

## Interactive comment on "The $\Delta^{17}$ O and $\delta^{18}$ 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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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. 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.

Generally speaking, I find the article unclear and confusing, with too many figures and

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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. 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). 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 an/ d/or modeling.

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. 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. Replicated samples were pooled at two sites (Genesee and Vauxhall) making even more difficult to know what plotted data really represent.

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".

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. 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  $\Delta$ 170 than HNO3. It is thus difficult to understand why authors want to explain the greater  $\Delta$ 170 of HNO3 in summer over p-NO3. Furthermore, the discussion falls short to give an acceptable explanation (lines 10 to 25 of page 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. 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. 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

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a true atmospheric model modeled  $\Delta$ 170 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  $\Delta$ 170 of nitrate (1 to 2 ‰ at most). Clearly, this section needs more and deeper investigations and critical review of published works.

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? 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.

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). Finally, the idea that low values of  $\Delta$ 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.

For all these reasons, I do not support the publication in acp.

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