

Interactive comment on “The $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of simultaneously collected atmospheric nitrates from anthropogenic sources – Implications for polluted air masses” by Martine M. Savard et al.

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1-I maintain that this article should have been submitted to AE as a Part II for coherency but this is a minor comment

REP- We do not see the advantage for the readership in this proposition. Publishing two articles dealing with distinct issues of atmospheric science isotopic applications, with several months in between, is commonly done through different journals, even if reporting data from a single region.

2-I don't think that “new and novel” data are sufficient arguments to guaranty their

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publications. New and novel does not mean correct and I have major reserves about their correctness (see point 5)

REP- We mean 'New and novel' implying that the data is QA/QC checked, i.e., correct (also see point 5).

3-I don't think that the authors demonstrated in any way that they have collected nitrate from specific sources whatever O isotopes track or not these sources. To pretend that, they need to provide observations that either NO_x, nitrate (or any other tracers, CO, O₃) are different than background atmosphere. According to the set-up of their experiment, I have serious doubts that sampling air from hours to days will guaranty a permanent sampling of the plume emissions. Conditional sampling based on wind direction is not enough. In this way, I found the title misleading, firstly because as said above, there is no guaranty they have sampled specific anthropogenic sources and secondly, as they mentioned, the scrambling of the oxygen atoms erases source fingerprints.

REP- We did not claim a "permanent sampling" of plume emissions, as we agree that would be unrealistic. The goal was to isolate emissions from sources at their respective location, with the emissions subject to some atmospheric processing (i.e. not stack sampling). By necessity there will be contributions from background nitrate as well. For comparison, background particle nitrate and nitric acid concentrations at Wood Buffalo National Park in northern Alberta, where CAPMoN began sampling in 2014, averaged 0.071 and 0.089 $\mu\text{g m}^{-3}$, respectively, for >2 years of monitoring. Concentrations from the conditional sampling at the sampling sites studied here were 4-40 times higher, suggesting that the collected samples have significantly greater p-NO₃ and HNO₃ concentrations than background. Moreover, back trajectory runs using the HYSPLIT model for every hour of sampling were used to rule out significant air mass transfer from other potential emission sources outside of the targeted wind sector, as discussed in section 2.2 of the original article.

4-Giving the Pearson's correlation in a table is not enough to judge the correctness of

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the correlation. Readers need to see the dispersion of the data and species time-series within the sampling time windows to connect sources with sampling.

REP- We have carefully examined the data dispersion before interpreting the statistical correlations. The main graphs (or stats) illustrating the dispersion can be shown in the Supl. Info. If required by the editor and reviewers.

5 (merged with comment 9; see below) -It is wrong to think that denuders are best used in urban area. Denuders to collect HNO₃ are used in the most remote regions of world (eg Antarctica, Jourdain and Legrand, 2002, Legrand et al., 2017). Denuders that are operational at 1m³/h exists (URG or Thermo Chemcomb), thus minimizing the collection time. Proper set up can limit passive sampling and restricted it to gas diffusion, exactly their purpose. The denuder tubes are the norm to collect acid gases with minimal interferences. They are promoted by the largest atmospheric aerosol networks (EMEP, EPA-method IO4-2). The method used by the authors (1st filter for p-NO₃ and 2nd nylon filter for HNO₃) is not the reference set up used to separate p-NO₃ and HNO₃. It is a set up used mainly to collect total nitrate. The difference in 17O between p-NO₃ and HNO₃ is not a guaranty that the different phases are sampled correctly. Finally, as already mentioned, the fact that a method is published and accepted does not exempt the authors to show us that they can correctly reproduce it. Authors should be able to provide the data and demonstrate that blanks, interferences, efficiencies etc. can be quantified and/or corrected (Finlayson-Pitts&Pitts, 2000). Jourdain, B., and Legrand, M.: Year-round records of bulk and size-segregated aerosol composition and HCl and HNO₃ levels in the Dumont d'Urville (coastal Antarctica) atmosphere: Implications for sea-salt aerosol fractionation in the winter and summer, *J. Geophys. Res.*, 107, 4645, 10.1029/2002jd002471, 2002. Legrand, M., Preunkert, S., Wolff, E., Weller, R., Jourdain, B., and Wagenbach, D.: Year-round records of bulk and size-segregated aerosol composition in central Antarctica (Concordia site) – Part 1: Fractionation of sea-salt particles, *Atmos. Chem. Phys.*, 17, 14039-14054, 10.5194/acp-17-14039-2017, 2017. EMEP manual for sampling and chemical analysis, Norwegian Institute for Air Re-

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search, Kjeller, Norway EMEP/CCC-Report 1/95, 2001. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air (EP A/625/R-96/010a) – method IO4-2 Finlayson-Pitts, B. J., and Pitts, J. N.: Chemistry of the upper and lower atmosphere: Theory, experiments and applications, Academic Press, San Diego, CA, 969 pp., 2000. 9- I will give one example where ^{17}O of nitrate can be modified. If a nitrate particle seating on the filter is hit by a sulfuric acid droplet and the pH of this sulfuric acid is low enough, then isotopic exchange between HNO_3 and H_2O can be triggered. I'm not saying it is what is happening with the author's sampling system but again my main point is that ^{17}O cannot be at the same time the causal and the effect, i.e. the variable to be explained and the variable to explain: the observed difference between ^{17}O HNO_3 and $p\text{-NO}_3$ can't be used as an argument to validate a sampling system. Where is the constrain showing me that such difference simply exists and it is not an artifact? For me it is a self-realization observation.

REP- We have responded to points 5 and 9 together since we interpreted them as raising closely-related issues. We acknowledge that it is possible to use denuders in remote areas, our point was that there are specific and well-regarded networks of rural and remote stations that continue to use filter-based sampling. Since our system was using the established methods of one of those networks (CAPMoN), and evaluation of the method blanks, collection efficiencies and interferences have been previously reported, it seems excessive to us to require repetition of these tests in every report using the same method. Where we developed a new method (for NO and NO_2 active sampling, not reported here), blanks and breakthrough tests were done and evaluated before reporting results. Again, denuders were considered but we chose not to use them for several reasons: (1) we were not certain of the denuder capacity or the ambient levels of HNO_3 in this region prior to the study; (2) given the potential for long periods without flow in the conditional sampling setup, denuders open to the atmosphere would be likely to passively sample during non-pumped periods, while (3) denuders with size-selective impactors at the inlets would result in screening out nitrate on some particles, with the size cutoff varying as the pumps cycled on and off in (sometimes) 5-

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min periods. Note that isotopic results based on collection with filter packs are not new. For instance, isotopic values for dry deposition (pNO_3 and HNO_3) actively collected with filter packs over a week have previously been reported in eastern USA (Elliott et al., JGR, vol 114, 2009).

Our primary concern with this system was the volatilization that is well documented, and that would affect both the O and N isotopes in a mass dependent and highly temperature dependent way. Therefore, as we stated, we evaluated the relative HNO_3 and pNO_3 $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values (as well as $\delta^{15}\text{N}$ in NH_3 and pNH_4), and their pattern with temperature, to judge whether this was strongly affecting the results. We did not draw conclusions about the artifact based on $\Delta^{17}\text{O}$ values, just stated that mass-dependent volatilization would not affect the value, which is correct. While the reviewer does suggest a possible mechanism that would affect $\Delta^{17}\text{O}$ (exchange with H_2O due to highly acidic particles), this scenario is unlikely in this region. Where we analyzed a complete suite of major ion data from the particle filter (2 of the 4 sites), the charge balance was always positive due to both relatively high Ca^{2+} and NH_4^+ . In any case, this scenario would similarly influence pNO_3 collected in a denuder-filter pack sampling system.

6-If the main point of the paper has nothing to do with targeted source types, title of the paper should not give the opposite impression. The authors did not convince me that they have sampled “true” anthropogenic plumes. Nothing in the presented data indicate such thing

REP- The main point of the article is not to address potential differences between various anthropogenic sources, but to examine isotopic trends in anthropogenic sources sampled at different periods, with the specific objective of verifying if low $\Delta^{17}\text{O}$ values exist in such contexts. Yes, they do and this finding has implications for interpreting isotopic data collected downwind from anthropogenic sources. The title refers to this aspect, which the article largely discusses.

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7-When I said what the data mean, I mean what atmospheric context are they representing? Not how have they been obtained? Plotting altogether data that represent averaged hours, averaged days, mix of nighttime or daytime in different proportion etc. does not help the reader to contextualize the observations.

REP- Merged parallel samples (Genesee and Vauxhall) constitutes a physical average of atmospheric characteristics at a given area, which can be compared with the calculated average through 4 parallel samples (4 other sites) which only had as a goal to determine the reproducibility of our sampling and analytical protocols. We have judged this type of care determinant and crucial in guaranteeing the quality of the data. Not clear what the reviewer means in the second point. There is no other way to plot the data since each sample is integrated over a variety of conditions. We would agree that higher-frequency field measurements would add to our understanding of the processes, though it would be challenging to collect enough material for isotopic analysis as methods currently stand.

10- Again I do not see any systematic trend in 17O difference between p-NO₃ and HNO₃ with season (fig3). In summer, two out of four have 17O nitrate > 17O HNO₃ and in winter they have only two events, a very weak statistic. I may not see the same data than the authors and any help from the other reviewers will be welcome. I have no explanation (as I'm not convinced by the correctness of the data by the way) but I can easily found one if I pile up few none demonstrated hypothesis, like the authors did with 1- HNO₃ is formed from non-equilibrated NO_x/O₃ system and 2- HNO₃ is faster scavenged. I can propose the formation of lower 17O p-NO₃ by the heterogeneous reaction $2\text{NO}_2 + \text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{ads}) + \text{HONO}$ (Finlayson-Pitts, 2009), or higher 17O HNO₃ by $\text{NO}_3 + \text{RH} \rightarrow \text{HNO}_3$ in gas phase nighttime oxidation. Finlayson-Pitts, B. J.: Reactions at surfaces in the atmosphere: integration of experiments and theory as necessary (but not necessarily sufficient) for predicting the physical chemistry of aerosols, PCCP, 11, 7760-7779, 10.1039/b906540g, 2009.

REP- The trends are various and each deserves attention. We discuss all of them in

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the article.

13- Well, I disagree again with the authors. One of the strongest argument used in this paper is to claim that $\text{NO}_x\text{-O}_3$ are not in isotopic equilibrium, using mainly Michalski paper as support. So, it is up to the authors to first question Michalski's paper and its conclusions. In Michalski, the atmospheric application of their model is really poorly described. It is not mentioned if at initialization, ozone has already its isotopes at equilibrium (as it should be in the atmosphere considering the life-time of O_3 vs NO_x). Yet ozone formation is the only reaction creating ^{17}O -excess, and since chemical steady state is quickly reached, equilibrium of ^{17}O among all species can't be reached faster than O_3 own equilibrium time in Michalski's model. Clearly, the limiting step in Michalski's model to propagate ^{17}O is ozone formation and not NO_x/O_3 interaction. If ozone is in isotopic equilibrium, any new population of NO_2 formed by O_3+NO (modulo the two-to-one atom transfer) will have the same isotopic composition that the O-atom transfer (if kinetic fractionation is neglected). It is thus simply a question of reservoir of NO_2 versus flux of NO_2 to reach equilibrium. Isotopic abundance has nothing to do here. Let's imagine that O_3 is already in isotopic equilibrium, further formation/destruction have no effect on ozone ^{17}O . Let's imagine further that NO_x and O_3 are in chemical/isotopic equilibrium (new O_3 formed has the same isotopic composition than consumed O_3 as O_3 isotope is controlled by pressure and temperature only). Suddenly, a new pool of NO is emitted. NO will be converted to NO_2 by O_3 contained in the surrounding atmosphere upon mixing and thus NO_2 will be formed at the rate of the Leighton cycle in this system. The characteristic time of the isotopic transfer from O_3 to NO_2 is simply twice the time of the Leighton cycle. Obviously, a plume model is necessary to calculate air mass mixing but as a first approximation, we can assume that the plume is continuously replenished by surrounding O_3 so that O_3 stays constant. The characteristic time, τ , at which the non-equilibrated isotopic NO_x reservoir is replaced by the isotopic equilibrated NO_2 is simply twice the size of NO_2 reservoir divided by the speed of Leighton cycle, either $\text{NO}+\text{O}_3$ reaction or JNO_2 depending on the chemistry context, as one of these reactions is the limiting step.

Using Michalski first simulations, NO = 23 ppbv (assumed NO₂/NO_x = 0.3 for fresh plume), NO₂ = 10 ppbv, O₃ = 50 ppbv and $k = 2e-14$ molecules cm⁻³ s⁻¹, $J = 0,007$ s; then $\tau = 2/J = 4,8$ min. In 20 min NO₂ is at 98 % in isotopic equilibrium. Using Michalski second simulations NO₂ = 0,03ppb, NO = 0,003 ppb (assumed NO₂/NO_x = 0.9 for remote place), O₃ = 5 ppb, $\tau = 2 [\text{NO}_2]/(k[\text{NO}][\text{O}_3]) = 120$ min; 8h to reach 98 % of equilibrium. Apparently, a much less favorable situation (due to the very low NO, strongly limiting the recycle speed) but this simulation at low ozone, 5 ppb, is taken as an illustration of Morin's observation (Morin et al., 2007). However, such situation corresponds to an ozone depletion event (due to the high concentration of bromine) for which NO_x are recycled through the BrO + NO and not NO+O₃ reaction. In a more rural situation (Rohrer et al., 1998), NO₂ = 1,4 ppb, NO = 0,3 ppb, O₃ = 25 ppb, $\tau = 11$ min Rohrer, F., Brüning, D., Grobler, E. S., Weber, M., Ehhalt, D. H., Neubert, R., Schüßler, W., and Levin, I.: Mixing Ratios and Photostationary State of NO and NO₂ Observed During the POPCORN Field Campaign at a Rural Site in Germany, *Journal of Atmospheric Chemistry*, 31, 119-137, 10.1023/a:1006166116242, 1998.

REP- We do not want to discuss the fundamentals of Michalski et al.'s paper here, this is not the place. However, we trust that the conclusion of Michalski's experiments open up the possibility of seeing isotopic disequilibrium in natural samples under certain conditions. In fact, given the unknowns, the back-of-envelope calculations above (20 min and 8 h to 98% of equilibrium in the two scenarios) are roughly in agreement with the timescales shown in Michalski et al. (Fig. 8), so it is not clear why the reviewer is not comfortable with the results of their simulations. Given that transit times from the closest point sources to our measurement sites averaged 25 minutes (range 9-55), and that we were sampling the fraction of NO_x that had been converted to nitrate and therefore "frozen" in $\Delta^{17}\text{O}$ at the point of conversion, contributions from unequilibrated NO_x are not ruled out by the τ of 11 minutes suggested by the reviewer for similar conditions.

We would like to be clear that we are not claiming to present definitive evidence of

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this phenomenon in the atmosphere. Indeed, we do suggest in a few places in the manuscript that the contribution from enhanced RO₂ could also give a similar result, as has been previously hypothesized. However, since the possibility of incomplete NO_x equilibration retained in nitrate field samples was a new idea, it was highlighted. We will carefully review the wording of the document to be sure not to overstate our confidence in the mechanism, as was suggested in the earlier comments.

In summary, authors' reply did not change my position and did not convince me. Because the idea that 1- HNO₃ has a different ¹⁷O composition than p-NO₂ and 2- NO_x is not in isotopic equilibrium are strong and important conclusions, before propagating these idea in the literature, strong lines of evidence should be provided. I don't think the current work carries such guaranty.

REP- Point 1 refers to measurements; the difference in isotopic signals is an observation, it is not an idea inferred through an interpretation. We have shown that the data are valid. Point 2 is a suggestion for which all arguments are exposed in the article; the reader gets substantial information allowing for a personal opinion to be made; this suggestion may create a debate (indeed, it already has) and spur further testing of the hypothesis through additional measurements and plume modelling, a healthy outcome in science.

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