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 HNO_3) 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: $\delta^{15}N(NO_2)$ 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 $\delta^{15}N$ 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 $\delta^{15}N$ 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 $\delta^{15}N(NO_x)$ 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 $\delta^{15}N(NO_x)$ 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 $\delta^{15}N(NO_x)$ source emission values.

As previous studies of vehicles exhausts showed that the variability of $\delta^{15}N$ 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 ± 1.7) ‰ (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 $\delta^{15}N$ signature of natural gas combustion determined by Walters et al. (2015) ((−16.5 ± 1.7) ‰). 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 ± 12.2) ‰ 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 NO +RO_2 rxn contributions to $\Delta^{17}O$

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 O_3 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 NO_2). 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 RO_2 measurements, the NO + RO_2 pathway can be accounted for in the estimation of nitrogen isotopic fractionation using $\Delta^{17}O$ measurements. Thus, the description of $\Delta^{17}O$ values must be presented before the section concerning $\delta^{15}N$. 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.