Nitrogen Stable Isotope Composition (δ^{15}N) of Vehicle-Emitted NO_x

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Supporting Information

ABSTRACT: The nitrogen stable isotope ratio of NO_x (δ^{15}N-NO_x) has been proposed as a regional indicator for NO_x source partitioning; however, knowledge of δ^{15}N values from various NO_x emission sources is limited. This study presents a detailed analysis of δ^{15}N-NO_x emitted from vehicle exhaust, the largest source of anthropogenic NO_x. To accomplish this, NO_x was collected from 26 different vehicles, including gasoline and diesel-powered engines, using a modification of a NO_x collection method used by the United States Environmental Protection Agency, and δ^{15}N-NO_x was analyzed. The vehicles sampled in this study emitted δ^{15}N-NO_x values ranging from −19.1 to 9.8‰ that negatively correlated with the emitted NO_x concentrations (8.5 to 286 ppm) and vehicle run time because of kinetic isotope fractionation effects associated with the catalytic reduction of NO_x. A model for determining the mass-weighted δ^{15}N-NO_x from vehicle exhaust was constructed on the basis of average commute times, and the model estimates an average value of −2.5 ± 1.5‰, with slight regional variations. As technology improvements in catalytic converters reduce cold-start emissions in the future, it is likely to increase current δ^{15}N-NO_x values emitted from vehicles.

INTRODUCTION

Nitrogen oxides (NO_x = NO and NO_2) are important trace gases that affect atmospheric chemistry, air quality, and climate.¹ NO_x play a key role in the troposphere by acting to control the concentrations of ozone (O_3) and the hydroxyl radical (OH) as well as forming nitrate (NO_3⁻) aerosols.² The reactions between NO_x and hydrocarbons (HC) are major sources of tropospheric O_3, which is a greenhouse gas, an oxidizing pollutant, and an influence of the lifetimes of other greenhouse gases.³–⁵ Ultimately, NO_x is oxidized to nitric acid (HNO_3) and deposited as acid rain, leading to degradation of drinking water, soil acidification, lacustrine and estuarine eutrophication, and biodiversity changes in terrestrial ecosystems.⁶

Sources of NO_x are both natural and anthropogenic, but there are uncertainties in the relative importance of these sources.⁶–⁸ Natural sources of NO_x include lightning, soil nitrification/denitrification, and wildfires.⁶,⁸ Anthropogenic sources of NO_x include fossil fuel and biofuel combustion (mainly emitted from power plants), transport (vehicles, ships, and aircraft), and industry.⁷ Since the industrial revolution, anthropogenic emissions of NO_x have surpassed natural NO_x emissions.⁶,⁷ Although significant improvements have been made to reduce NO_x emissions from stationary and mobile sources, further progress is needed to reduce the health and ecosystems impacts associated with NO_x emissions;⁹ however, the uncertainty of total NO_x emissions is relatively high, with an estimated uncertainty on the order of 30–50%.⁹ To estimate the relative importance of various NO_x sources and to assess the effectiveness of NO_x reduction technologies, a way of partitioning NO_x sources on the basis of nitrogen (N) deposition studies is required.

Once emitted into the atmosphere, NO_x is primarily oxidized to HNO_3 and subsequently removed from the atmosphere via wet or dry deposition. Therefore, analysis of the N stable isotopes of atmosphere-derived nitrate (δ^{15}N-NO_3⁻) could be used as a regional indicator for partitioning NO_x sources, which would help identify the contribution of various NO_x sources to local/regional N deposition as well as help evaluate the effectiveness of NO_x emission reductions. Previous works have observed spatial variations in δ^{15}N-NO_3⁻ in wet and dry deposition that correlated with the δ^{15}N-NO_x of the surrounding areas stationary NO_x emission sources (one-tailed, t test, p < 0.001), suggesting that δ^{15}N-NO_3⁻ is linked to NO_x sources.¹⁰,¹¹ Although the impact of kinetic and equilibrium isotopic fractionation of NO_x sink processes (chemical reactions and photolysis) on δ^{15}N during the conversion of NO_x to NO_3⁻ must also be considered,¹²,¹³ few fractionation factors for these sink processes have been determined. Previous measurements of δ^{15}N-NO_x from various NO_x sources are limited, but these indicate that NO_x sources may have a wider range of δ^{15}N values than previously thought (Figure 1).¹⁴–²² Although these prior measurements of δ^{15}N-NO_x allow for an approximation of relative source contributions, further characterization of δ^{15}N-NO_x is required to minimize
uncertainty in partitioning NOₓ source contributions and to understand the impact of NOₓ oxidation to HNO₃ on δ¹⁵N values. Furthermore, it is possible that technology developments could influence the δ¹⁵N-NOₓ values of various NOₓ sources, thus preventing the application of previous δ¹⁵N-NOₓ measurements to all regions.

In this study, the δ¹⁵N-NOₓ values of vehicle exhaust, the main source of anthropogenic emitted NOₓ, were measured. The source of N in vehicle exhaust is air with δ¹⁵N = 0‰; thus, it was previously assumed that NOₓ formed by the oxidation of air would also have δ¹⁵N near 0‰. However, previous measurements of δ¹⁵N-NOₓ emitted directly from vehicle exhaust, indicate a rather large range of δ¹⁵N-NOₓ from −13 to 3‰. Initial studies reported δ¹⁵N-NOₓ values of 3.7 and −1.8‰, supporting the assumption that δ¹⁵N-NOₓ emitted from vehicle exhaust is close to 0‰. However, a subsequent study reported a much wider range of δ¹⁵N-NOₓ values, from −13 to −2‰, suggesting that δ¹⁵N-NOₓ from vehicle exhaust may not be as close to the previously assumed value of 0‰. Recent studies of δ¹⁵N-NOₓ from vehicle exhaust have measured the δ¹⁵N in plant material, tree rings, and/or the δ¹⁵N from roadside NOₓ and indicate that vehicle-derived δ¹⁵N-NOₓ may have positive values as high as 17‰. Such inferences should be treated cautiously because they measure the δ¹⁵N of a secondary product formed from vehicle-emitted NOₓ that may be subject to kinetic and equilibrium isotope fractionation factors that can alter the initial δ¹⁵N-NOₓ value and, in plant material δ¹⁵N studies, because plant N requirements are likely not entirely derived from NOₓ precursors. To characterize the δ¹⁵N-NOₓ emitted from modern vehicles, we measured in this study the δ¹⁵N-NOₓ directly emitted from vehicle exhaust for model years 1995 to 2015.

MATERIALS AND METHODS

NOₓ Collection and Processing. NOₓ was collected from the tailpipes of 26 different vehicles that included 15 passenger cars, 7 sports-utility vehicles (SUVs), and 4 trucks, using a modification of the United States Environmental Protection Agency (US EPA) Method 7 at West Lafayette, Indiana, USA (40.45° N, 86.91° W) between June 20, 2014 and September 26, 2014. The majority of exhaust samples were collected while vehicles were in neutral (n = 22), and a smaller set of exhaust samples were collected while vehicles were driven (n = 4); under both modes, the engine speed was kept between 2000 to 2500 rpm during sampling. Nineteen of the vehicles sampled had a “cold engine” (running less than 2 min prior to sampling), and seven had a “warm engine” (running longer than 2 min prior to sampling). The model years of the sampled vehicles ranged from 1995 to 2015, and all vehicles had gasoline-powered engines except for one that had a diesel-powered engine. Every vehicle sampled was equipped with a 3-way catalytic converter. (For a complete list of sampled vehicles, see the Supporting Information.)

The sampling method used in this study was modified from US EPA Method 7 (Determination of Nitrogen Oxide Emissions from Stationary Sources). Briefly, exhaust samples were collected into evacuated 2 L borosilicate bottles. The 2 L bottles were connected to a Teflon tube (length of 35 cm and an inlet diameter of 1 cm) attached to a borosilicate probe with a length of 20 cm and an inlet diameter of 0.5 cm. The probe was placed into the tailpipes of each vehicle, and the stopcock to the borosilicate probe was opened, allowing the exhaust to be collected. After a sampling period of approximately 10 s, the stopcock was closed. Because in the limiting case, the diameter of the sampling apparatus (0.5 cm) is approximately 73 500 times larger than the molecular mean-free path at ambient pressures (68 nm), the and the sampling time is approximately 1520 times quicker than the lifetime of NO diffusion through air (τdiff = L²/D ≈ 15216.3 s, where L = length of diffusion and D is the diffusion constant = 0.1988 cm²/s) for the total sampling apparatus length of 55 cm, diffusion isotope effects are negligible in this setup. Additionally, the estimated volume of the Teflon tube and the borosilicate probe was 30 mL, making the volume of sampled air in the probe negligible compared to that of the collected exhaust. The sampling bottles contained 10 mL of a NOₓ absorbing solution, which was synthesized by mixing 2.8 mL of concentrated sulfuric acid (H₂SO₄) with 0.6 mL of 30% hydrogen peroxide (H₂O₂) that was diluted to 1 L using high-purity Millipore water. The absorbing solution quantitatively oxidizes NOₓ into NO₃⁻. Triplicate samples were collected for each vehicle, approximately 30 s apart.

After NOₓ exhaust collection, the containers were allowed to stand for at least 72 h with occasional shaking every 10 to 12 h to facilitate the conversion of NOₓ to NO₃⁻. The residual NOₓ headspace concentration was then measured using a Thermo Environmental Instrument Chemiluminescence NO-NOₓ–NO Analyzer. The absorbing solution was collected and neutralized using 1 mL of 1 M sodium bicarbonate, and the NO₃⁻ concentration was measured using a Cary 5000 UV–vis spectrometer. Using the residual NOₓ and NO₃⁻ concentrations, the percent of NOₓ conversion to NO₃⁻ was calculated. Every sample had over 97.5% of the NOₓ collected converted to NO₃⁻; therefore, the N isotopic fractionation resulting from this conversion should be minimized. A potential interference that could impact the collected δ¹⁵N-NOₓ is the oxidation of ammonium (NH₄⁺) to NO₃⁻. Ammonia (NH₃) is known to be a major component of vehicle-emitted exhaust, and once dissolved in the absorbing solution, it would presumably form NH₄⁺. Because H₂O₂, a strong oxidizer, was a component of the absorbing solution, control tests were conducted to determine the possible conversion of NH₄⁺ to NO₃⁻. The results of the control tests indicated that in the absorbing solution used in this study no detectable NO₃⁻ formed from relatively high NH₄⁺ concentrations (100 ppm). Therefore, NH₃ should have a minimal, if any, influence on the measured δ¹⁵N-NO₃⁻. Overall, our control studies indicate that our absorbing solution and successive neutralization induces no N isotope fractionation.

![Figure 1. Range of δ¹⁵N values for various NOₓ sources.](Image)
Isotopic Analysis. For N isotopic analysis, approximately 250 nmol of NO$_3^-$ was injected into a 12 mL vial containing 1 mL of a denitrifying strain of bacteria (P. aureofaciens) that converts NO$_3^-$ to nitrous oxide (N$_2$O)\textsuperscript{28}. The N$_2$O was extracted and purified using an automated head-space gas chromatography system and analyzed for $\delta^{15}$N values by a Thermo Delta V continuous-flow isotope ratio mass spectrometer (CF-IRMS) at the Purdue Stable Isotopes lab.\textsuperscript{29} Values of $\delta^{15}$N are reported in parts per thousand relative to atmospheric N$_2$, represented as

$$\delta^{15}N_{sample} (\text{‰}) = \frac{(15N/14N)_{sample} - (15N/14N)_{air}}{(15N/14N)_{air}} \times 1000$$  \hspace{1cm} (1)$$

Working lab standards calibrated to NIST isotope reference nitrites USGS34 and USGS35 were used to correct for isotopic fractionation resulting from the denitrification of NO$_3^-$ and the subsequent N$_2$O purification process. The working standards had an average standard deviation of 0.3‰ for $\delta^{15}$N.

## Results and Discussion

Table 1 details the vehicle information and the data measured from the vehicles sampled in this study. The text below summarizes the NO$_x$ concentrations and $\delta^{15}$N-NO$_x$ values of the collected samples and discusses our interpretation of these results.

**NO$_x$ Exhaust Concentration.** The average concentration of NO$_x$ for individual vehicles ranged from 8.5 to 286 ppm, with standard deviations ranging from 0.2 to 250 ppm for triplicate samples. The large range and variance of emitted NO$_x$ can be explained by the run times of the engine prior to sampling that were divided into either cold engines (running less than 2 min prior to sampling) or warm engines (running longer than 2 min prior to sampling). Vehicles with cold engines emitted significantly more NO$_x$ (95 ± 70 ppm, n = 19) compared to warm engines (17 ± 8.6 ppm, n = 7), a finding that was statistically significant at a confidence level of 0.01 (p < 0.01). In the case of vehicles with cold engines, the highest NO$_x$ concentrations were always collected from the first sample, and NO$_x$ concentrations drastically decreased for subsequent samples. Alternatively, warm-engine vehicles generally emitted NO$_x$ at a consistent concentration for all samples collected. Overall, emitted NO$_x$ concentrations exhibited an exponential decay that moderately correlated with the vehicle run time prior to sampling for all samples (Figure 2). These results are consistent with other studies that have shown that cold engines have higher emissions of NO$_x$\textsuperscript{30–33}. This occurs because of a rich air–fuel ratio in cold engines and is due to the inefficiency of the 3-way catalytic converters at reducing NO$_x$ emissions under cold-engine conditions\textsuperscript{30–33}. Generally, when an engine is first started, the fuel does not completely vaporize, and this causes higher emissions of hydrocarbons (HC), NO$_x$, and carbon monoxide (CO). As the engine reaches its operating temperature, the air–fuel ratio reaches the stoichiometric point for combustion, and catalytic converters become efficient, and the emissions of HC, CO, and NO$_x$ diminish.\textsuperscript{30–33} Despite the progress made at reducing HC, CO, and NO$_x$ emissions with the 3-way catalytic converter, vehicles account for roughly 50% of the emissions of these gases,\textsuperscript{32,34} with approximately 60–80% of the total emissions...
for a typical vehicle occurring during the first 200 s of cold-start operation, on the basis of the New European Driving Cycle.35

δ15N-NOx Values. The average δ15N-NOx measured for each vehicle ranged from −19.1 to 9.8‰, and the standard deviation ranged from 0.4 to 8.7‰ for triplicate samples. For most cases, the reported standard deviation was much greater than the analytical uncertainty of ±0.3‰. This large δ15N-NOx variance can be explained in terms of the emitted NOx concentration. A strong, negative logarithmic correlation is observed between δ15N-NOx values and NOx concentrations for gasoline- (R2 = 0.84) and diesel-powered engines (R2 = 0.98) (Figure 3). There was no significant difference between vehicles sampled while in neutral or while driven because both modes resulted in δ15N-NOx that similarly correlated with emitted NOx concentration (Figure 3). The measured δ15N-NOx values are hypothesized to have arisen from the thermal production of NOx in the combustion chamber that would result in NOx depleted in 15N and from the subsequent equilibrium isotope effects and the catalytic reduction of NOx to N2 that would enrich 15N relative to the thermally produced NOx. This hypothesis was tested using theoretical isotope-fractionation factors in kinetic and Rayleigh distillation models.

Thermal Production of NO. The most well-known chemical pathway for the formation of NOx in internal combustion engines is the Zeldovich mechanism,36 in which NO is formed by the reaction between nitrogen and oxygen in the intake air, represented as

\[ \text{N}_2 + \text{O} \rightarrow \text{NO} + \text{O} \]  

(R1)

\[ \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} \]  

(R2)

\[ \text{N} + \text{OH} \rightarrow \text{NO} + \text{H} \]  

(R3)

Under temperatures of the thermal production of NO (T > 2000 K), it has been previously assumed that N2, O2, and NO exist at isotopic equilibrium, represented as12,23

\[ \text{N}_2 + \text{O}_2 \leftrightarrow 2\text{NO} \]  

(R4)

The calculated equilibrium exchange fractionation factor for this reaction is extremely small (<1.69‰); therefore, the thermally produced NO should have a δ15N value close to that of air (0‰). However, the majority of our measured NOx was depleted in 15N, especially for cold-engine vehicles. This suggests that the thermal production of NO in a combustion chamber in a vehicle engine is not always achieving equilibrium, and its formation is kinetically limited by the large amount of energy required to break the triple bond of N2 (R1).

A previous study that measured depleted 15N abundances in vehicle exhaust NOx attributed the 15N depletion to the kinetic isotope effect associated with the breaking of the triple bond of N2.14 Because of the difference in zero-point energies (ZPE), this bond breaking is faster for the lighter isotopologues (15N14N, ZPE = 1175.7 cm⁻¹)38 relative to the heavier isotopologue (15N15N, ZPE = 1156.0 cm⁻¹).38 If the difference between N2 bond dissociation for 14N14N molecule and 15N15N molecule is significant at combustion temperatures, then the thermally produced NO will tend to have δ15N values lower than those of atmospheric N2. To quantify this kinetic isotope effect, so as to understand its impact on δ15N-NOx, the kinetics of the thermal production of NOx were simulated using Kinteus, a kinetics compiler that can be used to model chemical kinetic processes.39 Table 2 summarizes the reactions included in this model and the corresponding Arrhenius rate parameters.40–43 Rate constants for the molecules involving 14N were taken from the NIST Chemical Kinetics Database.3 These rate constants were adjusted for 15N by calculating the relative reaction rates and, therefore the fractionation factors (α), of the heavy isotope to the light isotope from the inverse of the reduced masses (μ) of the activated complex at the transition state (eq 2), subsequently scaling the reaction rate of the light isotope for the heavier isotope (eq 3).

\[
\alpha_{H/L} = \frac{k_H}{k_L} = \sqrt{\frac{\mu_L}{\mu_H}}
\]

(2)

\[
k(T)_{\text{heavy}} = \alpha_{H/L} A \left( \frac{T}{298} \right)^n e^{-E_a/RT}
\]

(3)

In eq 2, k is the reaction rate, μ± is the reduced mass of the activated complex, H represents the heavier N isotopologue (15N), and L represents the lighter N isotopologue (14N). In eq 3, A is the Arrhenius pre-exponential factor, T is temperature (in degrees Kelvin), n is the temperature dependence, E_a is the activation energy, and R is the gas constant. Kinetic isotope effects are caused by differences in the activation energy for
δ15N-NO values than what our thermal production of NOx model predicts. The NOx samples from diesel-powered vehicles analyzed in this study had δ15N-NOx values that ranged from −23.3 to −15.9‰, and in a previous study, measured δ15N-NOx values ranged from −13 to −12‰ for the kinetically limited thermal production of NOx. These lower δ15N-NOx values likely occur because of the different combustion conditions in diesel vehicles compared to those in gasoline-powered vehicles. Diesel-powered vehicles primarily operate at lower combustion temperatures than gasoline-powered vehicles. This is likely to increase N isotope fractionation and result in lower δ15N-NOx values from the thermal production of NOx compared to those from gasoline-powered engines. Although the exact δ15N-NOx produced from combustion is difficult to predict because of the variability in combustion conditions, the kinetically limited thermal NOx production should result in negative δ15N values.

**Catalytic Reduction of NO.** Another kinetic isotope effect to consider is that from the reaction of NOx with a 3-way catalytic converter. A 3-way catalytic converter uses a metal catalyst, typically platinum and rhodium, to reduce NOx emissions upward of 90%. The catalytic reduction of NOx to N2 can be described as NO decomposition on the catalyst surface followed by the removal of the oxygen on the catalyst surface by a reducing agent such as carbon monoxide (CO). Infrared studies of NO adsorption on aluminum- and silica-supported rhodium have provided evidence for stable molecular adsorption of NO on rhodium. and temperature-programmed desorption studies have provided evidence for the dissociation of NO on rhodium to form N and O. For NO to be reduced to N2, it has to first undergo adsorption onto the metal catalyst surface. For this process to occur, NOx has to diffuse through a washcoat layer approximately 10–50 μm thick and then bind onto the catalyst surface, likely leading to isotopic fractionation. The lighter molecules (14NO) will diffuse through the washcoat diffusion layer of the catalyst and undergo adsorption more quickly onto the catalyst surface than the heavier molecules (15NO) because of differences in mass and zero-point energies, respectively. This will cause the lighter NO molecules to preferentially decompose to their elemental components with the heavier NO molecules to be emitted when the catalytic converter is effectively operating, thus causing the emitted NOx to be enriched in 15N relative to the

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**Table 2. Data for the Reactions and the Rate Constants for the Thermal Production of NO**

<table>
<thead>
<tr>
<th>reaction</th>
<th>α</th>
<th>A</th>
<th>n</th>
<th>Ei (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 14N2 → 214N</td>
<td>1</td>
<td>9.86 × 10^-10</td>
<td>−3.33</td>
<td>940</td>
</tr>
<tr>
<td>2 14N2 → 14N + 15N</td>
<td>0.983</td>
<td>9.86 × 10^-10</td>
<td>−3.33</td>
<td>940</td>
</tr>
<tr>
<td>3 O2 + O → 15NO + 14N</td>
<td>1</td>
<td>3.01 × 10^-10</td>
<td>0</td>
<td>318</td>
</tr>
<tr>
<td>4 O2 + O → 15NO + O</td>
<td>0.997</td>
<td>1.51 × 10^-10</td>
<td>0</td>
<td>318</td>
</tr>
<tr>
<td>5 15N + OH → 14NO + H</td>
<td>0.994</td>
<td>4.47 × 10^-12</td>
<td>0</td>
<td>27.19</td>
</tr>
<tr>
<td>6 15N + OH → 15NO + H</td>
<td>0.999</td>
<td>4.70 × 10^-10</td>
<td>0</td>
<td>−0.71</td>
</tr>
</tbody>
</table>

δ(T) = αA(T/298)e^(-Ei/RT), and α represents the relative reaction rate for the N isotopologues.
thermally produced NO. The number of potentially fractionating reactions and difficulties in assessing catalytic isotope effects for each step is beyond the scope of this work. Rather, the observed $\delta^{15}$N-NO$_x$ and NO$_x$ concentration were used in a Rayleigh distillation model to determine the catalytic converter’s net isotope effect, which includes diffusion, equilibrium, and kinetic effects.

$\delta^{15}$N-NO$_x$, Exhaust Fractionation Factor. The results of this study indicate a strong relationship between the emitted NO$_x$ concentration and $\delta^{15}$N-NO$_x$ (Figure 3): in general, the more concentrated the NO$_x$ emission, the lower the $\delta^{15}$N-NO$_x$ value. Our kinetics model indicates that thermally produced NO is depleted in $^{15}$N. In the absence of a 3-way catalytic converter or under conditions of inefficient NO$_x$ reduction (cold engine and catalytic converter), the kinetically limited NO$_x$ production is likely to result in a negative $\delta^{15}$N-NO$_x$ value. As the vehicle engine becomes more efficient and the catalytic converter warms up, NO$_x$ emissions are reduced, and the NO$_x$ becomes enriched in $^{15}$N relative to thermally produced NO$_x$, likely as a result of the equilibrium isotope effect between N$_2$ and NO (R4) as well as the kinetic isotope effect associated with the diffusion and adsorption of NO$_x$ onto the catalytic converter surface as previously discussed.

To quantitatively determine the $\delta^{15}$N isotope fractionation associated with the reduction of NO$_x$ caused by the warming of a vehicle engine and catalytic converter, this process was modeled according to a Rayleigh type fractionation, represented as.

$$\delta^{15}N_f = \delta^{15}N_i - \varepsilon \ln[NO_x]$$

where $\delta^{15}N_f$ is the measured $\delta^{15}$N-NO$_x$, $\delta^{15}N_i$ is $\delta^{15}$N-NO$_x$ value that vehicle-emitted NO$_x$ reaches as NO$_x$ emissions approach zero, and $\varepsilon$ is the enrichment factor for $\delta^{15}$N as the concentration of NO$_x$ decreases. The enrichment factor ($\varepsilon$) is related to the fractionation factor ($\alpha$) of the reduction of NO$_x$ by the relationship represented as.

$$\varepsilon \ (	ext{‰}) = (\alpha - 1) \times 1000$$

From Figure 3, the enrichment factor ($\varepsilon$) for the production of vehicle-emitted NO$_x$ was calculated for gasoline- and diesel-powered engines to be 5.2(±0.3)% and 6.13(±0.8)% respectively. This indicates that as the engine and catalytic converter warm up, the lighter molecules of NO$_x$ are preferentially decomposed, leaving the emitted NO$_x$ enriched in $^{15}$N compared to atmospheric air. This suggests that vehicle-emitted NO$_x$ has likely become enriched in the $^{15}$N isotope relative to the vehicle-emitted NO$_x$ produced prior to 1975 because of the advent of the 3-way catalytic converter.

Implications for $\delta^{15}$N-NO$_x$. The data obtained from this study are limited and do not represent the $\delta^{15}$N-NO$_x$ emitted from all types of vehicles, but they are useful for $\delta^{15}$N-NO$_x$ source characterization of vehicle exhaust. In this study, we measured a rather large range of $\delta^{15}$N-NO$_x$ for individual samples, ranging from −15.1 to 10.5‰ for gasoline-powered vehicles and −23.3 to −15.9‰ for diesel-powered vehicles. In general, the lowest $\delta^{15}$N-NO$_x$ values came from cold-start vehicles that were emitting high concentrations of NO$_x$. As previously mentioned, approximately 60–80% of the total emissions for a typical vehicle occur during the first 200 s of cold-start operation. Therefore, in order to estimate the mass-weighted $\delta^{15}$N-NO$_x$ emitted from vehicles, the mass balance of the emitted NO$_x$ concentration needs to be accounted for. To this end, a model was constructed on the basis of numerical integration methods to relate the concentration of emitted NO$_x$ (Figure 2) as a function of vehicle run time with the instantaneous vehicle-emitted $\delta^{15}$N-NO$_x$ for gasoline-powered vehicles. Specific details on the construction of this model can be found in the Supporting Information. This model predicts the mass-weighted $\delta^{15}$N-NO$_x$ emitted from vehicles to have the following relationship with vehicle run time represented as.

$$y = -12.35 + 3.02 \ln(t + 0.455)$$

where $y$ is the mass-weighted $\delta^{15}$N-NO$_x$ (%e) emitted from vehicles and $t$ is vehicle run time (min). This model shows the importance of NO$_x$ mass-balance to the overall $\delta^{15}$N-NO$_x$. Because NO$_x$ emissions are highest and are lowest in $^{15}$N during the cold-start period, this will lower the overall emitted $\delta^{15}$N-NO$_x$ from vehicles. A similar type of analysis was not carried out for diesel-powered engines because of the small sample size measured in this study ($n = 3$).

The average commute time varies regionally in the USA, and this likely leads to slight differences in the emitted $\delta^{15}$N-NO$_x$ from vehicle exhaust. The United States Census Bureau American Community Survey’s zip code one-way commute time inventory was used with the $\delta^{15}$N-NO$_x$ cumulative release time function (eq 8), to estimate the $\delta^{15}$N-NO$_x$ of vehicle exhaust emissions in each zip code in the continental USA (Figure 4). Overall, the average one-way commute time in the United States is approximately 25.4 min, corresponding with a $\delta^{15}$N-NO$_x$ value of $−2.5 \pm 1.5$‰. Although this average commute time represents all modes of transportation, the majority of transportation is from vehicles (86.1%), so this should be an adequate estimate for the regional $\delta^{15}$N-NO$_x$ emitted from vehicle exhaust. This $\delta^{15}$N-NO$_x$ approximation only accounts for gasoline-powered engines. Our few measurements of diesel-powered engines had lower $\delta^{15}$N-NO$_x$ values than those of gasoline-powered engines. Therefore, if these measurements are representative of all diesel-powered engines, inclusion of diesel-powered engines to the overall mass-weighted $\delta^{15}$N-NO$_x$ would lead to a lower $\delta^{15}$N-NO$_x$ value. However, the percentage of diesel-powered passenger vehicles in the U.S. is roughly 2.8%, so the impact of diesel-powered vehicles on the mass-weighted $\delta^{15}$N-NO$_x$ from passenger vehicle exhaust is likely to be small.

Several studies have measured the $\delta^{15}$N-NO$_x$ in wet and dry deposition, and these values range from −9.5 to 14.1‰, outside of the mass-weighted $\delta^{15}$N-NO$_x$ value of vehicle-emitted NO$_x$. Additionally, a recent highway-tunnel
$\delta^{15}\text{N-NO}_2$ study measured $\delta^{15}\text{N}$ values that ranged from 10.2 to 17%, which is higher than the majority of the $\delta^{15}\text{N-NO}_2$ measurements made in this study. This discrepancy in $\delta^{15}\text{N-NO}_2$ of vehicle-emitted $\text{NO}_x$ and of $\delta^{15}\text{N-NO}_2$ deposition and $\delta^{15}\text{N-NO}_2$ roadside studies are likely explained either by equilibrium $^{13}$ and/or kinetic isotope effects $^{12}$ that slightly alter the $\delta^{15}\text{N}$ of the original NO source or by the contribution of other NO sources with different $\delta^{15}\text{N-NO}_2$ values (Figure 1). The exact cau$\text{tation}$ of the alteration of $\delta^{15}\text{N}$ is beyond the scope of this work; however, if the $\delta^{15}\text{N}$ of atmospheric $\text{NO}_3^-$ is controlled by the source $\delta^{15}\text{N-NO}_2$, then Figure 4 suggests that 1) there will be spatial variations in the $\delta^{15}\text{N}$ of $\text{NO}_3^-$ tied to commute time and vehicle $\text{NO}_x$ mitigation efficiency, 2) there would be temporal variations in $\delta^{15}\text{N}$ of $\text{NO}_3^-$ related to the transition from nonvehicle to vehicle $\text{NO}_x$ production during the day and week, and 3) the $\delta^{15}\text{N}$ of atmospheric $\text{NO}_3^-$ produced between 1950 and 1975 should be significantly lower relative to $\text{NO}_3^-$ produced after 1980, which should be detectable in the northern hemisphere ice core record $^{19,59}$.

The continual improvements of the 3-way catalytic converter will likely have a future impact on $\delta^{15}\text{N-NO}_2$ values. Once catalytic converters are warmed up, they are up to 97% effective at reducing toxic gas emissions. However, these high conversion rates are only achieved when the converter is at a temperature of (typically) 300°C or greater, which can take several minutes to achieve. This results in more than 60–80% of total emissions occurring during cold-start emissions. Decreasing these cold-start emissions is the objective of future catalytic converter improvements. As these technological advancements become commonplace for catalytic-converter-equipped vehicles, it will likely lead to an increase of the $\delta^{15}\text{N-NO}_2$ value relative to the current value because of the fractionation factor associated with the catalytic reduction of $\text{NO}_x$.

**ASSOCIATED CONTENT**

5 Supporting Information

Appendix table and mass-weighted $\delta^{15}\text{N-NO}_2$ emission model. This material is available free of charge via the Internet at http://pubs.acs.org.

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