

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 NO → NO₂ conversion is dominated by O₃? Do the authors have information available to clarify this here? i.e. is the observed NO/NO₂ ratio close to that given by the Leighton ratio approximation based on NO₂ photolysis and NO+O₃? 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 NO₂ 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 NO + RO₂ 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 NO + RO₂ 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 NO + RO₂ 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-ime expression is that, despite that 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.

3) Line 267: Is there any kinetic / mechanistic theoretical explanation that supports the suggestion that NO+RO₂ fractionation is similar to that of NO+O₃? 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 NO + O₃ reaction falls within the family of “normal kinetic isotope fractionation” with the NO₂ produced being depleted in ¹⁵N (Walters and Michalski, 2016) compared to residual reactant NO. To our knowledge, no such experiment has been carried out for the NO + RO₂ reaction. Nonetheless, considering the very close, and both very low, activation energies for the reaction NO + O₃ and NO + RO₂ (2.60 kcal mol⁻¹ and -0.71 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 NO + RO₂. This work will improve our comprehension of nitrogen isotopes fractionations during the atmospheric nitrogen cycle and thus to better quantify NO_x sources from δ¹⁵N 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 O₃ concentrations generated into the simulation chamber under UV-light (NO₂ 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 NO₂ 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 NO₂ + OH to produce HNO₃ is termolecular, involving a third body. i.e. NO + OH + M -> HNO₃ + M. See e.g. Atkinson et al., (2004).

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

6) Line 369: Derivation of [RO₂] and discussion. The diurnal behaviour of the derived RO₂ seems surprising. What is assumed for $k_{\text{NO}+\text{RO}_2}$ in Equation 10? How sensitive is RO₂ to the assumed speciation of RO₂? i.e. is the value assumed to simply be that for HO₂ 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, RO₂ + 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, HO₂ + 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 RO₂ concentration calculated with Eq.(6) to more than ± 2 pptv. Consequently, we consider RO₂ and HO₂ as one group (RO₂) and calculated the corresponding rate constant values according to the rate constant expression reported for the NO + CH₃O₂ 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.