby chemiluminescent monitors (ThermoScientific 42i-TL) mounted on top of Rockefeller Library on the campus of Brown University by Rhode Island Department of Environmental Management (RI-DEM, 2014).

2.3 Isotopic Analysis

Nitrite concentration from the Westco Analyzer was used to calculate injection volumes for isotopic analysis of 10 nanomoles of nitrite. Isotopes were analyzed using the bacterial denitrifier method (Sigman et al., 2001), which utilizes denitrifying bacteria (*Pseudomonas aureofaciens*) that lack the N₂O reductase enzyme to convert NO₃⁻(aq) and NO₂⁻(aq) to N₂O(g):

N₂O(g) was then sparged via helium carrier gas, passed through water and carbon dioxide traps, cryogenically concentrated, and analyzed via a Thermo Finnegan Delta V Plus Isotope Ratio Mass Spectrometer (IRMS) at *m/z* 44, 45 and 46 in continuous flow mode. Isotope ratios are reported using delta (δ) notation: $[\delta = (\frac{R_{sample}}{R_{reference}} - 1) \times 1000 \text{‰}]$, where R = ¹⁵N/¹⁴N or ¹⁸O/¹⁶O for δ¹⁵N and δ¹⁸O, and references are atmospheric nitrogen (N₂) and Vienna Standard Mean Ocean Water (VSMOW), respectively. The Δ¹⁷O is also reported for samples with sufficient concentration (50 nanomoles nitrite injections), where Δ¹⁷O = δ¹⁷O - 0.52 × δ¹⁸O. The Δ¹⁷O is determined by decomposing the analyte N₂O described above into N₂ and O₂ in a furnace heated to 770°C (Kaiser et al., 2007), which is then passed into the IRMS and resolved at *m/z* 32, 33, 34 to compute Δ¹⁷O from δ¹⁷O and δ¹⁸O of the O₂. Nitrate reference materials (Böhlke et al., 2003) IAEA-N3 (δ¹⁵N=4.7‰, δ¹⁸O =25.6‰), USGS34 (δ¹⁵N =-1.8‰, δ¹⁸O =-27.9‰, Δ¹⁷O =-0.292‰) and USGS35 (δ¹⁸O=57.5‰, Δ¹⁷O=21.6‰), are run with each sample

run and samples are corrected based upon the scheme outlined in Kaiser et al. (2007) and discussed in brief below. The precision of the isotopic method is excellent and captured as pooled standard deviations for each of the reference materials: 0.1‰ and 0.1‰ for $\delta^{15}\text{N}$ of IAEA-N3 and USGS34, respectively; 0.3‰, 0.5‰, and 0.4‰ for $\delta^{18}\text{O}$ of IAEA-N3, USGS34, and USGS35, respectively; and 0.1‰ and 0.4‰ for $\Delta^{17}\text{O}$ of USGS34 and USGS35, respectively.

As discussed in detail in Kaiser et al. (2007), the nitrogen and oxygen isotopic data are corrected for isobaric and blank interferences. For the isobaric corrections we include the $\Delta^{17}\text{O}$ (means for summer and winter samples) that are resolved independent of the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. The $\delta^{18}\text{O}$ is also corrected for isotopic fractionation and exchange related to the bacterial processing of the sample. The conversion of NO_3^- and NO_2^- to N_2O is quantitative; however oxygen isotopic fractionation occurs in the removal of oxygen atoms in the reduction to N_2O via the pathway described in R9 (Casciotti et al., 2002). Because the nitrite reduction represents a smaller fractional loss of oxygen atoms, the isotope effect for this step is lower than that for nitrate to N_2O (Casciotti et al., 2007). Casciotti et al. (2007) demonstrate that a calibration curve based on nitrate isotopic reference materials will return values for $\delta^{18}\text{O}$ of nitrite that are 25-30‰ lower than the true values. For this study, the nitrite isotopes for all samples are corrected for this difference in isotopic fractionation compared to the nitrate reference materials. The implication of this correction to the data is discussed below.

3. RESULTS AND DISCUSSION

Table 1 summarizes the meteorological conditions, NO_2^- concentrations (in μM), and NO_x and NO_2 concentrations (in ppbv) measured via the passive NO_x and NO_2 sensors for each sampling period. During summer the mixing ratios are approximately 11 ppbv for NO_x and 7 ppbv for NO_2 , compared to values around 16 ppbv and 11 ppbv during the winter collections. Overall, the passively collected NO_x and NO_2 concentrations in ppbv compare well with mean concentrations determined from high temporal resolution, nearby monitoring by the Rhode Island Department of Environmental Management (RI-DEM). The root mean square error comparing the means is 1 ppbv and 0.6 ppbv for NO_x and NO_2 in summer, and 0.2 ppbv and 0.9 ppbv for NO_x and NO_2 in winter. The higher concentrations found on the pads likely reflects the location of the passive collectors proximal to vehicular emissions of NO and NO_2 , compared to more well mixed air at the rooftop location of the RI-DEM chemiluminescent monitors.

Table 1: Summer (July - August '14) and Winter (December '14 - January '15) mean meteorological conditions (± 1 S.D. based on hourly data), observed NO_x and NO_2 concentrations from Ogawa samplers (± 1 S.D. based on duplicate sampling), and mean concentrations from DEM monitors based on hourly data.

Dates of Exposure	Temp. (°C)	Relative Humidity (%)	[NO ₂] (μM)		[NO ₂ or NO _x] (ppbv)		DEM Observations (ppbv)	
			NO _x pads	NO ₂ pads	NO _x pads	NO ₂ pads	NO _x	NO ₂
Jul 11-Jul 18	21.4±2.6	67.8±16.9	5.4 ± 0.2	2.3 ± 0.8	10.2 ± 0.5	4.2 ± 1.5	9.2	6.7
Jul 11-Jul 25	21.1±3.1	72.6±15.6	11.2 ± 0.1	7.6 ± 0.1	11.0 ± 0.2	7.3 ± 0.1	10.8	7.0
Jul 11-Aug 1	21.8±3.1	70.9±15.9	14.9 ± 1.2	11.1 ± 0.2	10.0 ± 0.8	7.3 ± 0.1	9.4	6.7
Jul 11-Aug 8	20.3±3.3	71.4±16.8	21.0 ± 1.9	14.3 ± 0.7	10.7 ± 1.0	7.1 ± 0.4	10.5	6.7
Dec 9-Dec 16	3.3±3.2	82.9±12.5	11.5*	5.7*	27.6*	12.0*	21.7	12.2
Dec 9-Dec 24	3.8±3.6	83.5±12.9	16.1 ± 1.5	11.7± 0.03	17.4 ± 0.8	12.3± 0.03	18.8	12.9
Dec 9-Dec 30	4.1±4.0	78.8±16.4	20.6 ± 3.1	15.1± 0.08	15.0 ± 1.8	10.9± 0.05	17.7	11.0
Dec 9-Jan 5	3.3±4.6	76.2±18.9	27.1 ± 5.7	19.2 ± 0.5	15.6 ± 3.9	10.8 ± 0.3	17.2	11.7

*Only one sampler deployed

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3.1 $\delta^{15}\text{N}$ of NO_x and NO_2

Mean $\delta^{15}\text{N}$ - NO_x for duplicate samples collected in summer for seven days, fourteen days, twenty-one days, and twenty-eight days ranged from -8.9 ‰ to -10.6 ‰, with an overall mean and 1 S.D. of -9.7 ± 0.7 ‰ (Figure 1). For winter, $\delta^{15}\text{N}$ - NO_x ranged from -11.6 ‰ to -12.1 ‰, with an overall mean and 1 S.D. of -11.9 ± 0.7 ‰ (Figure 1). We expect vehicle emissions, and in particular diesel delivery trucks, to be a dominant source of NO_x in these collections. These values are within the range of recently reported values based upon active tailpipe collections of NO_x from a range of transportation combustion sources in the U.S. (Walters et al., 2015a, 2015b; also see Introduction above). Using a different, active collection technique, Fibiger et al. (2014) reported a range -16.7 to -19.2 ‰ for NO_x produced from a diesel generator and collected via a laboratory smog chamber. In addition, Fibiger et al. (2014) reported a range of -0.6 to -7.7 ‰ for $\delta^{15}\text{N}$ - NO_x in urban air near downtown Providence, RI (rooftop location 1.9 km from the location of this study). Finally, Snape et al. (2003) reported a range for thermally produced NO_x in a controlled setting of -6.5 to -8.5 ‰. Overall, based on a variety of collection techniques, we would expect urban air heavily influenced by vehicles to carry fairly negative $\delta^{15}\text{N}$ - NO_x and $\delta^{15}\text{N}$ - NO_2 . Our observations likely reflect a significant influence of thermally produced NO_x from vehicles, with diesel vehicles contributing importantly to the overall low $\delta^{15}\text{N}$ found.

Mean $\delta^{15}\text{N}$ - NO_2 for duplicate NO_2 samplers deployed outside during summer ranged from -7.6 ‰ to -9.0 ‰, with an overall mean of -8.3 ± 0.9 ‰ (n=8). For winter, $\delta^{15}\text{N}$ - NO_2 ranged from -3.6 ‰ to -7.5 ‰, with an overall mean of -6.4 ± 1.4 ‰ (n=7).

Figure 1: $\delta^{15}\text{N}$ of NO_x (open square with X) and NO_2 (open circle) from Ogawa samplers deployed in summer (a) and (b) winter sampling periods. Error bars reflect ± 1 S.D. based upon duplicate samplers.

These values are very different than that reported by Felix and Elliott (2014) using Ogawa passive NO₂ pads to quantify $\delta^{15}\text{N}$ -NO₂ associated with vehicle emissions in Pittsburgh, PA. Mean values of $\delta^{15}\text{N}$ -NO₂ for pads exposed for ~1 month inside and outside of a traffic tunnel were $+14.4 \pm 1.9$ ‰ and $+15.7 \pm 0.8$ ‰, respectively (Felix and Elliott, 2014). In a passive roadside study in PA, Redling et al. (2013) found $\delta^{15}\text{N}$ -NO₂ values in a range of -5.1 to +7.3 ‰ at a location 2 m away from the road, and in a range of -11.9 to -24.6 ‰ 460 m away from the road. Both the Felix and Elliott and Redling et al. studies report that their observations are representative of a signature associated with vehicle emissions. But the clearly different values found in this study suggest that neither study is truly representative of an isotopic source signature for vehicle emissions.

The passive sampling technique necessarily collects both locally generated NO and NO₂, as well as background NO_x that would have been generated upwind of the sampling location. Ogawa recommends exposure of the NO₂ and NO_x pads for at least 24 hours, and typical minimum exposure times in an urban area (e.g. 10 ppbv NO_x) for isotopic determination via the denitrifier method would require a minimum exposure of ~36 hours, but dependent upon the ambient concentrations (i.e. lower concentrations would yield longer necessary exposure times). Therefore, passive sampling collections cannot be used to directly assess isotopic signatures associated with emission sources, unless those pads are only exposed to air resulting from a single emission source, and likely over short time scales (e.g., Homyak et al., 2016). Furthermore, NO_x sources primarily emit NO, with formation of NO₂ consequently occurring within minutes in the presence of an oxidant. Under equilibrium (photochemically driven) conditions, N isotopic exchange and fractionation can occur for NO and NO₂ (see Walters et al., 2015c and references therein). Thus, collection of NO₂ alone may not yield direct information on the $\delta^{15}\text{N}$ -NO associated with the emission source (more on this below). Our NO₂ and NO_x sampling is representative of urban air heavily influenced by vehicle emissions, particularly diesel vehicles. Our results suggest that overall these vehicle emissions contribute to a negative $\delta^{15}\text{N}$ of NO_x and NO₂ in the environment.

3.2 $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of NO_x and NO₂

Mean $\delta^{18}\text{O}$ -NO_x for duplicate samples collected in summer ranged from +33.4 ‰, to +38.5 ‰, with an overall mean of $+36.3 \pm 2.4$ ‰ (Figure 2). For winter, $\delta^{18}\text{O}$ -NO_x ranged from +34.2 ‰ to +41.4 ‰, with an overall mean of $+38.7 \pm 2.9$ ‰. The $\delta^{18}\text{O}$ -NO₂ for samples collected in summer ranged between +47.3 ‰ and +54.6 ‰, with an overall mean of $+50.5 \pm 3.2$ ‰. In winter, $\delta^{18}\text{O}$ -NO₂ ranged from +46.0 ‰ to +54.6 ‰, with an overall mean of 47.4 ± 1.2 ‰ (Figure 2). For the twenty-one day and twenty-eight day samples, enough sample remained following $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ analysis to complete $\Delta^{17}\text{O}$ measurements. These are the first $\Delta^{17}\text{O}$ observations reported for passively collected NO_x and NO₂. For samples collected in summer, the twenty-one day mean $\Delta^{17}\text{O}$ -NO₂ was 11.2 ± 0.6 ‰ and for twenty-eight days the mean $\Delta^{17}\text{O}$ -NO₂ was 10.4 ± 0.4 ‰, based upon duplicate samplers. As with $\delta^{18}\text{O}$, the $\Delta^{17}\text{O}$ -NO_x during the same collection

periods was always lower than for NO_2 with a twenty-one day mean of 6.9 ± 0.1 ‰, and twenty-eight day mean of 5.6 ± 0.7 ‰. The winter samples were systematically lower than the summer samples and tended to show greater variability between the duplicate samplers: $\Delta^{17}\text{O}\text{-NO}_2$ had a twenty-one day mean of 6.9 ± 1.1 ‰ and twenty-eight day mean of 8.4 ± 1.9 ‰; $\Delta^{17}\text{O}\text{-NO}_x$ had a twenty-one day mean of 3.7 ± 0.1 ‰ and twenty-eight day mean of 5.9 ± 1.2 ‰.

Figure 2: $\delta^{18}\text{O}$ of NO_x (square with crosshatch) and NO_2 (open diamond) from Ogawa samplers (a) deployed during summer and (b) winter sampling periods. Error bars (often smaller than symbols) reflect ± 1 S.D. based upon duplicate samplers.

As discussed in the Methods section above, determination of the $\delta^{18}\text{O}$ of nitrite via the denitrifier method must be corrected for fractionation that takes place due to the removal of oxygen atoms in the production of N_2O . Because *nitrate* isotopic reference materials are commonly used in the denitrifier method, an additional correction must be made to account for the loss of less oxygen in the conversion from nitrite samples to N_2O compared to nitrate to N_2O (Casciotti et al., 2007). We find that if this is not done, $\delta^{18}\text{O}$ -nitrite (i.e. $\delta^{18}\text{O}\text{-NO}_2$ and $\delta^{18}\text{O}\text{-NO}_x$) values are ~ 25 ‰ lower than the true values (Figure 3). It is not clear if recently reported $\delta^{18}\text{O}\text{-NO}_2$ (Felix and Elliott, 2014) or $\delta^{18}\text{O}\text{-NO}$ values (Homyak et al., 2016) from collections as nitrite have undergone this correction. The $\delta^{18}\text{O}\text{-NO}_2$ values found in our study are very different than that reported in Felix and Elliott (2014), which are in the range of -17.5 to -8.4 ‰ and -8.4 to $+7.8$ ‰ inside and outside the tunnel, respectively. Another important consideration when dealing with nitrite samples for isotopic analysis is that nitrite readily exchanges oxygen atoms with water, depending on pH and temperature, such that the storage of samples before analysis is important to consider (see Casciotti et al., 2007 for details).

Figure 3: Demonstration of difference in results due to correction of $\delta^{18}\text{O}$ of nitrite using $\delta^{18}\text{O}$ of nitrate reference materials (see section 2.4). Uncorrected data (triangles) are biased low by ~25 ‰.

A priori, the oxygen isotopic composition of NO_x would be expected to reflect that of the oxidants influencing the conversion of NO to NO_2 (Alexander et al., 2009; Hastings et al., 2003). Based upon the RIDEM monitoring data, both summer and winter ozone concentrations exceed that of NO and NO_2 (e.g. ~35 ppbv compared to 5-20 ppbv, respectively). Under conditions in this study, we would expect ozone to dominate the production of NO_2 via R1, and that the photochemical cycling of NO and NO_2 (R1, R2) occurs on the order of thousands of times before NO_2 is lost from the atmosphere to other products (e.g. R5-R7). As such, the expectation then is that NO , NO_2 and ozone should be in isotopic equilibrium and the oxygen isotopic composition will therefore reflect that of ozone primarily (see also Michalski et al., 2003; Alexander et al., 2009; Vicars and Savarino, 2014). Typical tropospheric values for bulk ozone are close to 110 ‰ for $\delta^{18}\text{O}$ and 25 ‰ for $\Delta^{17}\text{O}$ (39 ‰ for the terminal oxygen) (Vicars and Savarino, 2014 and references therein). In comparison, other oxidants such as OH , HO_2 , RO_2 , O_2 , etc. all have $\ll \delta^{18}\text{O}$ and $\Delta^{17}\text{O} \sim 0$ ‰. Atmospheric nitrate isotopic observations in the mid-latitudes also support the idea that NO_x should primarily reflect ozone-related chemistry, except under special circumstances where another oxidant (e.g., hydroxy and peroxy radicals) occurs in high enough concentrations relative to reaction rates (Alexander et al, 2009; Michalski et al., 2011). The $\delta^{18}\text{O}\text{-NO}_3^-$ typically ranges from 50-90 ‰ in the mid-latitudes (see Michalski et al., 2011 for a compilation), reflecting the predominance of ozone chemistry influence on NO_x and dilution of the ozone signal with further oxidation to NO_3^- via R4 or R5-R7. Therefore, even after the correction described above, the mean $\delta^{18}\text{O}\text{-NO}_2$ ($\Delta^{17}\text{O}$) of 47.4 ‰ (9.2 ‰) and mean $\delta^{18}\text{O}\text{-NO}_x$ of 38.7 ‰ (5.6 ‰) are surprisingly low. Three potential explanations arise for the lower than

expected oxygen isotopic composition for both NO_2 and NO_x . First, if the results are indicative of the isotopic composition of atmospheric NO_2 and NO_x , then there must be significant influence of an oxidant other than ozone. The other two possibilities are that the collection technique and/or the storage of samples influence the isotopic composition such that the isotopes do not directly reflect the atmospheric composition of NO_2 and NO_x .

In the first case, given the relatively high ozone values observed in and around the collection site (20–40 ppbv based on RIDEM monitoring data), and modeling studies such as Alexander et al. (2009) and Michalski et al. (2003), we would expect a predominance of R1 for NO_2 production, particularly on average over seven to twenty-eight day timescales. Peroxy or hydroxyl radicals can potentially compete with R1 to oxidize NO to NO_2 when concentrations are high enough. Whether ozone is the dominant oxidant or not, it is difficult to explain the consistently lower $\delta^{18}\text{O}\text{-NO}_x$ compared to $\delta^{18}\text{O}\text{-NO}_2$ since under sunlit conditions we would expect NO and NO_2 to cycle rapidly and come into isotopic equilibrium with the primary oxidant. The consistently lower values for $\delta^{18}\text{O}\text{-NO}_x$ are therefore better explained as resulting from the chemical conversion of NO_2 and NO_x to nitrite on the pads or because of exchange with water during storage. Both the NO_2 and NO_x are converted to nitrite on the pads and then stored in water. Nitrite in solution can readily exchange oxygen atoms with water, the timescale of which is dependent upon temperature and pH (Casciotti et al., 2007). At room temperature (i.e. 22°C) the $\delta^{18}\text{O}$ value of the nitrite in equilibrium with water will result in nitrite that is $\sim 14\text{‰}$ higher than that of the water ($\delta^{18}\text{O}\text{-H}_2\text{O}$) (Casciotti et al., 2007). Ultrapure water from our lab has a $\delta^{18}\text{O}$ of -6‰ , suggesting that the final $\delta^{18}\text{O}\text{-NO}_2^-$ would be $+8\text{‰}$. All samples in this study had slightly basic pH and were stored at room temperature prior to analysis. However, the summer samples were stored for ~ 3 weeks prior to isotopic analysis, while the wintertime samples were analyzed within 1 week of collection. Based on the detailed experiments of Casciotti et al. (2007), we would expect less than 5% exchange with water within the first 3 weeks of storage. Furthermore, the summer samples would have had a much greater chance for equilibration than the winter samples, yet the summer $\delta^{18}\text{O}\text{-NO}_x$ and $\delta^{18}\text{O}\text{-NO}_2$ values are similar to or higher than that in the winter. We conclude then that equilibration with water in solution was limited and cannot explain the overall lower than expected isotopic results for NO_2 and NO_x . We suggest then that chemistry on the passive sampling pads (i.e. conversion of NO and NO_2 to nitrite) contributes to the oxygen isotopic composition observed. In the case of NO_x , NO is converted to NO_2 and then reacted to produce nitrite (R8, Section 2). The influence of the chemical reactions on the oxygen isotopic composition of nitrite can also help explain why the $\delta^{18}\text{O}\text{-NO}_x$ (and $\Delta^{17}\text{O}$) is always less than the $\delta^{18}\text{O}\text{-NO}_2$ (and $\Delta^{17}\text{O}$). To lower the $\delta^{18}\text{O}\text{-NO}$ and $\delta^{18}\text{O}\text{-NO}_2$ so significantly, this likely involves either exchange of oxygens with the reactants or with atmospheric water vapor, or equilibrium fractionation during reaction with PTIO and TEA. If we expect that NO and NO_2 would be in isotopic equilibrium with ozone in the atmosphere, then the PTIO chemistry lowers the final $\delta^{18}\text{O}\text{-NO}_x$ by at least $\sim 15\text{‰}$. If the oxygen isotopic composition of the reactants were known and/or if the

fractionation or exchange during capture of NO and NO₂ were determined to be consistent, than it could be corrected for to calculate isotopic values that reflect atmospheric abundance in NO₂ and NO_x.

Additionally, it should be considered that isotopic fractionations could occur during NO_x/NO₂ collection. Previous studies of concentration have determined that the environmental settings under which samplers are deployed plays an essential role for effective NO₂ collection. Environmental parameters such as temperature and/or humidity can limit the capture of NO₂ or alter the chemistry between adsorbent (TEA) and NO₂ to produce compounds other than nitrite (NO₂⁻). For instance, TEA can effectively capture NO₂ unless the TEA is frozen (aqueous TEA freezes at -10°C) (Kirby et al., 2000) and this should be taken into consideration if samplers are deployed in environments where temperatures reach or fall below -10°C. Total water vapor content in the air during the reaction with NO₂ is likely the most important factor for effective quantitative conversion of NO₂ to NO₂⁻. Gold (1977) collected NO₂ with TEA in a dry solvent (N(CH₂CH₂OH)₃) and immersed the complex into water, which resulted in the production of NO₂⁻ and NO₃⁻. In another study, Aoyama et al. (1983) found that neither nitrite nor nitrate was formed when NO₂ was collected in dry air, but N-nitrosodiethanolamine is formed. Finally, chemical interferences from peroxyacetyl nitrate (PAN) and HONO converted to NO₂⁻ via TEA might also alter the isotopic composition of the collected analyte (Hisham et al., 1983; Sickles et al., 1990). Controlled laboratory studies would be ideal to address whether any of the processes significantly influence the isotopic composition collected via passive sampling.

4. CONCLUSIONS

The reproducibility, precision and ease of use of the Ogawa samplers suggest they can be an effective tool for environmental monitoring to quantify isotopic compositions of atmospheric NO₂/NO_x. We have provided a description of how colorimetric analysis and the denitrifier method can be utilized to measure $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ of atmospheric NO_x and NO₂ samples that are collected with Ogawa passive samplers. Several important precautions are necessary to consider when using these methods. While some authors suggest that passively collected results are representative of isotopic signatures of source emissions (e.g., vehicles, agricultural soils), passive sampling necessarily reflects a mix of sources (and possibly fractionation associated with NO to NO₂ conversion) given exposure times of days to weeks. The characteristic blue color of oxidant PTIO caused chemical interference during colorimetric analysis, which was removed via extraction by adding 3mL of diethyl ether into an aliquot of the aqueous analytical solution for colorimetric analysis only. For isotopic analysis via the denitrifier method, both nitrate and nitrite concentrations must be determined since if nitrate is present it will influence the final isotopic values obtained. Nitrite is the primary analyte of interest with the Ogawa passive samplers, and the oxygen isotopic data must be corrected if samples are run against nitrate reference materials. The presence of positive $\Delta^{17}\text{O}$ values is indicative of NO_x and ozone chemical cycling in the atmosphere.

However, the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of NO_2 and NO_x obtained via the passive samplers is much lower than would be expected in the atmosphere. The final $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of NO_2 and NO_x reflect a combination of atmospheric abundances and oxygen exchange or fractionation associated with the chemistry that takes place upon the conversion of the gas phase reactants to the nitrite analyte. Meteorological conditions such as very low temperatures ($<-10^\circ\text{C}$) or very low humidity are known to affect the collection of NO_2 by passive samplers and may also influence isotopic values. Ideally, future controlled laboratory experiments can quantitatively determine the extent to which passive sampling changes the isotopic composition of NO_x compounds compared to atmospheric abundances.

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