

## ***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.***

### **Anonymous Referee #3**

Received and published: 6 February 2018

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 NO<sub>x</sub>, nitrate (or any other tracers, CO, O<sub>3</sub>)

C1

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 HNO<sub>3</sub> are used in the most remote regions of world (eg Antarctica, Jourdain and Legrand, 2002, Legrand et al., 2017). Denuders that are operational at 1m<sup>3</sup>/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-NO<sub>3</sub> and 2nd nylon filter for HNO<sub>3</sub>) is not the reference set up used to separate p-NO<sub>3</sub> and HNO<sub>3</sub>. It is a set up used mainly to collect total nitrate. The difference in  $\Delta^{17}\text{O}$  between p-NO<sub>3</sub> and HNO<sub>3</sub> 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 HNO<sub>3</sub> 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,

C2

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, 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.

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  $\Delta^{17}\text{O}$  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  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  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  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}$   $\text{HNO}_3$  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.

10- Again I do not see any systematic trend in  $\Delta^{17}\text{O}$  difference between p- $\text{NO}_3$  and

C3

$\text{HNO}_3$  with season (fig3). In summer, two out of four have  $\Delta^{17}\text{O}$  nitrate >  $\Delta^{17}\text{O}$   $\text{HNO}_3$  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-  $\text{HNO}_3$  is formed from non-equilibrated  $\text{NO}_x/\text{O}_3$  system and 2-  $\text{HNO}_3$  is faster scavenged. I can propose the formation of lower  $\Delta^{17}\text{O}$  p- $\text{NO}_3$  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  $\Delta^{17}\text{O}$   $\text{HNO}_3$  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.

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  $\text{O}_3$  vs  $\text{NO}_x$ ). Yet ozone formation is the only reaction creating  $^{17}\text{O}$ -excess, and since chemical steady state is quickly reached, equilibrium of  $\Delta^{17}\text{O}$  among all species can't be reached faster than  $\text{O}_3$  own equilibrium time in Michalski's model. Clearly, the limiting step in Michalski's model to propagate  $\Delta^{17}\text{O}$  is ozone formation and not  $\text{NO}_x/\text{O}_3$  interaction. If ozone is in isotopic equilibrium, any new population of  $\text{NO}_2$  formed by  $\text{O}_3 + \text{NO}$  (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  $\text{NO}_2$  versus flux of  $\text{NO}_2$  to reach equilibrium. Isotopic abundance has nothing to do here. Let's imagine that  $\text{O}_3$  is already in isotopic equilibrium, further formation/destruction have no effect on ozone  $\Delta^{17}\text{O}$ . Let's imagine further that  $\text{NO}_x$

C4

and O<sub>3</sub> are in chemical/isotopic equilibrium (new O<sub>3</sub> formed has the same isotopic composition than consumed O<sub>3</sub> as O<sub>3</sub> isotope is controlled by pressure and temperature only). Suddenly, a new pool of NO is emitted. NO will be converted to NO<sub>2</sub> by O<sub>3</sub> contained in the surrounding atmosphere upon mixing and thus NO<sub>2</sub> will be formed at the rate of the Leighton cycle in this system. The characteristic time of the isotopic transfer from O<sub>3</sub> to NO<sub>2</sub> 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<sub>3</sub> so that O<sub>3</sub> stays constant. The characteristic time, Tau, at which the non-equilibrated isotopic NO<sub>x</sub> reservoir is replaced by the isotopic equilibrated NO<sub>2</sub> is simply twice the size of NO<sub>2</sub> reservoir divided by the speed of Leighton cycle, either NO+O<sub>3</sub> reaction or JNO<sub>2</sub> depending on the chemistry context, as one of these reactions is the limiting step. Using Michalski first simulations, NO = 23 ppbv (assumed NO<sub>2</sub>/NO<sub>x</sub> = 0.3 for fresh plume), NO<sub>2</sub> = 10 ppbv, O<sub>3</sub> = 50 ppbv and  $k = 2 \times 10^{-14}$  molecules cm<sup>-3</sup> s<sup>-1</sup>,  $J = 0,007$  s; then  $\tau = 2/J = 4,8$  min. In 20 min NO<sub>2</sub> is at 98 % in isotopic equilibrium. Using Michalski second simulations NO<sub>2</sub> = 0,03ppb, NO = 0,003 ppb (assumed NO<sub>2</sub>/NO<sub>x</sub> = 0.9 for remote place), O<sub>3</sub> = 5 ppb,  $\tau = 2 [NO_2]/(k[NO][O_3]) = 120$  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<sub>x</sub> are recycled through the BrO + NO and not NO+O<sub>3</sub> reaction. In a more rural situation (Rohrer et al., 1998), NO<sub>2</sub> = 1,4 ppb, NO = 0,3 ppb, O<sub>3</sub> = 25 ppb,  $\tau = 11$  min

Rohrer, F., Brüning, D., Grobler, E. S., Weber, M., Ehhalt, D. H., Neubert, R., Schübler, W., and Levin, I.: Mixing Ratios and Photostationary State of NO and NO<sub>2</sub> Observed During the POPCORN Field Campaign at a Rural Site in Germany, *Journal of Atmospheric Chemistry*, 31, 119-137, 10.1023/a:1006166116242, 1998.

C5

In summary, authors' reply did not change my position and did not convince me. Because the idea that 1- HNO<sub>3</sub> has a different  $\Delta^{17}O$  composition than p-NO<sub>2</sub> and 2- NO<sub>x</sub> 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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Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2017-1103>, 2018.

C6