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

Anonymous Referee #3

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Bullet points refer to first authors’ reply.

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

2-I don’t think that “new and novel” data are sufficient arguments to guaranty their publications. New and novel does not mean correct and I have major reserves about their correctness (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 NOx, nitrate (or any other tracers, CO, O3)

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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.

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

5-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 Δ17O 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 Research, Kjeller, NorwayEMEP/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.

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

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.

9- I will give one example where Δ17O of nitrate can be modified. If a nitrate particles 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 HNO3 and H2O 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 Δ17O 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 Δ17O HNO3 and p-NO3 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.

10- Again I do not see any systematic trend in Δ17O difference between p-NO3 and

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HNO3 with season (fig3). In summer, two out of four have Δ17O nitrate > Δ17O 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 NOx/O3 system and 2- HNO3 is faster scavenged. I can propose the formation of lower Δ17O p-NO3 by the heterogeneous reaction 2NO2 + H2O(s) –> HNO3(ads) + HONO (Finlayson-Pitts, 2009), or higher Δ17O HNO3 by NO3 + RH –> HNO3 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.

13- Well, I disagree again with the authors. One of the strongest argument used in this paper is to claim that NOx-O3 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 O3 vs NOx). Yet ozone formation is the only reaction creating 17O-excess, and since chemical steady state is quickly reached, equilibrium of Δ17O among all species can't be reached faster than O3 own equilibrium time in Michalski's model. Clearly, the limiting step in Michalski's model to propagate Δ17O is ozone formation and not NOx/O3 interaction. If ozone is in isotopic equilibrium, any new population of NO2 formed by O3+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 NO2 versus flux of NO2 to reach equilibrium. Isotopic abundance has nothing to do here. Let's imagine that O3 is already in isotopic equilibrium, further formation/destruction have no effect on ozone Δ17O. Let's imagine further that NOx and O3 are in chemical/isotopic equilibrium (new O3 formed has the same isotopic composition than consumed O3 as O3 isotope is controlled by pressure and temperature only). Suddenly, a new pool of NO is emitted. NO will be converted to NO2 by O3 contained in the surrounding atmosphere upon mixing and thus NO2 will be formed at the rate of the Leighton cycle in this system. The characteristic time of the isotopic transfer from O3 to NO2 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 O3 so that O3 stays constant. The characteristic time, Tau, at which the non-equilibrated isotopic NOx reservoir is replaced by the isotopic equilibrated NO2 is simply twice the size of NO2 reservoir divided by the speed of Leighton cycle, either NO+O3 reaction or JNO2 depending on the chemistry context, as one of these reactions is the limiting step. Using Michalski first simulations, NO = 23 ppbv (assumed NO2/NOx = 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/NOx = 0.9 for remote place), O3 = 5 ppb, Tau = 2 [NO2]/(k[NO][O3]) = 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 NOx 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.

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In summary, authors' reply did not change my position and did not convince me. Because the idea that 1- HNO3 has a different Δ17O composition than p-NO2 and 2- NOx 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.

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