

Response to the anonymous referee #1 (ACP-2020-1143)

We thank anonymous referee #1 for his/her positive review of this work and relevant comments. Anonymous referee #1's comments/suggestions are given below in bold followed by our replies.

1) Lines 32-34: In the introduction, I think the authors should point out that there is also motivation to better constrain precursor emission contributions to nitrate deposition; thus, source apportionment is also important (and not just chemistry).

Agreed. The sentence has been changed to : “In order to better understand the reactive nitrogen (which includes NO_x and HNO₃) chemistry, the related AOC, and the contributions of precursors emissions to nitrate deposition, it is necessary to better constrain NO_x sources and individual chemical processes.”. The revised version of the manuscript has been modified accordingly.

2) Line 243: $\delta^{15}\text{N}(\text{NO}_2)$ range looks to be incorrect; I think it should be -11.8 to -4.9 ‰ (based on Table 1).

Thank you for pointing this typing mistake out. The range has been corrected accordingly.

3) Line 280: EPA IsoSource is a very simplistic model that cannot account for source uncertainty. I think the authors should consider applying a more advanced statistical (i.e., Monte-Carlo) mixing model such as SIMR or SIAR that has been commonly used in the $\delta^{15}\text{N}$ atmospheric community for the past few years. As a measurement report, I think it is important to showcase how advanced statistical modelling and be used to partition NO_x emission sources using the described sampling technique.

Thank you for pointing this out. As recommended, we performed a new estimation of the NO_x sources using the Bayesian isotope mixing model SIAR. Compared to the IsoSource simulation, for which the early morning rush hours sample was dissociated from the rest of the sampling period, we have considered $\delta^{15}\text{N}$ measurements as one group for the SIAR simulation. Based on a local NO_x emission inventory and energy balance, we have decided to consider three NO_x sources in our analysis: soil emissions, natural gas combustion and vehicle exhausts. Considering the time of the year (mid-march), we excluded NO_x emissions from biomass burning for home heating.

SIAR simulation results do not change much the overall interpretation of NO_x sources that might influence our site. Like for IsoSource simulation, traffic still being the major contributor in front of natural gas combustion and soil ((57 ± 8), (36 ± 12) and (7 ± 5) % respectively). The manuscript has been modified according to the new simulation results.

As you have pointed out, the dataset use for this paper is limited to one site during only one day of sampling. Therefore, a lot of caution has to be exercised when interpreting these measurements. As recommended, we have removed the lines where we compared the IsoSource simulation results to satellite data and focused on the method validity without speculating or generalising any early conclusions.

4) Lines 284-286: In recent years, there have been several updates to our $\delta^{15}\text{N}(\text{NO}_x)$ source emission values including for biogenic emissions (rural and urban; Yu and Elliott, ES&T, 2017; Miller et al., GRL, 2018) and traffic (Miller et al., JGR:Atmos, 2017). Perhaps consider using more up to date $\delta^{15}\text{N}(\text{NO}_x)$ values. Additionally, the fuel-combustion signature is for natural gas power plants. Please confirm that is an appropriate fuel-combustion source signature for your study region.

Following your comments, the SIAR simulation on estimating the relative contribution of NO_x sources was performed with updated $\delta^{15}\text{N}(\text{NO}_x)$ source emission values.

As previous studies of vehicles exhausts showed that the variability of $\delta^{15}\text{N}$ depends on the fuel type, the reduction emission technology, and the vehicle run time with values ranging from -21‰ to -2‰ . We use the value of Miller et al. (2017) who have estimated the U.S. vehicle-fleet NO_x isotopic source signature to $(-4.7 \pm 1.7)\text{‰}$ (integrated on 50-100 km during daytime summer conditions). We think this value can be to some extent representative of our sampling location, as 90 % of the Grenoble vehicle-fleet is composed of diesel-powered engines (85 % for the U.S. vehicle-fleet). According to Grenoble urban area emission inventory, NO_x emissions can be attributed to industries for 26 % and to the residential/tertiary sectors for 20 %. Local energy consumption indicates that industries are powered at 51 % by electricity (mainly produced by nuclear power plants and hydropower dams) and 34 % by natural gas combustion. Additionally, the two main NO_x energy emitters in the residential/tertiary sectors are biomass burning and natural gas combustion. As biomass burning, mainly use for home heating, can be considered negligible at this time of the year, we consider natural gas as the main NO_x emitter for both industry and residential/tertiary sectors. We use the characteristic $\delta^{15}\text{N}$ signature of natural gas combustion determined by Walters et al. (2015) ($(-16.5 \pm 1.7)\text{‰}$). In view of the large variability in the isotopic signature of biogenic NO_x emissions reported in the literature (from -59.8 to -19.9‰), we use a mean value of $(-33.8 \pm 12.2)\text{‰}$ as reported by Zong et al. (2017). The revised version of the manuscript has been modified accordingly.

5) Lines 376-377: Can you further elaborate and include specific details on the “additional more accurate measurements” that are needed to improve the interpretation of $\text{NO} + \text{RO}_2$ rxn contributions to $\Delta^{17}\text{O}$

To study the nitrogen chemistry and test the isotopic approach, the monitoring of atmospheric species as peroxy radicals, NO_3 radical or N_2O_5 , require state of the art instruments and an important technical development. We believe the method presented in this paper can bring a reliable complementary tool for studying the reactive nitrogen chemistry along with studies using the

classic “kinetic method” and which is easier to implement on the field. Nonetheless, to carry out reliable kinetic calculations from these isotopic measurements, we need to monitor precisely NO_x concentrations i.e. with a precision higher our very close to 1 ppb. As it was not the case during our campaign, an important recommendation for further investigations is to conduct isotopic measurements with precise atmospheric chemistry monitoring, at least for NO_x and O₃ concentrations. Additionally, the use of a chemical box-model is also recommended because it will allow to account for non-equilibrium effects in isotopic transfers and thus strengthen the interpretation of isotopic measurements in investigations of the nitrogen cycle in urban atmospheres. The revised version of the manuscript has been improved following your comment.

In the marks reviewed version, you will find in red the main modifications from the first version following your comments and the ones of reviewer #2. Additionally, we exchanged the order of the sub-sections of section 4 (Discussion of the multi-isotopic composition of atmospheric NO₂). This is because we have developed more general expressions for daytime and nighttime nitrogen isotopic fractionation. The interesting point of the daytime expression is that, despite the absence of RO₂ measurements, the NO + RO₂ pathway can be accounted for in the estimation of nitrogen isotopic fractionation using $\Delta^{17}\text{O}$ measurements. Thus, the description of $\Delta^{17}\text{O}$ values must be presented before the section concerning $\delta^{15}\text{N}$. We also added two appendixes (C and D). The first appendix presents the derivations of the more general nitrogen isotopic fractionation equations following Li et al., 2020, and the second appendix provides a table of the kinetic constants we use for our calculations.

References

Miller, D. J., Wojtal, P. K., Clark, S. C., and Hastings, M. G.: Vehicle NO_x emission plume isotopic signatures: Spatial variability across the eastern United States, 122, 4698–4717, <https://doi.org/10.1002/2016JD025877>, 2017.

Walters, W. W., Tharp, B. D., Fang, H., Kozak, B. J., and Michalski, G.: Nitrogen isotope composition of thermally produced NO_x from various fossil-fuel combustion sources, 49, 11363–11371, <https://doi.org/10.1021/acs.est.5b02769>, 2015.

Zong, Z., Wang, X., Tian, C., Chen, Y., Fang, Y., Zhang, F., Li, C., Sun, J., Li, J., and Zhang, G.: First Assessment of NO_x Sources at a Regional Background Site in North China Using Isotopic Analysis Linked with Modeling, Environ. Sci. Technol., 51, 5923–5931, <https://doi.org/10.1021/acs.est.6b06316>, 2017.

Response to the anonymous referee #2 (ACP-2020-1143)

We thank anonymous referee #2 for his/her positive review of this work and relevant comments. Anonymous referee #2’s comments/suggestions are given below in bold followed by our replies.

1) Line 80: Could add reference to e.g. Michoud et al., (2014) which is a more recent specific study on HONO and NO_y relevant to an urban France location (Paris)

Thanks for the reference, it is now added in the revised manuscript along the Huang et al., (2017) reference.

2) From what I understand, Eq.(3) assumes that $\text{NO} \rightarrow \text{NO}_2$ conversion is dominated by O_3 ? Do the authors have information available to clarify this here? i.e. is the observed NO/NO_2 ratio close to that given by the Leighton ratio approximation based on NO_2 photolysis and $\text{NO}+\text{O}_3$? Is the discussion on lines 370-373 also relevant here?

We agree that the overall presentation of this part was not clear. Eq.(3) is developed in Li et al., (2020) assuming that NO conversion to NO_2 is dominated by ozone. The main problem was that our detailed discussion of NO_x chemistry and isotopic transfers in the ‘Oxygen isotopic composition’ section was placed after the analysis of nitrogen isotopic results which actually requires a discussion of NO_x chemistry in order to be easily understood. In addition, the $\text{NO} + \text{RO}_2$ pathway was neglected in the analysis of nitrogen isotopic results whereas it was taken into account in the analysis of oxygen isotopic results. It is possible to account for the $\text{NO} + \text{RO}_2$ pathway in the estimation of the nitrogen isotopic fractionation during the day using a new equation linking the nitrogen isotopic fractionation to the oxygen isotopic anomaly. Since this new expression for daytime nitrogen isotopic fractionation contains $\Delta^{17}\text{O}$ variables, the discussion of $\Delta^{17}\text{O}$ (oxygen isotopic composition) must be presented before the discussion of $\delta^{15}\text{N}$ (nitrogen isotopic composition). Furthermore, we also add for completion a more general expression for the nighttime nitrogen isotopic fractionation. In summary, in order to make things clearer and more consistent, we reorganise parts of the paper and accounted for the $\text{NO} + \text{RO}_2$ pathway in the daytime nitrogen isotopic fractionation analysis. First, the ‘Oxygen isotopic composition’ section (in particular, the discussion of NO_x chemistry and $\Delta^{17}\text{O}$) is now before the ‘Nitrogen isotopic composition’ section. Second, extended expressions for estimating the daytime and nighttime nitrogen isotopic fractionation are now provided. Derivations of these expressions following Li et al., 2020 are now provided in the new appendix C. The interesting point of the day-time expression is that, despite that the absence of RO_2 measurements, the $\text{NO} + \text{RO}_2$ pathway can be accounted for in the estimation of nitrogen isotopic fractionation using $\Delta^{17}\text{O}$ measurements.

3) Line 267: Is there any kinetic / mechanistic theoretical explanation that supports the suggestion that $\text{NO}+\text{RO}_2$ fractionation is similar to that of $\text{NO}+\text{O}_3$? Might be worth mentioning here if so.

Bigeleisen and Wolfsberg (1957) have laid the foundations of the kinetic isotope fractionation theory within the framework of the transition state theory. Briefly, as a molecule vibrational frequency depends (inversely) on the mass of its atoms, zero point energy (ZPE) of isotopologues differs: the molecule with the heavier isotope has a lower ZPE than the molecule with the lighter isotope. As a result, the dissociation energy is lower for the light isotopologues which facilitates the reaction and increases its reaction rate compared with the heavier isotopologue resulting into an enrichment of the product in the lighter isotope compared to the residual reactant. However, “inverse kinetic isotope fractionation” can also occur leading to an

enrichment of the product in the heavier isotope. The range of these isotopic fractionations is defined by the ratio of rate constants for the isotopologue specific reactions.

Previous studies found that the $\text{NO} + \text{O}_3$ reaction falls within the family of “normal kinetic isotope fractionation” with the NO_2 produced being depleted in ^{15}N (Walters and Michalski, 2016) compared to residual reactant NO . To our knowledge, no such experiment has been carried out for the $\text{NO} + \text{RO}_2$ reaction. Nonetheless, considering the very close, and both very low, activation energies for the reaction $\text{NO} + \text{O}_3$ and $\text{NO} + \text{RO}_2$ ($2.60 \text{ kcal mol}^{-1}$ and $-0.71 \text{ kcal mol}^{-1}$, respectively), it is quite likely that the fractionation factors of these two reactions are similar. But we agree it is not proven. In the near future, we plan to carry out experiments in an atmospheric simulation chamber in order to access precisely the nitrogen fractionation factor associated with the reaction $\text{NO} + \text{RO}_2$. This work will improve our comprehension of nitrogen isotopes fractionations during the atmospheric nitrogen cycle and thus to better quantify NO_x sources from $\delta^{15}\text{N}$ measurements.

Also, can the authors comment on the similarity of the chemical environment in the Li et al., (2020) study to their study location?

Li et al., (2020) experimental conditions are comparable to multiple tropospheric environments (from clean to polluted sites). Indeed, NO_x and O_3 concentrations generated into the simulation chamber under UV-light (NO_2 photolysis rate equivalent to dawn) range between 0 to a few dozen of nmol mol^{-1} . This suggests that the fractionation factors determined by Li et al. (2020) can be used for our environment. Additionally, while Li et al., (2020) have not determined the temperature dependency of fractionation factors, the daytime temperature variability during our sampling period seems to be too small (from 10 to 17 °C) to have a significant impact on nitrogen fractionations and close enough to Li et al. (2020) experimental conditions (room temperature).

4) Line 292-299: Comparison with COVID lockdown satellite study seems a bit tenuous (i.e. comparing NO_2 column change over a large city to limited time measurements here). Are there other estimates of traffic contributions to urban NO_x that could be compared?

As also noted by referee #1, the comparison to satellite data was a step too far and has been removed now. We now report a 2016 NO_x emissions inventory of the Grenoble urban area. According to this survey, 52 % of NO_x emission are attributed to traffic. This estimation is in good agreement with the value estimated by the new isotopic mixing model (57 ± 8 % (model simulation carried out to estimate the relative contribution of NO_x sources from our nitrogen isotopic measurements). The relatively small difference of 5 % can be attributed to differences in the weather, the location of the sampling site, season and so on. See our replies to comments 3) and 4) from referee #1 for more details about our new estimation of the NO_x sources using the Bayesian isotope mixing model SIAR with updated $\delta^{15}\text{N}(\text{NO}_x)$ source emission values.

5) Line 325: The reaction $\text{NO}_2 + \text{OH}$ to produce HNO_3 is termolecular, involving a third body. i.e. $\text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$. See e.g. Atkinson et al., (2004).

Thanks for pointing out this error, this has been corrected.

6) Line 369: Derivation of $[\text{RO}_2]$ and discussion. The diurnal behaviour of the derived RO_2 seems surprising. What is assumed for $k_{\text{NO}+\text{RO}_2}$ in Equation 10? How sensitive is RO_2 to the assumed speciation of RO_2 ? i.e. is the value assumed to simply be that for HO_2 or is there some weighting for an assumed VOC mixture, and does this matter much? In general it might be useful to provide a Table (in the Appendix?) of values and sources of rate constant values used.

We agree. The dispersion partly originates from measurements uncertainties, which may not be accurate enough for our level of analysis. According to the literature, $\text{RO}_2 + \text{NO}$ reactions are relatively fast and do not vary significantly with the nature of the alkyl group (e.g. $k_{\text{NO}+\text{CH}_3\text{O}_2, 289} = 7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{298} = (8-9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for other alkyl groups; Atkinson et al., 2006, 2004). In comparison, $\text{HO}_2 + \text{NO}$ reaction has a slightly lower rate constant of $k_{\text{HO}_2+\text{NO}, 298} = 2.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ but it does not impact RO_2 concentration calculated with Eq.(6) to more than ± 2 pptv. Consequently, we consider RO_2 and HO_2 as one group (RO_2) and calculated the corresponding rate constant values according to the rate constant expression reported for the $\text{NO} + \text{CH}_3\text{O}_2$ reaction in Atkinson et al., (2006): $k_{\text{NO}+\text{RO}_2} = 2.3 \times 10^{-12} \exp(360/T)^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As you recommended, we have added an Appendix D reporting a table with the rate constant expressions used for the calculation in our study.

Typographical errors

7) Line 57: ang = and

Thank you for pointing this typing mistake out.

In the marks reviewed version, you will find in red the main modifications from the first version following your comments and the ones of reviewer #1. We also added two appendixes (C and D). The first appendix presents the derivations of the more general nitrogen isotopic fractionation equations and the second appendix provides a table of the kinetic constants we use for our calculations.

Reference

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O_x , HO_x , NO_x and SO_x species, 4, 1461–1738, <https://doi.org/10.5194/acp-4-1461-2004>, 2004.

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Huang, R.-J., Yang, L., Cao, J., Wang, Q., Tie, X., Ho, K.-F., Shen, Z., Zhang, R., Li, G., Zhu, C., Zhang, N., Dai, W., Zhou, J., Liu, S., Chen, Y., Chen, J., and O'Dowd, C. D.: Concentration and sources of atmospheric nitrous acid (HONO) at an urban site in Western China, *Science of The Total Environment*, 593–594, 165–172, <https://doi.org/10.1016/j.scitotenv.2017.02.166>, 2017.

Li, J., Zhang, X., Orlando, J., Tyndall, G., and Michalski, G.: Quantifying the nitrogen isotope effects during photochemical equilibrium between NO and NO₂: implications for $\delta^{15}\text{N}$ in tropospheric reactive nitrogen, 20, 9805–9819, <https://doi.org/10.5194/acp-20-9805-2020>, 2020.

List of changes

- Addition of an Appendix C presenting the derivations of more general nitrogen isotopic fractionation equations separated by daytime and nighttime
- Addition of an Appendix D presenting rate constants used for calculations
- The order of sub-sections 4.1 and 4.2 has been exchanged
- The sub-section named “Nitrogen isotope composition” has been modified in accordance to the equations developed in appendix C.
- Figure 4 has been replaced by Table 3
- NO_x emission sources have been estimated using a different model (the Bayesian isotopic mixing model SIAR) and Figure 5 has been modified accordingly