Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-1103-AC1, 2018

Atmospheric Chemistry and Physics Discussions

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.

Martine M. Savard et al.

martinem.savard@canada.ca

Received and published: 29 January 2018

Point-by-point REPLY to Anonymous Referee #3 Received and published: 21 January 2018 The manuscript presents a new data set on the isotopic oxygen composition of nitrates in the Alberta region, Canada. It focuses specifically on the speciation of nitrate (aerosols, gases, wet phases) in conjunction with a potential source effect. The manuscript can be considered as the second part of a previous manuscript published in Atmospheric Environment (Savard et al. 2017, doi: 10.1016/j. atmosenv. 2017.05.010) which dealt only with the 15N/14N ratio of the same samples.

1- As a first question, I wonder why the authors did not submit this second part to

AE for coherency reasons or add this part to above mentioned reference. rep- The option of adding this data set and interpretation to the AE paper on δ15N values of all N-species investigated (NH3/NH4 and all nitrates) was not feasible, as it would have made a much too long article. We are convinced there is a natural separation of the two articles. They are addressing different questions: the AE article aims at evaluating the source fingerprinting potential of δ15N values in all forms of N emission (reduced and oxidized) from various anthropogenic sources; whereas the article submitted to ACP aims at understanding better the NOx oxidation pathways and the NOx/HNO3/p-NO3 relationships.

2- Generally speaking, I find the article unclear and confusing, with too many figures and tables that are not all very informative and easy to read. The explanations given are often ad hoc and not supported by strong observations, experiments or theory. Overall, the article is not of sufficient interest with new and strong novelty to recommend its publication in ACP. rep- This article presents the first Δ17O values in HNO3, simultaneously sampled with p-NO3. These measurements are difficult to obtain as they require elaborated field collection campaigns and state-of-the-art analytical systems. The data presented are new and they prompted a new interpretation in terms of non-equilibrated NOx-O3, suggested for the first time for field samples. For these reasons, we believe the article is worth publishing in ACP.

3- A major flaw of the paper is the angle taken by the authors to present and interpret their data in relation with a source effect as they did in Savard et al. (2017). It is well accepted by the community that the oxygen isotopes of nitrate are driven by oxidations and not by source effect, an idea back up by a large number of experiments and observations from the first studies (Michalski et al. 2003) to most recent ones (Guha et al. 2017). rep- The anonymous reviewer agrees with a key statement of the introduction in the originally submitted article that O isotopes should reflect oxidation pathways (see Introduction second paragraph; and section 4.4 line 4). Confirming no direct source effect on the O isotopes was expected, and this confirmation IS NOT the main contribution highlighted in the article. The original introduction clearly states the rationale for sampling downwind from anthropogenic source: ÂńIn those studies, δ18O and ïĄĎ17O values were suggested to be useful to apportion the contribution of emission sources to regional atmospheric nitrate loads. However, the signals of precursor NOx emitted from the same sources may quickly get modified through isotopic equilibration with O3, so that the original source signals may be difficult to recognize.Âż In the new version of the article to be available when the open discussion period is over, we further explain the pertinence of evaluating source effects, not in terms of distinguishing the ultimate sources among themselves, but for assessing if low Δ17O values previously suggested as indicative of anthropogenic emissions are characterizing some or all anthropogenic emissions sampled here. Do low Δ17O values reflect a larger role of RO2 in the oxidation of anthropogenic NOx emissions in fresh plumes? This question is of interest to the scientific community and as it is still debated in the literature as (Proemse et al., 2013; Guha et al., 2017).

4- The authors should have eliminated the source effect in one or two sentences and concentrated on the oxidation mechanism by adding ancillary data such as NOx, O3 concentrations, photo-dissociation rates such JNO2 and/or modeling. rep- We have used O3 and NOx mixing ratios and presented our statistics in Table 6. The fraction of each sample collected during daylight hours (correlations also shown in Table 6) was judged to be a reasonable proxy for the amount of sample collected during active photochemistry. Detailed jNO2 calculations are of limited value for effort considering that we do not have radiation data on site to account for cloud cover. We do recognize the importance of modelling, but it was not the purpose of our research, and our data can be made available for modellers when the article is accepted (a table with all pertinent information can be placed in the supplemental information).

5- The sampling protocols are poorly described. Blanks are not given, neither pumped volumes. No filter breakthrough, saturation, interference, efficiency is evaluated (see Talbot et al. 1990 for the use of nylon filter), especially in response to RH which is known to greatly influence volatilization of p-NO3 (Cheng et al., 2012) and HNO3 collection efficiency (Appel et al., 1980) on filters. Actually, such samplings artefacts can alternatively be an argument to explain the tight correlation observed between HNO3/p-NO3 isotopes and RH (Table6). It is also surprising to see the use of filter pack system to differentiate p-NO3 and HNO3 collection as most modern systems and networks use impregnated denuder systems (Cheng et al., 2012, ChemComb (Thermo Fisher scientific), MARGA (Metrohm) or URG gas-aerosols denuder samplers)) to avoid loss p-NO3 by H2SO4 acidification or gain of HNO3 by adsorption on collected alkaline aerosols. rep-The filter pack system is based on the ones used by two long-standing networks (Environment and Climate Change Canada's CAPMoN and the U.S. Environmental Protection Agency's CASTNET), but we can certainly provide more background about the historical testing of these filters and the rationale for their use in this study. For example, Anlauf et al. (1986) found that breakthrough was ∼3% for filter loadings up to 3 times higher than the maximum loading in this study. Filter loadings and pumped volumes can be reported with the tabulated sample and ancillary data mentioned above.

Denuders were considered but were not used, partly because of the lack of capacity and established quality control protocols at the CAPMoN laboratory. Also because of the higher potential complications due to the longer deployments in these remote locations (necessary to collect sufficient material for isotopic analysis at low ambient concentrations) compared to the typical urban networks with high concentrations that allow using denuders. We had concerns about: (a) the likely positive artefact of "passive" sampling due to diffusion into the denuder during the periods without pumping in this sector-based approach; (b) the likelihood of capturing coarse PM on the denuder if no size-selective inlet was used (which was not wanted due to the desire to capture p-NO3 on coarse PM); and (c) the higher potential for condensation and dripping within the denuders during multiple day/night cycles and resulting loss of coating/sample. While we acknowledge that small part of the HNO3 is likely volatilized p-NO3, as discussed in the last paragraph of section 3.1, fractionation during this process would be negligible during winter sampling and bias the HNO3 δ18O values low relative to p-NO3 in summer, while the observations showed the opposite seasonal pattern. In addition, this would be a mass-dependent process and therefore have no effect on the Δ17O signals, so it cannot explain the correlations between RH and Δ17O values.

6- Location descriptions and context refers systematically to the Savard et al, 2017 papers which does not help to contextualize what the data plotted really mean. Samples cover different total air sampling time, from 21 to 360h and deployment times. We don't know if the sampling is dominated by nighttime or daytime chemistry, if they are rich/poor NOx/O3 atmospheres. rep-We can present a location map in the supplementary information and further describe the locations and contexts of sampling if judged pertinent by the reviewers and editor. However, the main point with our sampling protocol has nothing to do with the targeted source types, but with the fact that it allows collection of true anthropogenic plumes, without changes in NOx/nitrate source, which could modify the potential oxidation pathways. The submitted article therefore describes this aspect clearly.

We have explored the relationship between the isotopic results and daylight fraction and found a significant inverse correlation with isotopic values of p-NO3, but not with HNO3 (Table 6). We can provide all the data, including available O3 and NOx concentrations, in a summary table placed in supplemental information if judged necessary (opinion of the editor/reviewers required here).

7- Replicated samples were pooled at two sites (Genesee and Vauxhall) making even more difficult to know what plotted data really represent. Each point on the plots represents a single sampling period at a given site, whether several samples were pooled or not. Where samples were not pooled, the individual data were used to estimate the reproducibility of the combined sampling and analytical approach, but in the end, the average values were plotted. In brief, last paragraph of section 2.2 of the submitted article clearly explains what the data represent.

Printer-friendly version

Discussion paper

8- Section 3.3 is useless considering what the authors say in the first line of 3.2. It is thus detrimental to the understanding of the study to see an idea accepted by the whole community, namely that oxygen isotopes of nitrate are controlled by oxidation, starting to appear in the middle of the discussion. Discussion about source-driven effect should be evacuated as soon as possible with no more than one/two sentences, such as “we did not observe any significant correlations between O-isotopes and source types or wind direction”. rep-In the new version of the article to be posted when the article is accepted, we have now placed former Figure 1 in supplementary information (replaced in article by a location map), removed the emphasis previously put on the individual sources and merged together sections 3.2 and former section 3.3 for which the length is now much reduced.

9- The discussion about the different oxidation pathways to explain the season trends is classic and does not bring any new idea or interpretation. The only original observation is the difference in isotopic compositions between HNO3 and nitrate but it is questionable given the above reserve mentioned. rep-As mentioned in reply to point 5, as well as in the text, the recognized sampling artefacts cannot cause Δ17O differences between pNO3 and HNO3.

10- Moreover, there is no systematic trend about HNO3 being enriched or depleted as function of season and with respect to p-NO3. In figure 3, there is few cases where summer p-NO3 have higher _17O than HNO3. It is thus difficult to understand why authors want to explain the greater _17O of HNO3 in summer over p-NO3. Furthermore, the discussion falls short to give an acceptable explanation (lines 10 to 25 of page 11). rep-The data show both positive and negative values of Δ17O(HNO3)- Δ17O(pNO3), with a somewhat positive trend with temperature. While we hypothesize that negative values may be due to the larger contribution of the N2O5+H2O heterogeneous reaction to p-NO3, we felt it was necessary to propose a mechanism for the positive differences also observed in most spring and summer samples. At this stage, to our knowledge, the best hypothesis for explaining higher Δ17O values in HNO3 is that the deposition of HNO3 is greater than the one of p-NO3, a difference in rates that is much stronger during summer than winter. This mechanism combined with the NOx-O3 isotopic equilibrium can explain our data set. If readers want to suggestion different lines of interpretation, we will gladly receive them.

11- The idea that NO2 is not in isotopic equilibrium with O3 in summer is odd. First if equilibrium is not reached, it should be amplified in winter, not in summer when O3 is at max (Angle et al., 1989) and photolysis at its peak. rep-Agreed, but we should note that there was not a full year of data at any single site, and the two sites where summer samples were primarily gathered were the closest to the NOx sources (Table 1). This will be added to the discussion on p. 10 regarding the NO2 estimated Δ17O values.

12- Moreover, NO2 is the precursor of HNO3 and p-NO3, if not in equilibrium it should impact equally HNO3 and p-NO3. To twist this basic idea, the authors claim that HNO3 is faster scavenged from the atmosphere than p-NO3 but they have no quantitative data to show that is realistic in their environmental context. rep-We refer the reader again to articles cited in the manuscript (Zhang et., et al 2009; Benedict et al., 2013) showing the higher dry deposition rate for HNO3.

13- Neither the authors tested the hypothesis that NO2 is indeed not in equilibrium with O3. If Michalski et al. (2014) showed that the time-scale for equilibrium is strongly dependent on local sunlight conditions and NOx/O3 ratio and can be longer than 1h, they fall short to tell us why isotope equilibrium will take longer than chemical steady state (is it due to the time for ozone or NO2 to reach its isotopic equilibrium composition? or unrealistic O/O3/NO/NO2 ratios after model initialization since chemical steady state will be reached in min and will radically change the NO2/O3 ratio?). In another study, Morin et al. (2011) using a true atmospheric model modeled _17O of NO2 using different realistic atmospheric conditions and environments. They showed that NO2 is largely at isotopic equilibrium except during few night hours but with little impact on prognosticated _17O of nitrate (1 to 2 ‰ at most). Clearly, this section needs more and deeper investigations and critical review of published works. rep-The field mea-

Printer-friendly version

Discussion paper

surements reported here were not designed to test this hypothesis (they predate the Michalski et al. 2014 paper), but we look forward to other field data to further understanding of the real-world applicability of their model. Our understanding of Michalski et al.'s results (see Fig. 8 of their paper, which bracket the concentrations of NO2 and O3 observed in the current study) is that it is simply a matter of the number of interactions between NO2 and O3 required to achieve a statistical redistribution of the heavy isotopes – by necessity, due to the fewer number of heavy isotopes, this will be many more than are required to achieve chemical equilibrium. However, we would argue that it is not necessary to provide an explanation for others' findings when they are well presented in the original paper. Note that Morin et al. (2011) did not model any fresh NOx emissions and they used a 24-hour model spin up before reporting isotopic composition of NO2. Therefore, we are not able to compare their modeling results with the nitrates collected within minutes to hours of fresh NOx emissions.

Considering that this article represents the first investigation of simultaneously sampled nitrates in precipitation, gas and particulate forms for their δ18O and Δ17O values, we think it deserves to be available to the large readership of ACP. We have now clarified the lines of interpretation the article provides placing less emphasis on the types of sources from which the plumes were sampled.

14- Explanation of correlations with meteorological parameters are ad hoc and rough with a weak constrain on possible mechanisms. For instance, correlations with RH and T can be the result of the winter/summer meteorology. Summer is more oxidant but also warmer, sunnier and lower RH. Should all correlations be interpreted, as much of them are not independently related? rep-We judge it pertinent to suggest an interpretation for these correlations as they relate to reactions summarized in Table 5. The text describing this interpretation is short.

15- Correlations with co-pollutants are contradictory as mentioned by the authors (lines 27-35, page 12) and lead to no strong conclusions. In this regard and in my view, the authors should have reported O3, NOx and JNO2 time-series to give some context.

Only gross correlations are reported with most the variables interdependent. rep-We are not convinced that time series of O3, NOx and jNO2 would be meaningful in interpreting these integrated and intermittent samples, which is why we used average values over the sampling times for O3 and NOx analysis. However, those average values can be reported in the proposed data table to be placed in the supplementary information. The use of daylight fraction rather than jNO2 is discussed in point 4.

16- There is other imperfection that bother me. For instance, what was a hypothesis at the beginning (the none equilibrium of NO2 with O3) has now become a certainty (line 6 page 13). rep- Good point. The previous sentence was : Âń However, NO2 not in isotopic equilibrium with O3, and/or NO reacted with RO2 significantly influenced the overall results.Âż The sentence now reads: However, NO2 not in isotopic equilibrium with O3, and/or NO reacted with RO2 may have significantly influenced the overall results.Âż

17- Finally, the idea that low values of _17O can be linked to the rapid oxidation of anthropogenic NOx is attractive but would have merited more investigation such as following for example the NOx/NO3- ratio to give some clue about the aging of the air masses. rep- This is a good suggestion. A technique for actively sampling integrated NO2 and NO concentrations was developed with some success through the course of the study, but since it was an evolving methodology we have acceptable NO2 concentrations only at 2 of the 4 sites, both in the Edmonton urban area. Therefore, we could provide this ratio for the samples, where available on site, in the supplemental data table.

Cited references Anlauf, K.G., Fellin, P., Wiebe, H.A., Schiff, H.I., Mackay, G.I., Braman, R.S., Gilbert, R. A comparison of three methods for measurement of atmospheric nitric acid and aerosol nitrate and ammonium (1985) Atmospheric Environment (1967), 19 (2), pp. 325-333.

Anlauf, K.G., Wiebe, H.A., Fellin, P. Characterization of Several Integrative Sampling

Methods for Nitric Acid, Sulphur Dioxide and Atmospheric Particles (1986) Journal of the Air Pollution Control Association, 36 (6), pp. 715-723.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-1103, 2018.

Printer-friendly version

Discussion paper