Quantifying the nitrogen isotope effects during photochemical equilibrium between NO and NO_2: implications for $\delta^{15}N$ in tropospheric reactive nitrogen

Jianghanyang Li[1], Xuan Zhang[2], John Orlando[2], Geoffrey Tyndall[2] and Greg Michalski[1,3]

[1.] Department of Earth, Atmospheric and Planetary Sciences, Purdue University, West Lafayette, IN, 47907
[2.] Atmospheric Chemistry Observations and Modeling Lab, National Center for Atmospheric Research, Boulder, CO, 80301
[3.] Department of Chemistry, Purdue University, West Lafayette, IN, 47907

Correspondence to: Jianghanyang Li (li2502@purdue.edu)

Abstract. Nitrogen isotope fractionations between nitrogen oxides (NO and NO_2) play a significant role in determining the nitrogen isotopic compositions ($\delta^{15}N$) of atmospheric reactive nitrogen. Both the equilibrium isotopic exchange between NO and NO_2 molecules and the isotope effects occurring during the NO_x photochemical cycle are important, but both are not well constrained. The nighttime and daytime isotopic fractionations between NO and NO_2 in an atmospheric simulation chamber at atmospherically relevant NO_x levels were measured. Then, the impact of NO_x level and NO_2 photolysis rate to the combined isotopic fractionation (equilibrium isotopic exchange and photochemical cycle) between NO and NO_2 were calculated. It was found that the isotope effects occurring during the NO_x photochemical cycle can be described using a single fractionation factor, designated the Leighton Cycle Isotope Effect (LCIE). The results showed that at room temperature, the fractionation factor of nitrogen isotopic exchange is 1.0275±0.0012, and the fractionation factor of LCIE (when O_3 solely controls the oxidation from NO to NO_2) is 0.990±0.005. The measured LCIE factor showed good agreement with previous field measurements, suggesting that it could be applied in ambient environment, although future work is needed to assess the isotopic fractionation factors of NO + $RO_2/HO_2 \rightarrow NO_2$. The results were used to model the NO-NO_2 isotopic fractionations under several NO_x conditions. The model suggested that isotopic exchange was the dominate factor when NO_x >20 nmol mol^{-1}, while LCIE was more important at low NO_x concentrations (<1 nmol mol^{-1}) and high rates of NO_2 photolysis. These findings provided a useful tool to quantify the isotopic fractionations between tropospheric NO and NO_2, which can be applied in future field observations and atmospheric chemistry models.

1. Introduction

The nitrogen isotopic composition ($\delta^{15}N$) of reactive nitrogen compounds in the atmosphere is an important tool in understanding the sources and chemistry of atmospheric NO_x ($NO+NO_2$). It has been suggested that the $\delta^{15}N$ value of atmospheric nitrate (HNO_3, nitrate aerosols and nitrate ions in the precipitation and snow) imprints the $\delta^{15}N$ value of NO_x sources (Elliott et al., 2009; Kendall et al., 2007) thus many studies have used the $\delta^{15}N$ values of atmospheric nitrate to investigate NO_x sources (Chang et al., 2018; Felix et al., 2012; Felix & Elliott, 2014; Gobel et al., 2013; Hastings et al., 2004, 2009; Morin et al., 2009; Park et al., 2018; Walters et al., 2015, 2018). However, there remain questions about how isotopic fractionations that may occur during photochemical cycling of NO_x could alter the $\delta^{15}N$ values as it partitions into NO_y (NO_y = atmospheric nitrate, NO_3, N_2O_5, HONO, etc., Chang et al., 2018; Freyer, 1991; Hastings et al., 2004; Jarvis et al., 2008; Michalski et al., 2005; Morin et al., 2009; Zong et al., 2017). Similarily, other complex reactive nitrogen chemistry, such as nitrate photolysis and re-deposition in ice and snow (Frey et al., 2009), may impact the $\delta^{15}N$ of NO_y and atmospheric nitrate. The fractionation between NO and NO_2 via isotope exchange has been suggested to be the dominant factor in determining the $\delta^{15}N$ of NO_2 and ultimately atmospheric nitrate (Freyer, 1991; Freyer et al., 1993; Savarino et al., 2013; Walters et al., 2016). However, isotopic fractionations occur in most, if not all, NO_x and NO_y reactions, while most of these are still unknown or, if calculated (Walters and Michalski, 2015), unverified by experiments. Since the atmospheric chemistry of NO_y varies significantly in different environments (e.g., polluted vs. pristine, night vs. day), the isotopic fractionations associated with NO_y chemistry are also likely to vary in different environments. These unknowns could potentially bias conclusions about NO_x source apportionment reached when using nitrogen isotopes. Therefore, understanding the isotopic

fractionations between NO and NO_2 during photochemical cycling could improve our understanding of the relative role of sources versus chemistry for controlling the $\delta^{15}N$ variations of atmospheric NO_2 and nitrate.

In general, there are three types of isotopic fractionation effects associated with NO_x chemistry (Fig. 1A). The first type is the equilibrium isotopic effect (EIE), i.e., isotope exchange between two compounds without forming new molecules (Urey, 1947, Bigeleisen and Mayer, 1947), which for nitrogen isotopes in the NO_x system is the $^{15}NO + {}^{14}NO_2 \leftrightarrow {}^{14}NO + {}^{15}NO_2$ exchange reaction (Begun and Melton, 1956, Walters et al., 2016). The second type is the kinetic isotopic effect (KIE) associated with difference in isotopologue rate coefficients during unidirectional reactions (Bigeleisen & Wolfsberg, 1957). In the NO_x system this KIE would manifest in the oxidation of NO into NO_2 by $O_3/HO_2/RO_2$. The third type is the photochemical isotope fractionation effect (PHIFE, Miller & Yung, 2000), which for NO_x is the isotopic fractionation associated with NO_2 photolysis. All three fractionations could impact the $\delta^{15}N$ value of NO_2, and consequently atmospheric nitrate, but the relative importance of each may vary.

The limited number of studies on the EIE in the NO_x cycle have significant uncertainties. Discrepancies in the EIE for $^{15}NO + {}^{14}NO_2 \leftrightarrow {}^{14}NO + {}^{15}NO_2$ have been noted in several studies. Theoretical calculations predicted isotope fractionation factors (α) ranging from 1.035 to 1.042 at room temperature (Begun & Fletcher, 1960; Monse et al., 1969; Walters & Michalski, 2015) due to the different approximations used to calculate harmonic frequencies in each study. Likewise, two separate experiments measured different room temperature fractionation factors of 1.028±0.002 (Begun & Melton, 1956) and 1.0356±0.0015 (Walters et al., 2016). A concern in both experiments is that they were conducted in small chambers with high NO_x concentrations (hundreds of μmol mol^{-1}), significantly higher than typical ambient atmospheric NO_x levels

(usually less than 0.1 μmol mol^{-1}). Whether the isotopic fractionation factors determined by these experiments are applicable in the ambient environment is uncertain because of possible wall effects and formation of higher oxides, notably N_2O_4 and N_2O_3 at these high NO_x concentrations.

Even less research has examined the KIE and PHIFE occurring during NO_x cycling. The KIE of NO + O_3 has been theoretically calculated (Walters and Michalski, 2016) but has not been experimentally verified. The NO_2 PHIFE has not been experimentally determined or theoretically calculated. As a result, field observation studies often overlook the effects of PHIFE and KIE. Freyer et al. (1993) measured NO_x concentrations and the $\delta^{15}N$ values of NO_2 over a 1-year period at Julich, Germany and inferred a combined NO_x isotope fractionation factor (EIE+KIE+PHIFE) of 1.018±0.001. Freyer et al. (1993) suggested that the NO_x photochemical cycle (KIE and PHIFE) tends to diminish the equilibrium isotopic fractionation (EIE) between NO and NO_2. Even if this approach were valid, applying this single fractionation factor elsewhere, where NO_x, O_3 concentrations and actinic fluxes are different, would be tenuous given that these factors may influence the relative importance of EIE, KIE and PHIFE (Hastings et al., 2004; Walters et al., 2016). Therefore, to quantify the overall isotopic fractionations between NO and NO_2 at various tropospheric conditions, it is crucial to know 1) isotopic fractionation factors of EIE, KIE and PHIFE individually and 2) the relative importance of each factor under various conditions.

In this work, we aim to quantify the nitrogen isotope fractionation factors between NO and NO_2 at photochemical equilibrium. First, we measure the N isotope fractionations between NO and NO_2 in an atmospheric simulation chamber at atmospherically relevant NO_x levels. Then, we provide mathematical solutions to assess the impact of NO_x level and NO_2 photolysis rate ($j(NO_2)$) to the relative importance of EIE, KIE and PHIFE. Subsequently we use the solutions and chamber measurements to calculate the isotopic fractionation factors of EIE, KIE and PHIFE. Lastly, using

the calculated fractionation factors and the equations, we model the NO-NO_2 isotopic fractionations at several sites to illustrate the behavior of $\delta^{15}N$ values of NO_x in the ambient environment.

2. Methods

The experiments were conducted using a 10 m^3 Atmospheric Simulation Chamber at the National Center for Atmospheric Research (see descriptions in supplementary material and Zhang et al. (2018)). A set of mass flow controllers was used to inject NO and O_3 into the chamber. NO was injected at 1 L min^{-1} from an in-house NO/N_2 cylinder (133.16 μmol mol^{-1} NO in ultra-pure N_2), and O_3 was generated by flowing 5 L min^{-1} zero-air through a flow tube equipped with a UV Pen-Ray lamp (UVP LLC., CA) into the chamber. NO and NO_2 concentrations were monitored in real time by chemiluminescence with a detection limit of 0.5 ppb (model CLD 88Y, Eco Physics, MI) as were O_3 concentrations using an UV absorption spectroscopy with a detection limit of 0.5 ppb (model 49, Thermo Scientific, CO). In each experiment, the actual amounts of NO and O_3 injected were calculated using measured NO_x and O_3 concentrations after steady state was reached (usually within 1 h). The wall loss rate of NO_2 was tested by monitoring O_3 (29 nmol mol^{-1}) and NO_x (62 nmol mol^{-1}) over a 4-hour period. After the NO and NO_2 concentrations reached steady state, no decrease in NO_2 concentrations was observed showing that chamber wall loss was negligible.

Two sets of experiments were conducted to separately investigate the EIE, KIE and PHIFE. The first set of experiments was conducted in the dark. In each of these dark experiments, a range of NO and O_3 ($[O_3]<[NO]$) was injected into the chamber to produce NO-NO_2 mixtures with $[NO]/[NO_2]$ ratios ranging from 0.43 to 1.17. The N isotopes of these mixtures were used to

investigate the EIE between NO and NO_2. The second set of experiments was conducted under irradiation of UV lights (300-500 nm, see supplementary material for irradiation spectrum). Under such conditions, NO, NO_2 and O_3 reached photochemical steady state, which combined the isotopic effects of EIE, KIE and PHIFE. In addition, three experiments were conducted to measure the $\delta^{15}N$ value of the tank NO. In each of these experiments, a certain amount of O_3 was first injected into the chamber, then approximately the same amount of NO was injected into the chamber to ensure 100% of the NO_x was in the form of NO_2 with little O_3 (<3 nmol mol^{-1}) remaining in the chamber, such that the O_3+NO_2 reaction was negligible. The NO_2 in the chamber was then collected and its $\delta^{15}N$ value measured, which equates to the $\delta^{15}N$ value of the tank NO.

In all experiments, the concentrations of NO, NO_2 and O_3 were allowed to reach steady state, and the product NO_2 was collected from the chamber using a honeycomb denuder tube. The glass denuder tubes (Chemcomb 3500, Thermo Fisher Scientific) were coated with a solution of 10% KOH and 25% guaiacol in methanol and then dried by flowing N_2 gas through the denuder tube for 15 seconds (Williams and Grosjean, 1990, Walters et al., 2016). The NO_2 reacted with guaiacol coating and was converted into NO_2^- that was retained on the denuder tube wall (Williams and Grosjean, 1990). NO was inert to the denuder tube coating: a control experiment sampled pure NO using the denuder tubes, which did not show any measurable NO_2^-. The NO_2 collection efficiency of a single honeycomb denuder tube was tested in another control experiment: air containing 66 nmol mol^{-1} of NO_2 was drawn out of the chamber through a denuder tube, and the NO_2 concentration at the exit of the tube holder was measured and found to be below the detection limit (<1 nmol mol^{-1}), suggesting the collection efficiency was nearly 100% when [NO_2] <66 nmol mol^{-1}. Furthermore, when the denuder system consisted of two denuder tubes in series and NO_2^- in the second denuder was below the detection limit indicating trivial NO_2 breakthrough. The NO_2^-

148 was leached from each denuder tube by rinsing thoroughly with 10 ml deionized water into a clean
149 polypropylene container and stored frozen until isotopic analysis. Isotopic analysis was conducted
150 at Purdue Stable Isotope Laboratory. For each sample, approximately 50 nmol of the NO_2^- extract
151 was mixed with 2 M sodium azide solution in acetic acid buffer in an air-tight glass vial, then
152 shaken overnight to completely reduce all the NO_2^- to $N_2O_{(g)}$ (Casciotti & McIlvin, 2007; McIlvin
153 & Altabet, 2005). The product N_2O was directed into a Thermo GasBench equipped with cryo-
154 trap, then the $\delta^{15}N$ of the N_2O was measured using a Delta-V Isotope Ratios Mass Spectrometer.
155 Six coated denuders tubes that did not get exposed to NO_2 were also analyzed using the same
156 chemical procedure, which did not show any measurable signal on the IRMS, suggesting the blank
157 from both sampling process and the chemical conversion process was negligible. The overall
158 analytical uncertainty for $\delta^{15}N$ analysis was ±0.5 ‰ (1σ) based on replicate analysis of in house
159 NO_2^- standards.
160
161 **3. Results and Discussions**
162 **3.1. Equilibrium Isotopic Fractionation between NO and NO_2**
163 The equilibrium isotope fractionation factor, $\alpha(NO_2\text{-}NO)$, is the ^{15}N enrichment in NO_2
164 relative to NO, and is expressed as the ratio of rate constants k_2 / k_1 of two reactions:
165 $^{15}NO_2 + {}^{14}NO \rightarrow {}^{15}NO + {}^{14}NO_2$ R1, rate constant = k_1
166 $^{15}NO + {}^{14}NO_2 \rightarrow {}^{15}NO_2 + {}^{14}NO$ R2, rate constant = $k_2 = k_1 \times \alpha(NO_2\text{-}NO)$
167 where k_1 is the rate constant of the isotopic exchange, which was previously determined to be
168 8.14×10^{-14} cm^3 s^{-1} (Sharma et al., 1970). The reaction time required for NO-NO_2 to reach isotopic
169 equilibrium was estimated using the exchange rate constants in a simple kinetics box model
170 (BOXMOX, Knote et al., 2015). The model predicts that at typical NO_x concentrations used during

171 the chamber experiments (7.7-62.4 nmol mol^{-1}), isotopic equilibrium would be reached within 15
172 minutes (see supplementary material). Since the sample collection usually started 1 hour after NO_x
173 was well mixed in the chamber, there was sufficient time to reach full isotope equilibrium. The
174 isotope equilibrium fractionation factor is then calculated to be:

175 $$\alpha(NO_2 - NO) = \frac{[^{15}NO_2]\times[^{14}NO]}{[^{14}NO_2]\times[^{15}NO]} = \frac{R(NO_2)}{R(NO)} \quad \text{Eq. (1)}$$

176 where R(NO, NO_2) are the $^{15}N/^{14}N$ ratios of NO and NO_2. By definition, the
177 $\delta^{15}N(NO)=(R(NO)/R(reference)-1)\times1000‰$ and $\delta^{15}N(NO_2)=(R(NO_2)/R(reference)-1)\times1000$ ‰,
178 but hereafter, the $\delta^{15}N$ values of NO, NO_2 and NO_x will be referred as $\delta(NO)$, $\delta(NO_2)$ and $\delta(NO_x)$,
179 respectively. Eq. (1) leads to:

180 $$\delta(NO_2) - \delta(NO) = (\alpha(NO_2 - NO) - 1) \times 1000\,‰ \times (1 + \delta(NO))$$

181 $$= \varepsilon(NO_2 - NO) \times (1 + \delta(NO)) \quad \text{Eq. (2)}$$

182 where $\varepsilon(NO_2\text{-}NO)$ is the isotope enrichment factor ($\varepsilon(NO_2\text{-}NO) = (\alpha(NO_2\text{-}NO)-1)\times1000‰$, Hoefs,
183 2009). Using Eq. (2) and applying NO_x isotopic mass balance ($\delta(NO_x)=f(NO_2)\times\delta(NO_2)+(1-$
184 $f(NO_2))\times\delta(NO)$, $f(NO_2)=[NO_2]/([NO]+[NO_2])$ yields:

185 $$\delta(NO_2) - \delta(NO_x) = \varepsilon(NO_2 - NO) \times (1 + \varepsilon(NO_2 - NO)) \times (1 + \delta(NO_2)) \times (1 - f(NO_2)) \quad \text{Eq. (3)}$$

186 Here, $\delta(NO_x)$ equals to the $\delta^{15}N$ value of the cylinder NO and $f(NO_2)$ is the molar fraction of NO_2
187 with respect to total NO_x. Three experiments (see descriptions in method section) that measured
188 $\delta(NO_x)$ showed consistent $\delta(NO_x)$ values of -58.7±0.8 ‰ (n = 3), indicating $\delta(NO_x)$ remained
189 unchanged throughout the experiments (as expected for isotope mass balance). Thus, the $\delta(NO_x)$
190 can be treated as a constant in Eq. (3), and the linear regression of $(\delta(NO_2)-\delta(NO_x))/(1+\delta(NO_2))$
191 versus $1-f(NO_2)$ should have an intercept of 0 and a slope of $\varepsilon(NO_2\text{-}NO)/(1+\varepsilon(NO_2\text{-}NO))$.

The plot of $(\delta(NO_2)-\delta(NO_x))/(1+\delta(NO_2))$ as a function of $1-f(NO_2)$ values from five experiments yields an $\varepsilon(NO_2\text{-}NO)$ value of 27.5±1.2 ‰ at room temperature (Fig. 1B). This fractionation factor is comparable to previously measured values but with some differences. Our result agrees well with the $\alpha(NO_2\text{-}NO)$ value of 1.028±0.002 obtained by Begun and Melton (1956) at room temperature. However, Walters et al., (2016) determined the $\alpha(NO_2\text{-}NO)$ values of NO-NO_2 exchange in a 1-liter reaction vessel, which showed a slightly higher $\alpha(NO_2\text{-}NO)$ value of 1.035. This discrepancy might originate from rapid heterogeneous reactions on the wall of the reaction vessel at high NO_x concentrations and the small chamber size used by Walters et al. (2016). They used a reaction vessel made of Pyrex, which is known to absorb water (Do Remus et al., 1983; Takei et al., 1997) that can react with NO_2 forming HONO, HNO_3 and other N compounds. Additionally, previous studies have suggested that Pyrex walls enhance the formation rate of N_2O_4 by over an order of magnitude (Barney & Finlayson-Pitts, 2000; Saliba et al., 2001), which at isotopic equilibrium is enriched in ^{15}N compared to NO and NO_2 (Walters & Michalski, 2015). Therefore, their measured $\alpha(NO_2\text{-}NO)$ might be slightly higher than the actual $\alpha(NO_2\text{-}NO)$ value. In this work, the 10 m^3 chamber has a much smaller surface to volume ratio relative to Walters et al. (2016) which minimizes wall effects, and the walls were made of Teflon that minimize NO_2 surface reactivity, which was evidenced by the NO_2 wall loss control experiment. Furthermore, the low NO_x mixing ratios in our experiments minimized N_2O_4 and N_2O_3 formation. At NO and NO_2 concentrations of 50 nmol mol^{-1} the steady state concentrations of N_2O_4 and N_2O_3 were calculated to be 0.014 and 0.001 pmol mol^{-1}, respectively (Atkinson et al., 2004). Therefore, we suggest our measured $\alpha(NO_2\text{-}NO)$ value (1.0275±0.0012) may better reflect the room temperature (298 K) NO-NO_2 EIE in the ambient environment.

Unfortunately, the chamber temperature could not be controlled so we were not able to investigate the temperature dependence of the EIE. Hence, we speculate that the $\alpha(NO_2\text{-}NO)$ follows a similar temperature dependence pattern calculated in Walters et al. (2016). Walters et al. (2016) suggested that, the $\varepsilon(NO_2\text{-}NO)$ value would be 4.7 ‰ higher at 273 K and 2.0 ‰ lower at 310 K, relative to room temperature (298 K). Using this pattern and our experimentally determined data, we suggest the $\alpha(NO_2\text{-}NO)$ values at 273 K, 298 K and 310 K are 32.2±1.2 ‰, 27.5±1.2 ‰ and 25.5±1.2 ‰, respectively. This 6.7‰ variation at least partially contribute to the daily and seasonal variations of $\delta^{15}N$ values of NO_2 and nitrate in some areas (e.g., polar regions with strong seasonal temperature variation). Thus, future investigations should be conducted to verify the EIE temperature dependence.

3.2. Kinetic isotopic fractionation of Leighton Cycle

The photochemical reactions of NO_x will compete with the isotope exchange fractionations between NO and NO_2. The NO-NO_2 photochemical cycle in the chamber was controlled by the Leighton cycle: NO_2 photolysis and the NO + O_3 reaction. This is because there were no VOCs in the chamber so no RO_2 was produced, which excludes the NO + RO_2 reaction. Likewise, the low water vapor content (RH<10%) and the minor flux of photons < 310 nm results in minimal OH production and hence little HO_2 formation and subsequently trivial amount of NO_2 would be formed by NO + HO_2. Applying these limiting assumptions, the EIE between NO and NO_2 (R1-R2) were only competing with the KIE (R3-R4) and the PHIFE in R5-R6:

$^{14}NO_2 \rightarrow {}^{14}NO + O$ R3, rate constant=$j(NO_2)$

$^{15}NO_2 \rightarrow {}^{15}NO + O$ R4, rate constant=$j(NO_2)\times\alpha_1$

$^{14}NO + O_3 \rightarrow {}^{14}NO_2 + O_2$ R5, rate constant=k_5

$^{15}NO+O_3 \rightarrow {}^{15}NO_2+O_2$ R6, rate constant=$k_5 \times \alpha_2$

In which $j(NO_2)$ is the NO_2 photolysis rate (1.4×10^{-3} s^{-1} in these experiments), k_5 is the rate constant for the $NO+O_3$ reaction (1.73×10^{-14} cm^3 s^{-1}, Atkinson et al., 2004), and $\alpha_{1,2}$ are isotopic fractionation factors for the two reactions. Previous studies (Freyer et al., 1993; Walters et al., 2016) have attempted to assess the competition between EIE (R1-R2), KIE and PHIFE (R3-R6), but none of them quantified the relative importance of the two processes, nor were α_1 or α_2 values experimentally determined. Here we provide the mathematical solution of EIE, KIE and PHIFE to illustrate how R1-R6 affect the isotopic fractionations between NO and NO_2.

First, the NO_2 lifetime with respect to isotopic exchange with NO ($\tau_{exchange}$) and photolysis (τ_{photo}) was determined:

$$\tau_{exchange} = \frac{1}{k_1 \times [NO]} \quad \text{Eq. (4)}$$

$$\tau_{photo} = \frac{1}{j(NO_2)} \quad \text{Eq. (5)}$$

We then define an A factor:

$$A = \begin{cases} \frac{\tau_{exchange}}{\tau_{photo}} & \text{when } j(NO_2) \neq 0 \\ 0 & \text{when } j(NO_2) = 0 \end{cases} \quad \text{Eq. (6)}$$

Using R1-R6 and Eq. (1)-(6), we solved steady-state $\delta(NO_2)$ and $\delta(NO)$ values (see calculations in supplementary material). Our calculations show that the $\delta(NO_2)$-$\delta(NO)$ and $\delta(NO_2)$-$\delta(NO_x)$ values at steady state can be expressed as functions of α_1, α_2, $\alpha(NO_2\text{-}NO)$ and A:

$$\delta(NO_2) - \delta(NO)\ (‰) = \frac{(\alpha_2-\alpha_1)\times A+(\alpha(NO_2-NO)-1)}{A+1} \times 1000\ ‰ \quad \text{Eq. (7)}$$

$$\delta(NO_2) - \delta(NO_x)\ (‰) = \frac{(\alpha_2-\alpha_1)\times A+(\alpha(NO_2-NO)-1)}{A+1} \times (1 - f(NO_2)) \times 1000\ ‰ \quad \text{Eq. (8)}$$

Equation (7) shows the isotopic fractionation between NO and NO_2 ($\delta(NO_2)$-$\delta(NO)$) is largely determined by A, the EIE factor ($\alpha(NO_2\text{-}NO)$-1) and the (α_2-α_1) factor. This (α_2-α_1) represents a

combination of KIE and PHIFE, suggesting they act together as one factor; therefore, we name the (α_2-α_1) factor Leighton Cycle Isotopic Effect, i.e., LCIE. Using measured $\delta(NO_2)$-$\delta(NO)$ values, A values, and the previously determined EIE factor, we calculated that the best fit for the LCIE factor was -10±5 ‰ (showing the lowest Rooted Mean Square Error, RMSE, of 1.1‰, Fig. 1C). The uncertainties in the LCIE factor are relatively higher than that of the EIE factor, mainly because of the accumulated analytical uncertainties at low NO_x and O_3 concentrations, and low A values (0.10-0.28) due to the relatively low $j(NO_2)$ value (1.4×10^{-3} s^{-1}) under the chamber irradiation conditions.

This LCIE factor determined in our experiments is in good agreement with theoretical calculations. Walters and Michalski (2016) previously used an *ab initio* approach to determine an α_2 value of 0.9933 at room temperature, 0.9943 at 237 K and 0.9929 at 310 K. The variation of α_2 values from 273 K to 310 K is only ±0.7 ‰, significantly smaller than our experimental uncertainty. The α_1 value was calculated using a ZPE shift model (Miller & Yung, 2000) to calculate the isotopic fractionation of NO_2 by photolysis. Briefly, this model assumes both isotopologues have the same quantum yield function and the PHIFE was only caused by the differences in the $^{15}NO_2$ and $^{14}NO_2$ absorption cross-section as a function of wavelength, thus α_1 values do not vary by temperature. The $^{15}NO_2$ absorption cross-section was calculated by shifting the $^{14}NO_2$ absorption cross-section by the $^{15}NO_2$ zero-point energy (Michalski et al., 2004). When the ZPE shift model was used with the irradiation spectrum of the chamber lights, the resulting α_1 value was 1.0023. Therefore, the theoretically predicted α_2-α_1 value should be -0.0090, i.e., -9.0±0.7 ‰ when temperature ranges from 273 K to 310 K. This result shows excellent agreement with our experimentally determined room temperature α_2-α_1 value of -10±5 ‰.

This model was then used to evaluate the variations of α_1 value to different lighting conditions. The TUV model (TUV5.3.2, Madronich & Flocke, 1999) was used to calculate the solar wavelength spectrum at three different conditions: early morning/late afternoon (solar zenith angle=85 degree), mid-morning/afternoon (solar zenith angle=45 degree), noon (solar zenith angle=0 degree). These spectrums were used in the ZPE shift model to calculate the α_1 values, which are 1.0025, 1.0028, and 1.0029 at solar zenith angles of 85, 45 and 0 degree, respectively. These values, along with the predicted α_1 value in the chamber, showed a total span of 0.6‰ (1.0026 ±0.0003), which is again significantly smaller than our measured uncertainty. Therefore, we suggest that our experimentally determined LCIE factor (-10±5 ‰) can be used in most tropospheric solar irradiation spectrums.

The equations can also be applied in tropospheric environments to calculate the combined isotopic fractionations of EIE and LCIE for NO and NO_2. First, the NO_2 sink reactions (mainly NO_2+OH in the daytime) are at least 2-3 orders of magnitude slower than the Leighton cycle and the NO-NO_2 isotope exchange reactions (Walters et al., 2016), therefore their effects on the $\delta(NO_2)$ should be minor. Second, although the conversion of NO into NO_2 in the ambient environment is also controlled by NO + RO_2 and HO_2 in addition to NO+O_3 (e.g., King et al., 2001), Eq. (7) still showed good agreement with field observations in previous studies. Freyer et al. (1993) determined the annual average daytime $\delta(NO_2)$-$\delta(NO)$ at Julich, Germany along with average daytime NO concentration (9 nmol mol^{-1}, similar to our experimental conditions) to be +18.03±0.98 ‰. Using Eq. (7), assuming the daytime average $j(NO_2)$ value throughout the year was $5.0\pm1.0\times10^{-3}$, and a calculated A value from measured NO_x concentration ranged from 0.22-0.33, the average NO-NO_2 fractionation factor was calculated to be +18.8±1.4 ‰ (Fig. 1C), in excellent agreement with the measurements in the present study. This agreement suggests the

303 $NO+RO_2/HO_2$ reactions might have similar fractionation factors as $NO+O_3$. Therefore, we suggest
304 Eq. (7) and (8) can be used to estimate the isotopic fractionations between NO and NO_2 in the
305 troposphere.
306
307 **3.3 Calculating nitrogen isotopic fractionations of NO-NO_2**
308 First, Eq. (7) was used to calculate the $\Delta(NO_2\text{-}NO) = \delta(NO_2)\text{-}\delta(NO)$ at a wide range of
309 NO_x concentrations, $f(NO_2)$ and $j(NO_2)$ values (Fig. 2A-D). $j(NO_2)$ values of 0 s^{-1} (Fig. 2A),
310 1.4×10^{-3} s^{-1} (Fig. 2B), 5×10^{-3} s^{-1} (Fig. 2C) and 1×10^{-2} s^{-1} (Fig. 2D) were selected to represent
311 nighttime, dawn (as well as the laboratory conditions of our experiments), daytime average and
312 noon, respectively. Each panel represented a fixed $j(NO_2)$ value, and the $\Delta(NO_2\text{-}NO)$ values were
313 calculated as a function of the A value, which was derived from NO_x concentration and $f(NO_2)$.
314 The A values have a large span, from 0 to 500, depending on the $j(NO_2)$ value and the NO
315 concentration. When A=0 ($j(NO_2)=0$) and $f(NO_2)<1$ (meaning NO-NO_2 coexist and $[O_3]=0$), Eq.
316 (7) and (8) become Eq. (2) and (3), showing the EIE was the sole factor, the $\Delta(NO_2\text{-}NO)$ values
317 were solely controlled by EIE which has a constant value of +27.5 ‰ at 298K (Fig. 2A). When
318 $j(NO_2)>0$, the calculated $\Delta(NO_2\text{-}NO)$ values showed a wide range from -10.0 ‰ (controlled by
319 LCIE factor: $\alpha_2\text{-}\alpha_1$=-10 ‰) to +27.5 ‰ (controlled by EIE factor: $\alpha(NO_2\text{-}NO)\text{-}1$ = +27.5 ‰). Fig.
320 2B-D display the transition from a LCIE-dominated regime to an EIE-dominated regime. The
321 LCIE-dominated regime is characterized by low $[NO_x]$ (<50 pmol mol^{-1}), representing remote
322 ocean areas and polar regions (Beine et al., 2002; Custard et al., 2015). At this range the A value
323 can be greater than 200, thus Eq. (7) can be simplified as: $\Delta(NO_2\text{-}NO) = (\alpha_2\text{-}\alpha_1)\times1000$ ‰,
324 suggesting the LCIE almost exclusively controls the NO-NO_2 isotopic fractionation. The $\Delta(NO_2\text{-}$
325 NO) values of these regions are predicted to be <0 ‰ during most time of the day and < -5 ‰ at

noon. On the other hand, the EIE-dominated regime was characterized by high [NO_x] (>20 nmol mol^{-1}) and low $f(NO_2)$ (< 0.6), representative of regions with intensive NO emissions, e.g., near roadside or stack plumes (Clapp & Jenkin, 2001; Kimbrough et al., 2017). In this case, the $\tau_{exchange}$ are relatively short (10-50 s) compared to the τ_{photo} (approximately 100 s at noon and 1000 s at dawn), therefore the A values are small (0.01-0.5). The EIE factor in this regime thus is much more important than the LCIE factor, resulting in high $\Delta(NO_2\text{-}NO)$ values (>20 ‰). Between the two regimes, both EIE and LCIE are competitive and therefore it is necessary to use Eq. (7) to quantify the $\Delta(NO_2\text{-}NO)$ values.

Fig. 2 also implies that changes in the $j(NO_2)$ value can cause the diurnal variations in $\Delta(NO_2\text{-}NO)$ values. Changing $j(NO_2)$ would affect the value of A and consequently the NO-NO_2 isotopic fractionations in two ways: 1) changes in $j(NO_2)$ value would change the photolysis intensity, therefore the τ_{photo} value; 2) in addition, changes in $j(NO_2)$ value would also alter the steady state NO concentration, therefore changing the $\tau_{exchange}$ (Fig. 2C). The combined effect of these two factors on the A value varies along with the atmospheric conditions, and thus needs to be carefully calculated using NO_x concentration data and atmospheric chemistry models.

We then calculated the differences of $\delta^{15}N$ values between NO_2 and total NO_x, e.g. $\Delta(NO_2\text{-}NO_x) = \delta(NO_2)\text{-}\delta(NO_x)$ in Fig. 2E-H. Since $\Delta(NO_2\text{-}NO_x)$ are connected through the observed $\delta^{15}N$ of NO_2 (or nitrate) to the $\delta^{15}N$ of NO_x sources, this term might be useful in field studies (e.g., Chang et al., 2018; Zong et al., 2017). The calculated $\Delta(NO_2\text{-}NO_x)$ values (Fig. 2E-H) also showed a LCIE-dominated regime at low [NO_x] and an EIE-dominated regime at high [NO_x]. The $\Delta(NO_2\text{-}NO_x)$ values were dampened by the $1\text{-}f(NO_2)$ factor comparing to $\Delta(NO_2\text{-}NO)$, as shown in Eq. (3) and (8): $\Delta(NO_2\text{-}NO_x) = \Delta(NO_2\text{-}NO)\times(1\text{-}f(NO_2))$. At high $f(NO_2)$ values (>0.8), the differences between $\delta(NO_2)$ and $\delta(NO_x)$ were less than 5 ‰, thus the measured $\delta(NO_2)$ values were similar to

$\delta(NO_x)$, although the isotopic fractionation between NO and NO_2 could be noteworthy. Some ambient environments with significant NO emissions or high NO_2 photolysis rates usually have $f(NO_2)$ values between 0.4-0.8 (Mazzeo et al., 2005; Vicars et al., 2013). In this scenario, the $\Delta(NO_2\text{-}NO_x)$ values in Fig. 2F-H showed wide ranges of -4.8 ‰ to +15.6 ‰, -6.0 ‰ to +15.0 ‰, and -6.3 ‰ to +14.2 ‰ at $j(NO_2)$=1.4×10^{-3} s^{-1}, 5×10^{-3} s^{-1}, 1×10^{-2} s^{-1}, respectively. These significant differences again highlighted the importance of both LCIE and EIE (Eq. (7) and (8)) in calculating the $\Delta(NO_2\text{-}NO_x)$. In the following discussion, we assume 1) the α_1 value remain constant (see discussion above), 2) the $NO+RO_2/HO_2$ reactions have the same fractionation factors (α_2) as $NO+O_3$, and 3) both EIE and LCIE do not display significant temperature dependence, then use Equations (7) and (8) and this laboratory determined LCIE factor (-10 ‰) to calculate the nitrogen isotopic fractionation between NO and NO_2 at various tropospheric atmospheric conditions.

4. Implications

The daily variations of $\Delta(NO_2\text{-}NO_x)$ values at two roadside NO_x monitoring sites were predicted to demonstrate the effects of NO_x concentrations to the $NO\text{-}NO_2$ isotopic fractionations. Hourly NO and NO_2 concentrations were acquired from a roadside site at Anaheim, CA (https://www.arb.ca.gov) and an urban site at Evansville, IN (http://idem.tx.sutron.com) on July 25, 2018. The hourly $j(NO_2)$ values output from the TUV model (Madronich & Flocke, 1999) at these locations was used to calculate the daily variations of $\Delta(NO_2\text{-}NO_x)$ values (Fig. 3A, B) by applying Eq. (8). Hourly NO_x concentrations were 12-51 nmol mol^{-1} at Anaheim and 9-38 nmol mol^{-1} at Evansville and the $f(NO_2)$ values at both sites did not show significant daily variations (0.45±0.07 at Anaheim and 0.65±0.08 at Evansville), likely because the NO_x concentrations were controlled by the high NO emissions from the road (Gao, 2007). The calculated $\Delta(NO_2\text{-}NO_x)$

values using Eq. (8) showed significant diurnal variations. During the nighttime, the isotopic fractionations were solely controlled by the EIE, the predicted $\Delta(NO_2\text{-}NO_x)$ values were +14.5±2.0 ‰ and +8.7±2.1 ‰ at Anaheim and Evansville, respectively. During the daytime, the existence of LCIE lowered the predicted $\Delta(NO_2\text{-}NO_x)$ values to +9.8±1.7 ‰ at Anaheim and +3.1±1.5 ‰ at Evansville while the $f(NO_2)$ values at both sites remained similar. The lowest $\Delta(NO_2\text{-}NO_x)$ values for both sites (+7.0 ‰ and +1.7 ‰) occurred around noon when the NO_x photolysis was the most intense. In contrast, if one neglects the LCIE factor in the daytime, the $\Delta(NO_2\text{-}NO_x)$ values would be +12.9±1.5 ‰ and +10.0±1.6 ‰ respectively, an overestimation of 3.1 ‰ and 6.9 ‰. These discrepancies suggested that the LCIE played an important role in the NO-NO_2 isotopic fractionations and neglecting it could bias the NO_x source apportionment using $\delta^{15}N$ of NO_2 or nitrate.

The role of LCIE was more important in less polluted sites. The $\Delta(NO_2\text{-}NO_x)$ values calculated for a suburban site near San Diego, CA, USA, again using the hourly NO_x concentrations (https://www.arb.ca.gov, Fig. 3C) and $j(NO_2)$ values calculated from the TUV model. NO_x concentrations at this site varied from 1 to 9 nmol mol^{-1}. During the nighttime, NO_x was in the form of NO_2 ($f(NO_2) = 1$) because O_3 concentrations were higher than NO_x, thus the $\delta(NO_2)$ values should be identical to $\delta(NO_x)$ ($\Delta(NO_2\text{-}NO_x) = 0$). In the daytime a certain amount of NO was produced by direct NO emission and NO_2 photolysis but the $f(NO_2)$ was still high (0.73±0.08). Our calculation suggested the daytime $\Delta(NO_2\text{-}NO_x)$ values should be only +1.3±3.2 ‰ with a lowest value of -1.3 ‰. These $\Delta(NO_2\text{-}NO_x)$ values were similar to the observed and modeled summer daytime $\delta(NO_2)$ values in West Lafayette, IN (Walters et al., 2018), which suggest the average daytime $\Delta(NO_2\text{-}NO_x)$ values at NO_x = 3.9±1.2 nmol mol^{-1} should range from +0.1 ‰ to

+2.4 ‰. In this regime, we suggest the $\Delta(NO_2\text{-}NO_x)$ values were generally small due to the significant contribution of LCIE and high $f(NO_2)$.

The LCIE should be the dominant factor controlling the NO-NO_2 isotopic fractionation at remote regions, resulting in a completely different diurnal pattern of $\Delta(NO_2\text{-}NO_x)$ compared with the urban-suburban area. Direct hourly measurements of NO_x at remote sites are rare, thus we used total NO_x concentration of 50 pmol mol^{-1}, daily O_3 concentration of 20 nmol mol^{-1} at Summit, Greenland (Dibb et al., 2002; Hastings et al., 2004; Honrath et al., 1999; Yang et al., 2002), and assumed the conversion of NO to NO_2 was completely controlled by O_3 to calculate the NO/NO_2 ratios. Here the isotopes of NO_x were almost exclusively controlled by the LCIE due to the high A values (>110). The $\Delta(NO_2\text{-}NO_x)$ values displayed a clear diurnal pattern (Fig. 3D) with highest value of -0.3 ‰ in the "nighttime" (solar zenith angle >85 degree) and lowest value of -5.0 ‰ in the mid-day. This suggest that the isotopic fractionations between NO and NO_2 were almost completely controlled by LCIE at remote regions, when NO_x concentrations were <0.1 nmol mol^{-1}. However, since the isotopic fractionation factors of nitrate-formation reactions (NO_2+OH, NO_3+HC, N_2O_5+H_2O) are still unknown, more studies are needed to fully explain the daily and seasonal variations of $\delta(NO_3^-)$ at remote regions.

Nevertheless, our results have a few limitations. First, currently there are very few field observations that can be used to evaluate our model, therefore, future field observations that measure the $\delta^{15}N$ values of ambient NO and NO_2 should be carried out to test our model. Second, more work, including theoretical and experimental studies, is needed to investigate the isotope fractionation factors occurring during the conversion from NO_x to NO_y and nitrate: in the NO_y cycle, EIE (isotopic exchange between NO_2, NO_3 and N_2O_5), KIE (formation of NO_3, N_2O_5 and nitrate) and PHIFE (photolysis of NO_3, N_2O_5, HONO and sometimes nitrate) may also exist and

417 be relevant for the $\delta^{15}N$ of HNO_3 and HONO. In particular, the N isotope fractionation occurring
418 during the $NO_2 + OH \rightarrow HNO_3$ reaction needs investigation. Such studies could help us modeling
419 the isotopic fractionation between NO_x emission and nitrate, and eventually enable us to analyze
420 the $\delta^{15}N$ value of NO_x emission by measuring the $\delta^{15}N$ values of nitrate aerosols and nitrate in wet
421 depositions. Third, our discussion only focuses on the reactive nitrogen chemistry in the
422 troposphere, however, the nitrogen chemistry in the stratosphere is drastically different from the
423 tropospheric chemistry, thus future studies are also needed to investigate the isotopic fractionations
424 in the stratospheric nitrogen chemistry. Last, the temperature dependence of both EIE and LCIE
425 needs to be carefully investigated, because of the wide range of temperature in both troposphere
426 and stratosphere. Changes in temperature could alter the isotopic fractionation factors of both EIE
427 and LCIE, as well as contribute to the seasonality of isotopic fractionations between NO_x and NO_y
428 molecules.
429
430 **5. Conclusions**
431 The effect of NO_x photochemistry on the nitrogen isotopic fractionations between NO and
432 NO_2 was investigated. We first measured the isotopic fractionations between NO and NO_2 and
433 provided mathematical solutions to assess the impact of NO_x level and NO_2 photolysis rate ($j(NO_2)$)
434 to the relative importance of EIE and LCIE. The EIE and LCIE isotope fractionation factors, at
435 room temperature, were determined to be 1.0275±0.0012 and 0.990±0.005, respectively. These
436 calculations and measurements can be used to determine the steady state $\Delta(NO_2\text{-}NO)$ and $\Delta(NO_2\text{-}$
437 $NO_x)$ values at room temperature. Subsequently we applied our equations to polluted, clean and
438 remote sites to model the daily variations of $\Delta(NO_2\text{-}NO_x)$ values. We found that the $\Delta(NO_2\text{-}NO_x)$
439 values could vary from over +20 ‰ to less than -5 ‰ depending on the environment: in general,

the role of LCIE becoming more important at low NO_x concentrations, which tend to decrease the $\Delta(NO_2\text{-}NO_x)$ values. Our work provided a mathematical approach to quantify the nitrogen isotopic fractionations between NO and NO_2 that can be applied to many tropospheric environments, which could help interpret the measured $\delta^{15}N$ values of NO_2 and nitrate in field observation studies.

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Data Availability

Data acquired from this study was deposited at Open Sciences Framework (Li, 2019, DOI 10.17605/OSF.IO/JW8HU).

Author contribution

J. Li and G. Michalski designed the experiments, X. Zhang and J. Li conducted the experiments. X. Zhang, G. Michalski, J. Orlando and G. Tyndall helped J. Li in interpreting the results. The manuscript was written by J. Li and all the authors have contributed during the revision of this manuscript.

Competing interest

The authors declare no competing interest.

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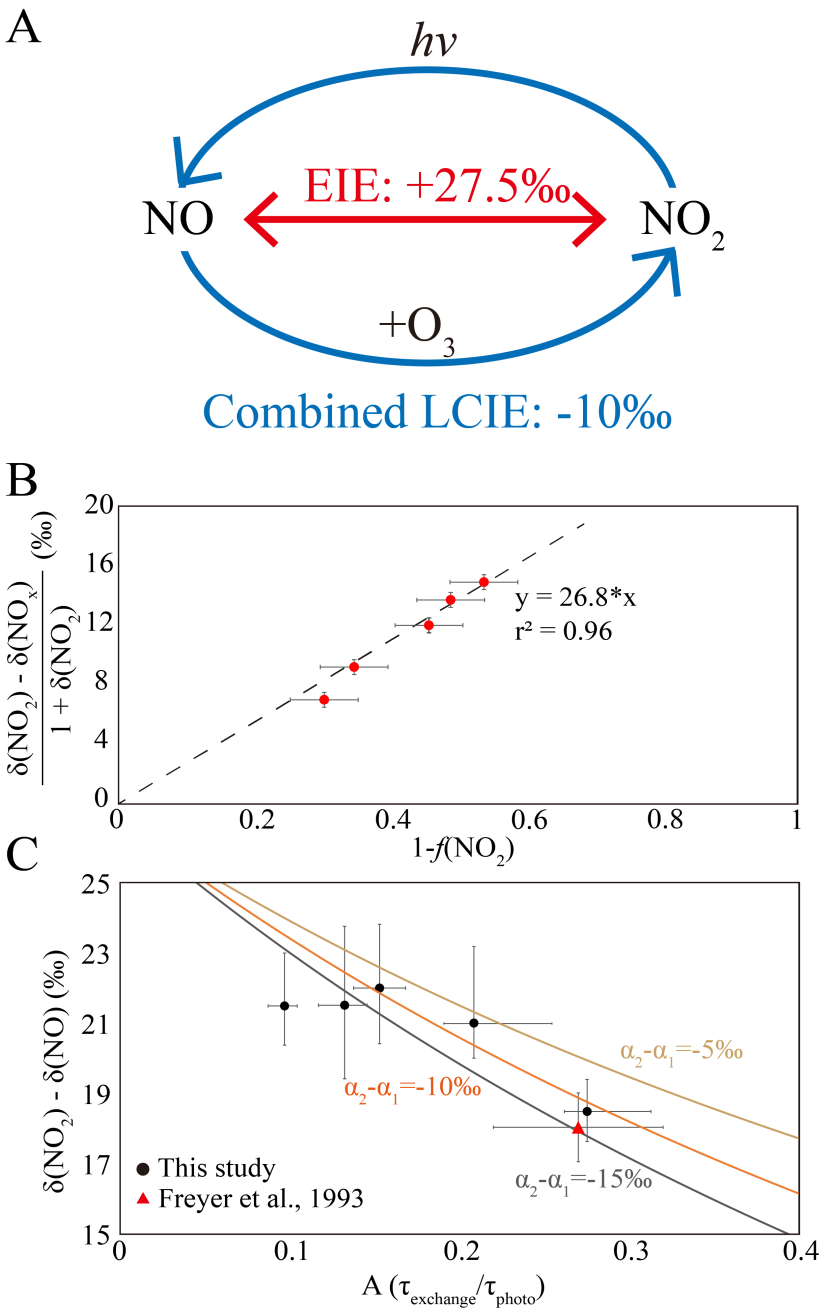

Fig. 1 A. a sketch of the isotopic fractionation processes between NO and NO_2, both fractionation factors are determined in this work. **B.** Results from five dark experiments yielded a line with $\varepsilon(NO_2\text{-}NO)/(1+\varepsilon(NO_2\text{-}NO))$ value of 26.8 ‰ and $\varepsilon(NO_2\text{-}NO)$ value of 27.5 ‰; **C.** Results from five UV irradiation experiments (black points) and a previous field study (red triangle). The three lines represent different (α_2-α_1) values: the (α_2-α_1)=-10 ‰ line showed the lowest RMSE to our experimental data as well as the previous field observation. The error bars in panels B and C represented the combined uncertainties of NO_x concentration measurements and isotopic analysis.

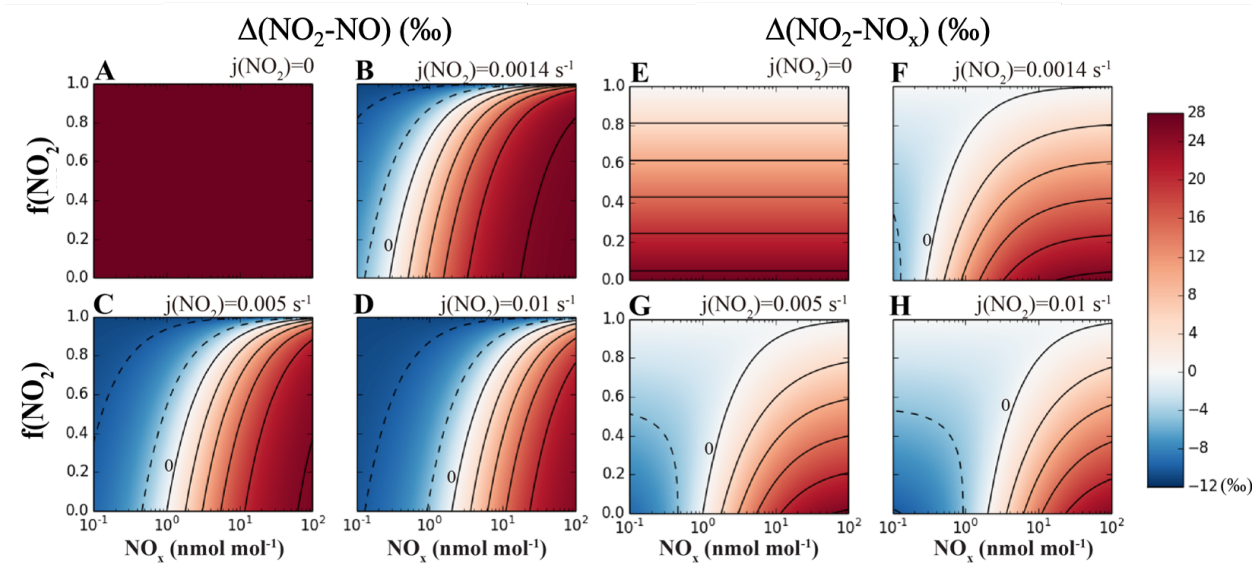

Fig. 2 Calculating isotopic fractionation values between NO-NO_2 ($\Delta(NO_2\text{-}NO)$, **A-D**) and NO_x-NO_2 ($\Delta(NO_2\text{-}NO_x)$, **E-H**) at various $j(NO_2)$, NO_x level and $f(NO_2)$ using Eq. (7) and (8). Each panel represents a fixed $j(NO_2)$ value (showing on the upper right side of each panel), and the fractionation values are shown by color. Lines are contours with the same fractionation values, at an interval of 5‰, the contour line representing 0‰ was marked on each panel except for A and E.

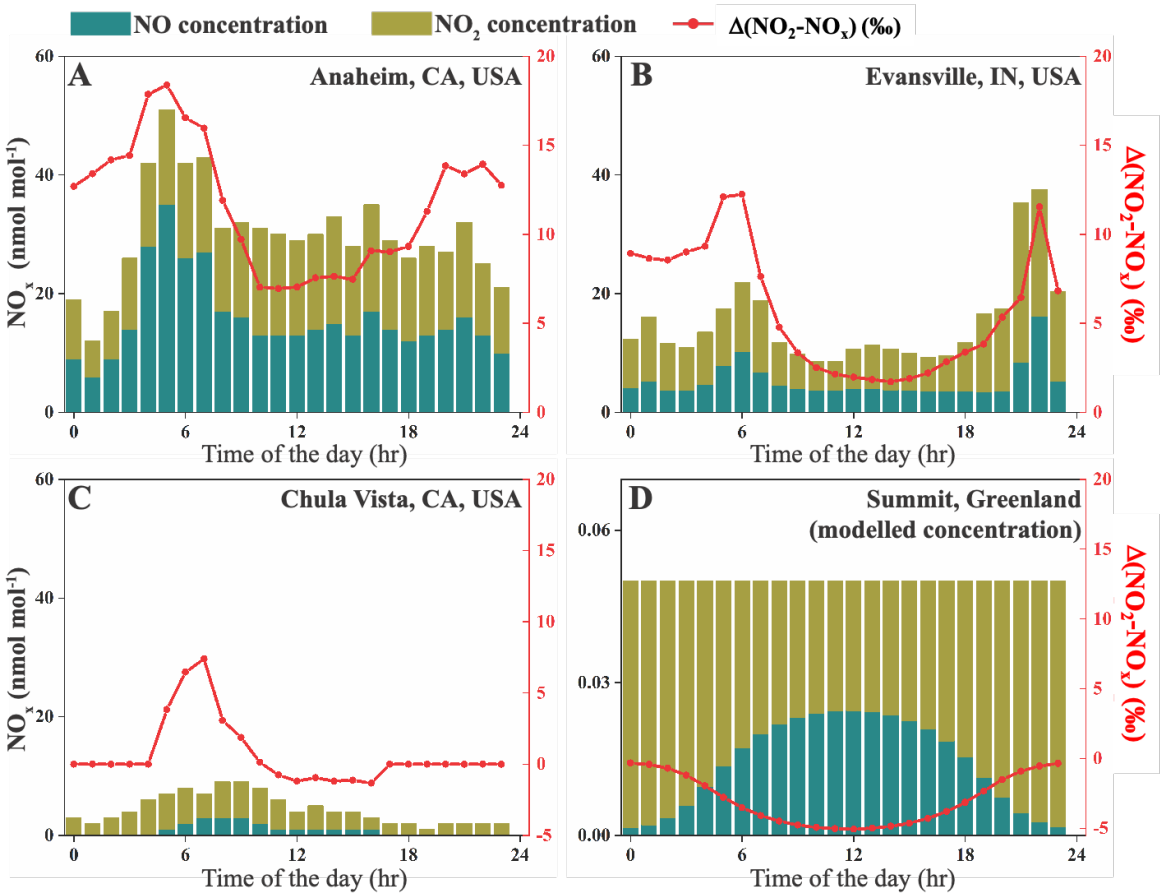

Fig. 3 NO_x concentrations and calculated $\Delta(NO_2\text{-}NO_x)$ values at four sites. Stacked bars show the NO and NO_2 concentrations extracted from monitoring sites (A-C) or calculated using 0-D box model (D); the red lines are $\Delta(NO_2\text{-}NO_x)$ values at each site. Note that the NO_x concentration (left-y) axis on panel D is different from the rest.