

**CHARACTERIZING THE $\delta^{15}\text{N}$ OF NO_x FROM
VEHICLE-RELATED EMISSIONS:
FIELD APPLICATION OF A NEW METHOD**

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Introduction

NO_x is a term that represents the mononitrogen oxide gases, NO and NO_2 . Both are short-lived in the atmosphere and rapidly exchange between each other in sunlight. N_2 is broken down and oxidized to NO in the atmosphere by combustion or lightning, which then is oxidized to NO_2 , usually by ozone (O_3). NO_2 then may photolyze to form NO, or deposit by reacting to form nitric acid (HNO_3). The result is that nitrogen formerly stable as atmospheric N_2 is deposited as acid rain (Jacob, 91). Understanding the life cycle of NO_x in the atmosphere furthers our understanding of acid rain, oxidative processes in the atmosphere, and potential impacts on the biosphere caused by nitrogen deposition, such as fertilization. NO_x is formed naturally by lightning and microbial processes in soils, and it is emitted by anthropogenic sources such as fossil fuel and biomass burning. Throughout the oxidative processes of NO_x , the nitrogen does not further exchange with N_2 in the atmosphere; as a result, the isotopic value (represented by $\delta^{15}\text{N}$, see below) of nitrogen in NO_x could be used to better understand the reactive nitrogen cycle, particularly the impact of natural versus human influences. $\delta^{15}\text{N}$ (read as “delta 15-N”) is calculated based on measurements of the ratio of isotopic species by mass-spectrometry, using the following equation, where N_2 in air is the reference gas in this case:

$$\delta^{15}\text{N} \equiv \left(\frac{\frac{^{15}\text{N}}{^{14}\text{N}}_{\text{sample}}}{\frac{^{15}\text{N}}{^{14}\text{N}}_{\text{reference}}} - 1 \right) \times 1000\text{‰}$$

$\delta^{15}\text{N}$ could potentially be used to track NO_x sources in nitrogen deposition. For example, since the industrial revolution, the isotopic signature of NO_3^- found in an ice core from Summit, Greenland has become increasingly more negative (Hastings et al., 2010). The most dramatic change occurred some time between 1950 and 1980, coinciding with a sharp increase in fossil fuel burning worldwide. NO_3^- and HNO_3 act as the sinks for NO_x . The change in $\delta^{15}\text{N}$ implies a shift in the global nitrogen budget – one

might hypothesize that the negative isotopic signature reflects a negative $\delta^{15}\text{N}$ of NO_x in fossil fuel burning. However, the current literature on $\delta^{15}\text{N}$ of different NO_x sources does not reflect the values observed in the ice cores, indicating that further research must be conducted in order to provide a better understanding of the $\delta^{15}\text{N}$ of NO_x sources and the nitrogen cycle.

Many in the scientific community have attempted to characterize source signatures for NO_x using $\delta^{15}\text{N}$. However, in order to compare the $\delta^{15}\text{N}$ range between sources for NO_x , the collection method must be consistent, it must collect only NO_x , and it must collect NO_x with 100% efficiency or a consistent efficiency that does not result in fractionation of the isotopes. In the current literature, these criteria are not met for NO_x collection. For vehicle emissions, there are only two papers that measure $\delta^{15}\text{N}$ for NO_x – Heaton (1990) and Ammann et al. (1999). Heaton actively collected NO_x using NaOH and H_2O_2 , while Ammann et al. collected NO and NO_2 separately using two denuder tubes coated with KOH and guaiacol. Because KOH /guaiacol only collects NO_2 , the Ammann study used a separate tube for NO collection that first converted NO to NO_2 using solid $\text{CrO}_3/\text{H}_3\text{PO}_4$. Ammann et al. collected emissions next to a highway in Norway, while Heaton collected directly from vehicle tailpipes in South Africa that lacked catalytic converters. Catalytic converters were added to cars in the late 1980s and lower the temperature of combustion, so they might also change how nitrogen fractionates in forming NO_x . No measurements of $\delta^{15}\text{N}$ of NO_x from vehicle emissions have been done in North America so far. Heaton collected NO_x from vehicles instantaneously, while Ammann et al. used two-week averages. For NO_2 , Ammann et al. found a range of (+2.9 to +8.5‰, n=9); for NO , he found a wider range of (-2.3 to +8.5‰, n=9). Heaton found a range for NO_x of (-13 to -2‰, n=8). Because of the different experimental methods and collection solutions used, it is not surprising that Heaton and Ammann et al. produced very different ranges for $\delta^{15}\text{N}$ of NO_x emitted by vehicles. It is impossible to distinguish which difference contributed to the different ranges – whether it is the collection method, type of collection (roadside vs. tailpipe, instantaneous vs. average), presence of catalytic converters, types of vehicles used, or another factor not known.

The lack of consistency among sampling methods in the current literature prevents comparison of $\delta^{15}\text{N}$ between sources. If different sources are measured using a consistent method, the resulting $\delta^{15}\text{N}$ values could potentially permit tracing of specific sources for NO_3^- in modern air pollution and deposition studies, as well as tracing the history of NO_x deposition in an ice core. This study investigates the application of a different method for NO_x collection than the methods used by Heaton and Ammann et al. Margeson et al. published an EPA method for NO_x collection using an Alkaline-Permanganate (A-P) sampling system, that uses 0.25M KMnO_4 - 0.5M NaOH solution, with a total collection efficiency of 99%-102% (Margeson et al., 1984). This technique was researched in the laboratory and adapted for collecting NO_x and measuring $\delta^{15}\text{N}$ (Fibiger et al., submitted). Because it collects with nearly 100% efficiency under a variety of flow rates, volumes and time, it can be used to collect NO_x without fractionation of the nitrogen. In addition to demonstrating 100% efficiency in a controlled laboratory setting, this method must also collect efficiently in the field under a variety of conditions, including variable temperature and humidity.

The primary goal of this study was to test the A-P method in the field under varying conditions, with multiple set-ups running at the same time, in order to investigate the reproducibility of the $\delta^{15}\text{N}$ values. We selected a site that is heavily influenced by vehicle emissions; the site is relatively close to two high-traffic highways in Providence, RI (Figure 1). Samples were collected during morning and evening rush hours when we expected that the majority of NO_x emissions in the area come from cars and trucks. We deployed Ogawa passive samplers at the same site for NO_2 and NO_x to have a sense of the ambient NO_x concentrations. In addition, we measured $\delta^{15}\text{N}$ values for the Ogawa pads in two different settings to examine reliability of these passive samplers for isotope analysis. Finally, we also collected NO_x emissions from a laboratory diesel chamber in order to test consistency in a different controlled setting with unknown ambient NO_x concentrations using different flow rates. While our primary goal was to evaluate the consistency of the A-P NO_x collection method, we hoped to also gain understanding of the potential nitrogen isotopic signature of both vehicle-influenced air and direct diesel fuel emissions.



Figure 1 – Location of Field Site (222 Richmond Street), Providence Jewelry District.

Methods

A. Active NO_x Collection Method

The method for collecting NO_x uses 100mL of A-P solution with a concentration of 0.25M KMnO₄ - 0.5MNaOH. Air is pulled through a glass bubbler with a coarse frit using a pump and a flow controller at a rate between 1L/min and 5L/min. Teflon tubing is used for all connections and inlets because NO_x is sticky but does not stick to Teflon. The top of the bubbler is fit with a Teflon Millipore hydrophobic filter to prevent solution loss. The inlet is fit with a Teflon particle filter and Nylasorb filter for preventing HNO₃ from reaching solution (however, the Nylasorb filter was only used for the diesel chamber collections) (Figure 2). NO and NO₂ are both oxidized to NO₃⁻ by the permanganate. The solution will also oxidize NH₃ and HNO₃, so we must either filter these compounds out or attempt to quantify their interference. Within 48 hours of the start of collection, the A-P solution is reduced by approximately 5mL of 30% H₂O₂. Precipitated MnO₂ is removed by centrifuge, and the resulting solution contains NaOH and NO₃⁻. Excess H₂O₂ is decomposed by MnO₂ in solution (Margeson, 1985). The

solution is then neutralized using 12.1N HCl before colorimetric analysis using a Smartchem Westco.

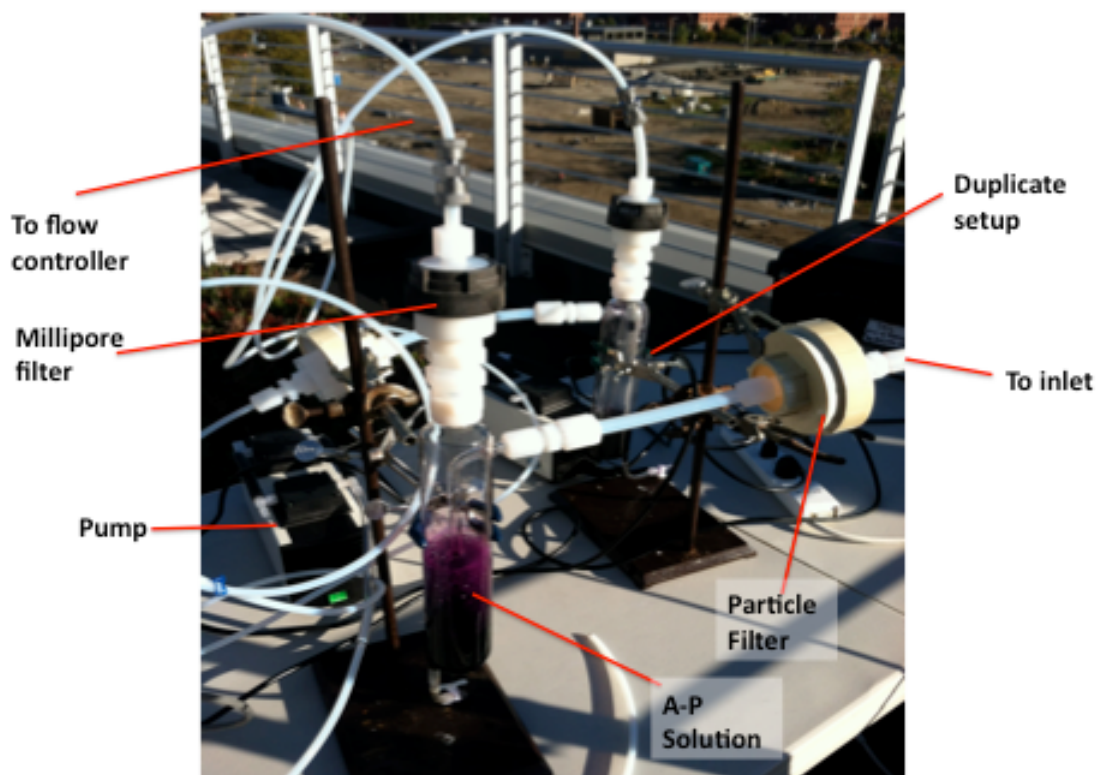


Figure 2 – Collection Method Setup at Field Site, Providence Jewelry District

$\delta^{15}\text{N}$ was measured using a bacteria denitrifier method that converts nitrite and nitrate to N_2O gas, which is then measured on an isotope-ratio mass-spectrometer (Sigman, 2001). We use 3mL vials of bacteria culture in nitrate-free tryptic soy broth, and inject solution with 10nmol of NO_3^- , alongside standards (USGS35, USGS34, IAEA N3).

The amount of moles of NO_x collected by the A-P solution is calculated using the following method, where C_c is the concentration of the solution after centrifuge, V_c is the volume of the solution after centrifuge, V_A is the volume of acid added after centrifuge, V_R is the volume reserved for analysis after collection, and V_f is the volume of the solution immediately after collection:

$$\frac{C_C(V_C + V_A)}{V_R} \times V_f$$

Because the KMnO_4 solution used (Fisher) had a nitrate blank, we measure a blank from the same bottle with every sample. The blank is then subtracted from the μmoles collected to obtain the net μmoles of nitrate in the final solution.

The following equation is used for blank correcting the $\delta^{15}\text{N}$ values, where the subscript S represents sample, B represents blank, and M refers to the amount of μmoles :

$$\frac{(\delta^{15}\text{N}_S \times M_S) - (\delta^{15}\text{N}_B \times M_B)}{M_S - M_B}$$

The blank corrected $\delta^{15}\text{N}$ value represents the $\delta^{15}\text{N}$ of the NO_x collected by the A-P solution. The entire method has been shown in the laboratory to have $\pm 1.5\%$ reproducibility from collection to isotopic determination (Fibiger et al., submitted).

B. Field Collection – Site Description

Field samples were collected on the fourth floor terrace of the Alpert Medical School building at 222 Richmond Street in the Jewelry District of Providence, Rhode Island. The building is approximately 0.4 miles north of the intersection of I-95 and I-195, two interstates with high traffic during rush hour, and the Jewelry District is the neighborhood just south of downtown Providence (Figure 1). Two solutions were set up using separate pumps for all days of collection except for the very first collection in July. We attempted to collect samples during rush hours for two consecutive days – 7:00AM to 9:30AM and 3:30PM to 6:00PM. When collection had to be paused during heavy rainfall, both setups were paused for the same length of time. These times were chosen in order to maximize the NO_x contributions from vehicles. A Davis Vantage Vue weather station was used to collect data on temperature, humidity, wind speed, wind direction,

and rainfall. The average daily humidity ranged from 45-85% humidity, and average temperature ranged from 37-67°F. Due to tall buildings in the area, wind direction was difficult to measure likely as a result of local eddies, but it is still reported.

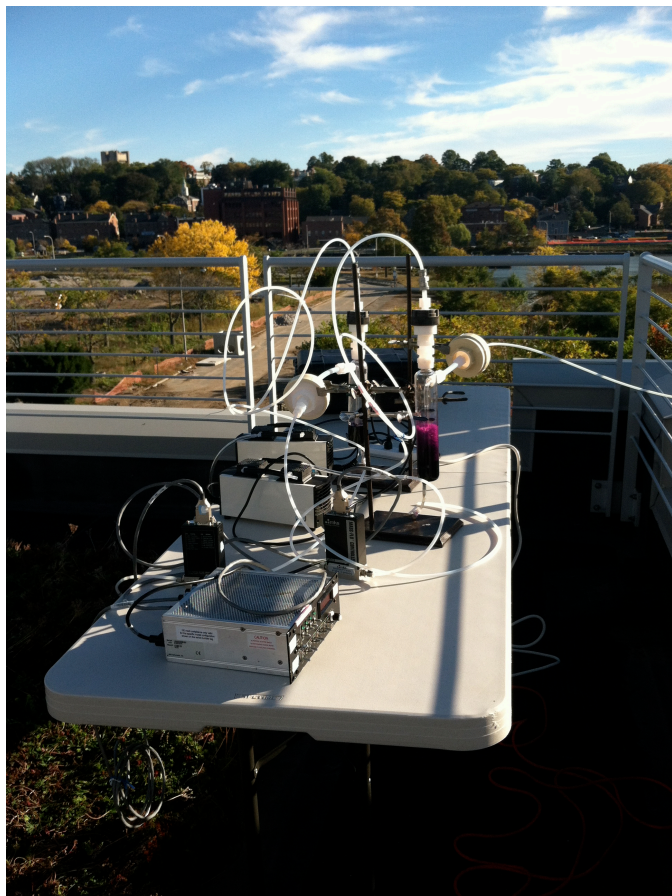


Figure 3 – Two Field Setups, Zoomed Out. The large metal box in the foreground measures the flow rate through the flow controllers. Teflon was used for all connections.

C. Passive NO_x Collection

Because the ambient concentrations of NO_x were unknown prior to collection, we decided to use Ogawa pads to measure the concentrations during collection in order to compare with the concentration of NO_x that can be calculated by the NO₃⁻ collected in the A-P solution, collection time, and flow rate. In addition, we planned to measure δ¹⁵N values of the nitrate and nitrite on the Ogawa pads in order to attempt to characterize the effectiveness of the Ogawa NO_x pads in isotopic analysis. However, Ogawa pads are

officially designed for measuring ambient concentration, not characteristic isotopic values of the gases. A labeled photograph of the Ogawa pads and holders can be seen in Figure 4.

Ogawa makes and distributes passive collection samplers for both NO_x and NO_2 and can be used to calculate ambient concentrations of NO_x , NO_2 and NO gas. The sampler is left outside with separate NO_x and NO_2 collection pads, protected from rain by a cup, for a minimum of 24 hours for typical concentrations and maximum of 30 days for low concentrations. Ogawa provides tables that use temperature, humidity, collection time in minutes, and concentration of nitrite on the pads to calculate these ambient concentrations.

For comparison to active collections, Ogawa NO_x and NO_2 pads were deployed at the same site for the entirety of active collection, but they were left out in between collection times. Pads were kept refrigerated before use, and were immediately put into 8mL of water following collection. NO_x pads are dyed purple by Ogawa to distinguish between NO_x and NO_2 pads. However, since we measure concentrations of nitrate using a colorimetric method, the purple dye interfered with the results, and often there was not enough sample to make additional measurements. The purple dye can be partially removed with 100% diethyl ether.

During active field collections, pads were deployed for 36 hours, the time from the first collection to the final collection. In addition, pads were deployed in 48 hours, week and month long intervals in order examine the consistency of $\delta^{15}\text{N}$ values for nitrite and nitrate captured on the NO_x and NO_2 pads.

The week and month long pad deployment occurred in the loading dock of the Geochemistry building. Two sets of NO_x and NO_2 pads were left out for an entire month; during this time, two new sets of NO_x and NO_2 pads were exchanged every 8-12 days. The entire length of the month-long deployment was equal to the sum of the weeklong deployments.

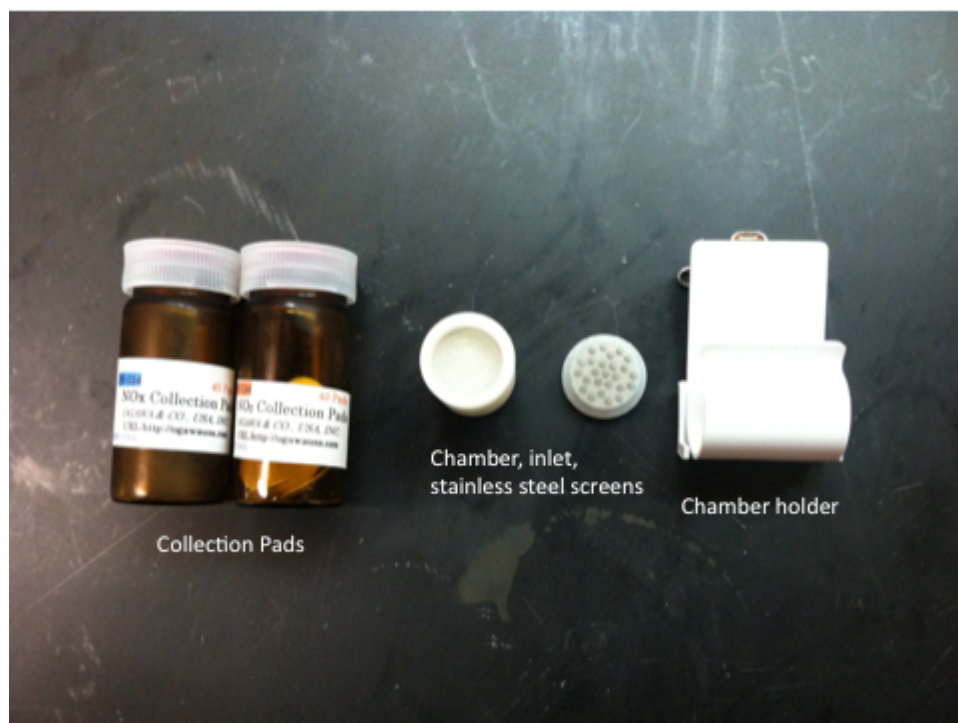


Figure 4 – Ogawa Pads and Holder (“chamber”). The pad is inserted between two stainless steel screens and secured in the chamber. The inlet has holes through which air can pass.

D. Diesel Smog Chamber Collections

NO_x emitted by diesel-burning engines was collected directly using a Teflon-lined smog chamber. The diesel smog was generated by a Yanmar diesel engine coupled to a Pramac generator with continuous 50% load. The diesel filled the chamber for 6 minutes, after which it was diluted for 2 minutes and ten seconds with air from the room. Air within the chamber was pulled directly using a Teflon inlet. Experiments were run for 30 minutes each. In order to attempt simulation of photochemical effects on NO_x, the smog chamber was illuminated by 144 ultraviolet lights for thirty minutes. Three experiments were run before turning on the UV lights, and two experiments were run after thirty minutes of UV exposure to the chamber. The flow rate was somewhat variable for the five experiments, probably as a result of a particle buildup on the Teflon filter at the start of the experiments. The flow rate of the first experiment was 4.07L/min, which decreased sharply for the second experiment to 1.91L/min but balanced out to a stable

average of 2.3L/min for the final three experiments. Very similar concentrations of NO_x were calculated for each run, despite the variable flow rate. The average ambient NO_x concentration of the chamber was 1.93ppm with a standard deviation of 0.21ppm.

E. Lab Experiments

Before going out into the field, we wanted to address two potential problems – the lengthy collection time required and potential interference of ammonia. Because the Fisher 1M KMnO_4 bottles have a small blank (5-10 μM of nitrate, depending on the bottle), we need to maximize the amount of NO_x collected for the blank correction step without compromising the solution by running for too long. In short lab experiments of two hours, about 10% of solution was lost by likely evaporation or solution loss. We performed several experiments to examine these effects – running the A-P solution for 6-8 hours over two days and either adding back water, adding back more A-P solution, or allowing evaporation to occur. In addition, we prepared a solution with small traces of ammonium added to the A-P solution, which was left out for four days. Over this time, aliquots were taken and the concentration was compared to the initial concentration. The purpose is to model the effect of ammonia in the air on the NO_x collected. In order to determine the amount of NH_4Cl to add to A-P solution, a study on ambient ammonia in New York City was used, which reported an average ambient NH_3 concentration of 0.8ppb (Li et al., 2004). New York City also ranges from 20-80ppb in ambient NO_x concentration. Since our target nitrate concentration in solution is 40 μmol , we added approximately $\frac{1}{5}$ of the expected nitrate, 8 μmol , to solution to quantify ammonia's effect on total nitrate in solution.

Results

A. Lab Experiments

Ammonia was shown to have little effect on the total nitrate of the A-P solution ($r^2 = .02$) (Figure 5).

In addition, adding back solution maintained high efficiency, while adding back water appeared to have diluted the solution, resulting in 88.3% efficiency. In addition, not adding back anything to the solution also decreased efficiency to 89.6%. The loss of solution was likely a combination of splashing with some evaporation. This problem did not come up during field collection, and solution loss was negligent.

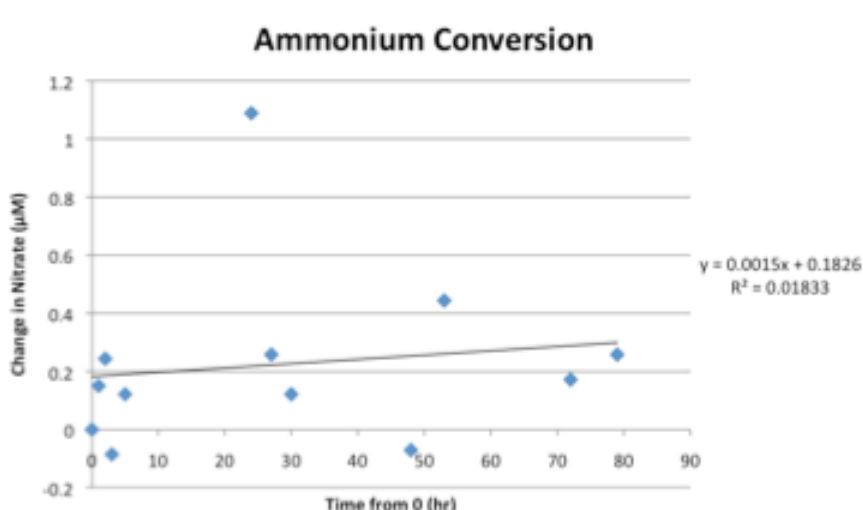


Figure 5 – Tests for Ammonium Conversion to Nitrate in A-P Solution.

B. Active Field Collections – Providence Jewelry District

Field samples were collected in Providence four times – once in July, once in October, and twice in November. The range of $\delta^{15}\text{N}$ values was (-0.6 to -7.7‰) for all collections (Table 1, Figure 6). On a specific day when two samples were collected at the same time, the resulting $\delta^{15}\text{N}$ value fell within a 1.5‰ range of each other. On 10/8-10/9, the standard deviation was 0.6‰; on 11/20-11/21, the standard deviation was 0.7‰. Although 11/6-11/7 resulted in some leaking solution, the estimated blank corrected $\delta^{15}\text{N}$ value for the second sample gives a standard deviation of 0.9‰. All of these samples lay within the 1.5‰ range that was found in the laboratory using the A-P method.

On 10/8, due to problems with the second sample's flow controller, only one setup was run that morning from 7:00-9:32AM. In order to have two setups running at the exact same time, fresh solution was made and that morning's solution was reserved

and set aside for later comparison. Most importantly, there is no collection overlap between the 10/8 sample and the two samples on 10/8-10/9.

On 11/6, one sample leaked after collecting in the morning for 2.5 hours. The remaining sample (about 30mL) was set aside and measured for concentration and isotopic ratio. However, because certain variables could not be directly measured (mass of solution after collection and mass of sample after centrifuge), the resulting blank corrected $\delta^{15}\text{N}$ had to be estimated. This sample does have collection overlap with the first sample collected on 11/6-11/7, which was collected for longer.

<i>Active Field Collections</i>						
<i>Dates</i>	<i>Time Run (hours)</i>	<i>$\delta^{15}\text{N}$ Sample 1</i>	<i>$\delta^{15}\text{N}$ Sample 2</i>	<i>Average Temp. (°F)</i>	<i>Average % Humidity</i>	<i>Average Wind Direction</i>
7/25-7/26	8.17	-5.6	-	67	82.5	105
10/8*	2.5	-1.9	-	60	53	199
10/8-10/9	6.75	-0.6	-1.3	60	57.5	133
11/6-11/7	5.25	-6.7	-7.7**	63	74	151
11/20-11/21	8.9	-7.1	-6.7	37	45	169

Table 1 – Active Field Collections, Providence Jewelry District.

* = morning only collection; ** = estimated calculation due to spilled solution

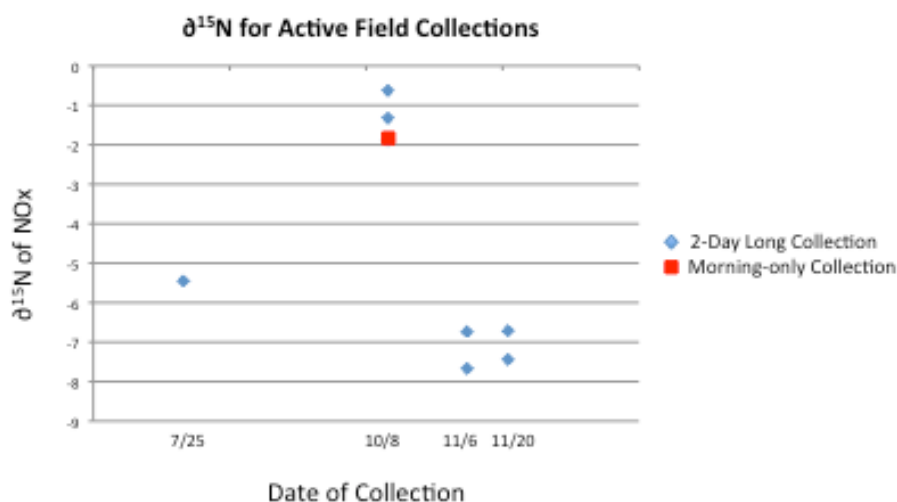


Figure 6 – Date of collection vs. $\delta^{15}\text{N}$

C. Active Laboratory Collection – Diesel Smog Chamber

For the diesel smog chamber samples, the average $\delta^{15}\text{N}$ value for the samples in which no “photochemistry” occurred was -17.4‰ with a standard deviation of 0.7‰. For all five samples, the average $\delta^{15}\text{N}$ value is -18.0‰ with a standard deviation of 1.0‰ (Table 2). These all are within the 1.5‰ previously observed for the method. The range of $\delta^{15}\text{N}$ values for all samples is (-16.7 to -19.2‰).

<i>Diesel Smog Chamber Collections</i>		
<i>Sample Name</i>	<i>Average Flow Rate (L/min)</i>	<i>$\delta^{15}\text{N}$</i>
A	4.03	-16.7
B	1.91	-17.5
C	2.42	-18.1
D*	2.27	-19.2
E*	2.20	-18.7

Table 2 – Active Collection, Diesel Smog Chamber.

** = sample was collected after UV lights were left on for thirty minutes.*

D. Passive Collections – Providence Jewelry District

There were many challenges in providing a complete dataset for these experiments, primarily as a result of the purple interference from dye on NO_x pads. However, the data collected and measured in presented in Table 3. The range of $\delta^{15}\text{N}$ values is -0.2 to -6.6‰. The average value was -2.6‰ with a standard deviation of 2.3‰. The average standard deviation for the replicated pads was 1.3‰ (Table 3).

<i>Passive Collection – Providence Jewelry District</i>					
<i>Dates</i>	<i>$\delta^{15}\text{N}$ of NO_x 1</i>	<i>$\delta^{15}\text{N}$ of NO_x 2</i>	<i>Time of Exposure (hours)</i>	<i>Conc. of NO_2 1 (ppb)</i>	<i>Conc. of NO_2 2 (ppb)</i>
8/6-8/7	-3.3	-0.9	48	8.9	11.5
8/13-8/14	-0.3	-0.2	48	7.0	5.8
10/8-10/10	-1.2	-4.1	76	6.5	13.7
11/6-11/7	-6.6	-	58	11.5	11.2
11/20-11/21	-	-4.1	58	4.0	3.7

Table 3 – Passive Collection, Providence Jewelry District. NO_2 is included here for concentrations instead of NO_x because few NO_x concentrations were reliably measured with a colorimetric method due to purple dye interference.

E. Passive Collections – Loading Dock, Geochemistry Building

The Ogawa pads set up in the loading dock had a $\delta^{15}\text{N}$ range from -10.7 to 13.9‰. The average value was -12.1‰ with a standard deviation of 1.1‰. The average standard deviation between replicated pads was 1.0‰. For the month long pads, the standard deviation between the two pads was 0.6‰, while the average standard deviation for the pads left out for 8-12 days was 1.2‰ (Table 4).

<i>Passive Collection – Loading Dock</i>					
<i>Dates</i>	<i>$\delta^{15}\text{N}$ of NO_x 1</i>	<i>$\delta^{15}\text{N}$ of NO_x 2</i>	<i>Time of Exposure (hours)</i>	<i>Conc. of NO_x 1 (ppb)</i>	<i>Conc. of NO_x 2 (ppb)</i>
11/20-12/2	-13.4	-12.4	290.5	-	-
12/2-12/10	-13.9	-10.7	198.5	34.8	53.7
12/10-12/18	-10.9	-11.9	191.5	26.8	30.7
Month (11/20-12/18)	-11.6	-12.4	680.5	27.0	26.8

Table 4 – Passive Collection, Geochemistry building loading dock.

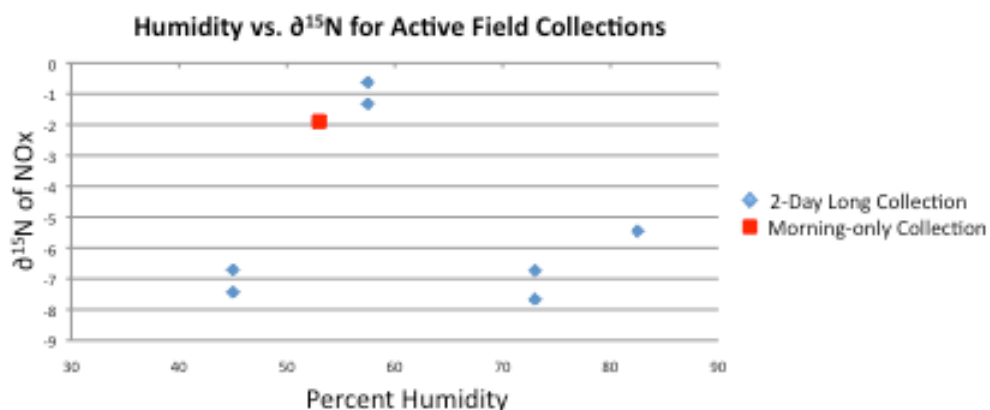
Discussion

A. Reproducibility in the Field

This method is reproducible in the field. It is evident that in experiments where two setups were run for the same amount of time, even with different flow rates, glassware and equipment, the $\delta^{15}\text{N}$ values remained within the expected 1.5‰ range. In addition, the setup is reproducible for a variety of conditions – temperature, humidity and wind direction. We anticipated that the change in values between days (~ -1 vs. -7‰) could be explained by a significant difference in some weather variable, but there does not appear to be any correlation between weather and $\delta^{15}\text{N}$ value (Figure 7). What our

data does suggest, however, is that the isotopic signature measured on 10/8, while distinctly outside the range collected from other experiments, had a sample only collected during the morning of the first collection day with no overlap in collection time. This sample is very similar in $\delta^{15}\text{N}$ value to the collection later in the day; this implies a relatively more positive $\delta^{15}\text{N}$ value of NO_x from that day, supporting the reproducibility.

In addition, the diesel smog chamber experiments resulted in an average $\delta^{15}\text{N}$ of -18.0‰ with a standard deviation of 1.0‰ , and the standard deviation is less significant when the “photochemistry” experiments are not taken into account ($\delta^{15}\text{N} = -17.4\text{‰}$ with a standard deviation of 0.7‰). There is no obvious change due to the photochemistry simulation. However, it is possible that the range of $\delta^{15}\text{N}$ values would vary distinctly from the previous experiments without photochemistry, and perhaps such a change would become more convincing with additional collections. As noted earlier, there was a large range of average flow rates used in the five experiments (1.91L/min to 4.03L/min) that still resulted in a consistent calculation of ambient NO_x concentration and consistent $\delta^{15}\text{N}$, indicating the effectiveness of the A-P method for variable flow rates. In this case, the flow rates were limited by experimental conditions and were not adjusted intentionally, so similar limitations from a field setting would not impact the consistency of the A-P method for NO_x collection.



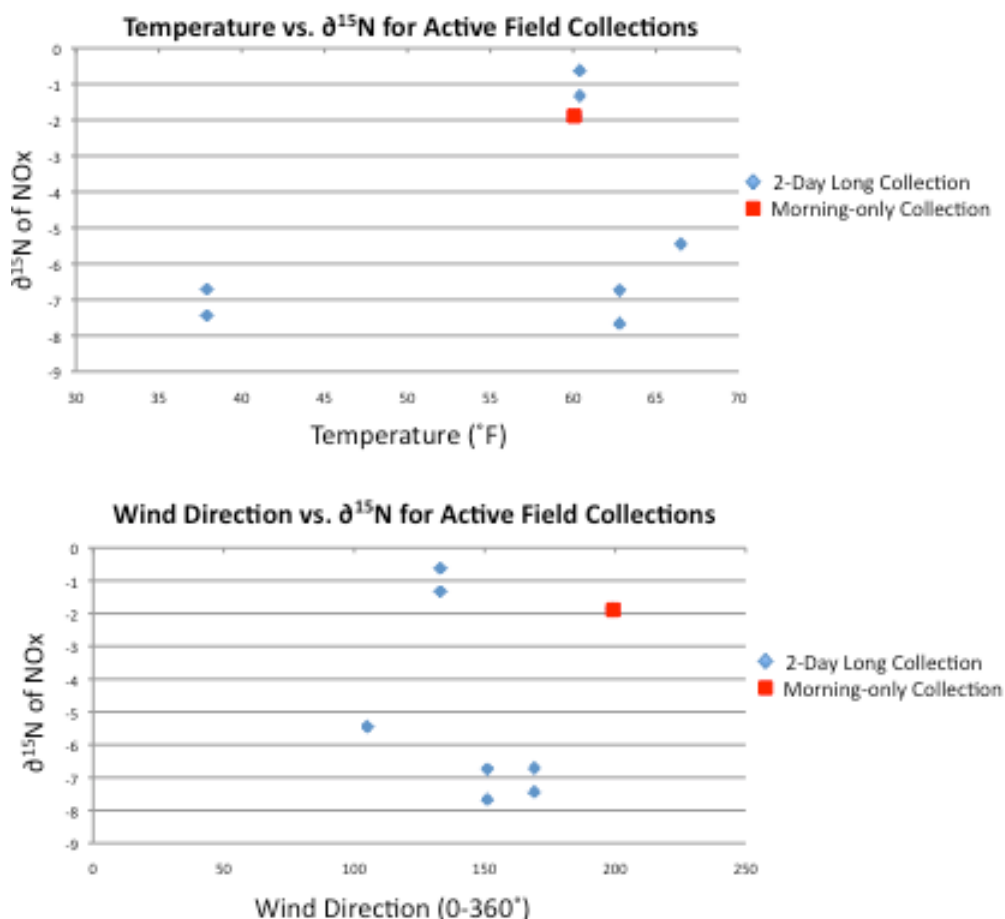


Figure 7 – Different weather variables and $\delta^{15}\text{N}$, graphed to show lack of correlation.

B. $\delta^{15}\text{N}$ of Vehicle Influenced Air

We are not presenting the values collected as a conclusive range of the $\delta^{15}\text{N}$ signature for NO_x for vehicle influenced air. The field samples collected represent a preliminary range for our understanding of NO_x . All samples collected exhibited negative $\delta^{15}\text{N}$ values from (-0.6 to -7.7‰) with an average of -4.9‰ and median of -6.1‰. In addition, because HNO_3 was not removed during the active field collections, the impact of HNO_3 on the $\delta^{15}\text{N}$ values is unknown and cannot be accounted for. Until the nitrate collected in the A-P solution reflects NO_x only with definitively no HNO_3 , these values cannot attempt to characterize source signatures of NO_x .

There are several problems with the site selected for field collections of vehicle emissions that cause hesitations in using these values as source signature ranges for NO_x .

from vehicles. A roadside collection that occurs much closer to the highway (perhaps several meters away instead of 0.4 miles) would more directly collect NO_x from the desired source (it would not, however, demonstrate how NO_x changes in the atmosphere). In addition, there are several other sources that could have interfered - in particular, there is ongoing construction in the Jewelry District where Brown University is building new administrative buildings. The construction area is the same distance from the collection site as the highway. Active collection pulled directly from a tailpipe of a car would provide a useful supplement to this data.

The average $\delta^{15}\text{N}$ values for the diesel collections are, however, consistent with the values from the field collections and the week/month long passive collections. The diesel samples exhibited a very negative $\delta^{15}\text{N}$ (-17.4‰ without photochemistry). We would expect diesel engines to contribute to the overall urban air in Downtown Providence, so it makes sense to have negative $\delta^{15}\text{N}$ values. In addition, this would imply that smaller vehicles that burn non-diesel fuel have a more positive $\delta^{15}\text{N}$ value for NO_x .

The month/week long passive collections using Ogawa NO_x and NO_2 pads occurred in the loading dock of Geochemistry, where the primary vehicles that enter are diesel-burning trucks. Therefore, we would also expect the NO_x of the loading dock to represent primary diesel source. Since the average $\delta^{15}\text{N}$ value for these experiments was -12.1‰ for NO_x , this implies that diesel is the primary source. However, the Ogawa pads have not been tested for $\delta^{15}\text{N}$ values in the laboratory, so this comparison is qualitative, pointing out a trend consistent with the active collection emissions from a diesel-burning engine.

While we cannot directly compare our vehicle-influenced NO_x range to the current literature, it appears that our range is closer to the range determined by Heaton than Ammann et al. Heaton reported a more negative $\delta^{15}\text{N}$ range (-13 to -2‰) than Ammann et al., whose average $\delta^{15}\text{N}$ was slightly positive. However, because different methods were used for NO_x collection, we cannot definitively evaluate the correctness of either range.

C. Usefulness of Ogawa Pads

Do the Ogawa pads collect NO_x such that they can accurately measure the overall $\delta^{15}\text{N}$ of NO_x emissions? This question cannot be answered until NO_x pads are measured in a controlled setting while collecting NO_x with a known isotopic value. However, when we tested the Ogawa pads in the loading dock, the resulting $\delta^{15}\text{N}$ values were fairly consistent and reproducible – these had much longer collection times at lower concentrations. However, samples left out for 48 hours in higher concentrations were much more variable and difficult to understand. Thus, we propose that the pads collect an average of the total air, and therefore are more reliable when left out for long periods of time in low concentrations. In addition, the concentrations remain more consistent for duplicated pads, even when isotopes vary greatly.

Conclusion and Further Work

The A-P method for collecting NO_x actively and efficiently for $\delta^{15}\text{N}$ analysis is reproducible under a variety of weather conditions for flow rates from 1.0L/min to 5.0L/min. In addition, preliminary results of vehicle NO_x emissions indicate a negative range for $\delta^{15}\text{N}$ of NO_x released by vehicles, while direct measurement of diesel emissions indicates a very negative $\delta^{15}\text{N}$ range with an average of -17.4‰.

While the reliability of using Ogawa pads for isotope analysis has not been tested fully, they appear to be more useful for longer periods at low concentrations (from one week to one month). Short deployments (36 to 48 hours) resulted in high variability for $\delta^{15}\text{N}$ values for pads left out the same amount of time.

There is much additional work that could be done to better understand the sources of NO_x isotopically. In order to characterize the $\delta^{15}\text{N}$ of NO_x , no HNO_3 should be collected, so a proper filter must be used to remove the nitric acid. In addition, more sites and experiments could provide a better understanding of the $\delta^{15}\text{N}$ of NO_x from roadside emissions. These could be done using more sites near multiple highways, perhaps at different times of day. Finally, to supplement the data of $\delta^{15}\text{N}$ for NO_x measured directly from a diesel smog chamber, emissions of cars burning regular fuel should be measured, either using a similar smog chamber setup or by pulling directly from a tailpipe of a car

under different amounts of loading. This type of experiment could be used alongside the diesel $\delta^{15}\text{N}$ values in order to give a fuller understanding of the roadside emissions, as they are likely a sum of cars and trucks. Finally, the A-P method can be used to measure additional sources. Some work has already been started on measuring biomass-burning NO_x using the A-P active collection method (Fibiger et al., submitted), but additional sources, such as soil emissions, lightning, and coal smoke stacks, have not been measured using the A-P collection method yet. The same method must be used for collections for quantitative comparisons across different sources. This study laid the foundation to support further use of the A-P method for NO_x collection from various emission sources.

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