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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.

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Comment 1: Title: I find the title to be somewhat misleading specifically “from anthropogenic sources – Implications for polluted air masses” As written this title implies direct plume emissions were sampled rather than air mass originating from anthropogenic emission regions. Due to the numerous sampling sites, I think the authors should instead highlight that this work is spatially-resolved.

REP – We can modify the title to: “The D17O and d18O values of simultaneously collected atmospheric nitrates from anthropogenic air masses”

Comment 2: Intro: I think the introduction could use a better framework. If speciating HNO3(g) and p-NO3- is a main motivation of this study (however likely not achieved), then I think the introduction needs to have a better critical analysis of HNO3(g) and p-NO3- dynamics in the atmosphere. What might _18O and _17O of speciated nitrate tell the atmospheric community that isn’t already known? Will this speciated work shed light into their separate formation pathways or will the phase separation reflect the inorganic thermodynamics of trace gases and PM driven by RH, temperature, [sulfate], [ammonia], etc.

REP – We can do that in the final version.

Comment 3: Sampling Methodology: I think it would be useful to quantitatively demonstrate that the collected nitrate truly originated from the targeted upwind region. Specifically, the lifetimes both for NOx oxidation to nitrate and nitrate lifetime should be considered. Based on these lifetimes, how much of the sampled nitrate reasonable originated from NOx oxidized from the upwind region? Was the emitted NOx converted to nitrate from these emission regions are is the sampled nitrate a mixture of “background” nitrate originated from NOx emitted further upwind that the targeted region due to a relatively long nitrate lifetime (3-5 days). I think this is incredible important especially considered the sampling distance from the targeted sources (1 to 125 km).

REP – We aimed at isolating emissions from sources at their respective location, with the emissions subject to some atmospheric processing (i.e., not stack sampling). By necessity, it is clear that background contributed to the sampled load, but not in significant proportions. 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 μg 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 greater p-NO3 and HNO3 concentrations than background. Moreover, back trajectory runs using the HYSPLIT model for every hour of sampling served 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.

Comment 4 (MAJOR): Sampling Protocols: I'm not convinced that nitrate speciation (HNO3 ad p-NO3-) was actually achieved with the sampling filter pack method. The problem, as the authors have pointed out, that the collected p-NO3- can easily volatize as HNO3 that is collected on the filter designated for HNO3(g) collection. Additionally, there is the possibility of gaseous reactions on the PM filter especially as the filter accumulates PM. The authors point out that they don't expect volatilization of p-NO3- to play a major role on their results because p-NO3- isotope ratios are higher during winter than during summer and that the difference between p-NO3- and HNO3 is opposite than expected, but this is not proper justification. First, I wonder what the expected p-NO3- and HNO3 isotope difference is? This process is likely driven by an equilibrium effect rather than a kinetic effect since the volatilization of p-NO3- as HNO3 is due to the system being at non-equilibrium. I think this would change the authors expectation that the difference p-NO3- and HNO3 is driven by a kinetic effect (I assumed this was the authors assumption). Additionally, which "isotopic ratios" did the authors use to evaluate the p-NO3- and HNO3 difference? I'm assuming mass-dependent _18O but this information is not provided in text. Also, suggesting that this filter pack method has previously been used for isotopic analysis of p-NO3- and HNO3 (Elliot et al., 2009) does not mean the sampling method is correct and optimal for this isotopic analysis. Elliot et al., 2009 did not quantify this method for phase separation for isotopic analysis; thus, this argument should not be used to justify the work in this manuscript. Also, there is a general lack of information regarding the authors sampling protocols. What types of filters were used (and size)? How were these filters prepared and processed? Were field and laboratory blanks taken? At what flow rates was sampling conducted? How was the requirement that sample air volumes be within 15% quantitatively determined and could the authors elaborated on the experienced flow problems, specifically was this related to mechanical malfunctions or filter build-up? If samplers were placed out for an extended period of time, how might potential for passive HNO3(g) absorption on

the Nylon filter play a role in their results?

REP - A potential complication from the air sampling method could arise if there was significant dissociation of ammonium nitrate on the particle filter into nitric acid and ammonia, with subsequent collection on the downstream nitric acid and ammonia filters. This may result in isotopic fractionation between the particle and gaseous components (Heaton et al., 1997; Kundu et al., 2010). For instance, ammonium nitrate formed on the Teflon particle filters may dissociate and release NH3 and HNO3, particularly with changes in the ambient temperature and humidity. In that equilibrium process, the p-NH4+ and p-NO3- remaining on the Teflon filters would preferentially retain 15N, and 15N-depleted HNO3 and NH3 would accumulate on the downstream nylon and citrated Whatman filters. This phenomenon could generate artificially low δ15N values in HNO3 and NH3 and high values in the particulate ions. At higher temperature, the effect should increase due to enhanced volatilization, assuming that the effect of temperature on the solid/gas or solution/gas equilibrium is larger than the effect of temperature on the fractionation factor of the atmospheric reactions (typically smaller as the temperature increases; Savard et al., 2017; Atm Env). In the present study, when all source types are considered, or when several data from a single source are examined, the opposite relationship is observed; NH4 δ15N values are low at higher temperature (10 to 20 C), and high at low temperature (-10 to 0 C). In contrast, the NH3 values are slightly higher or practically unchanged at high temperature. In addition, there is no observed systematic change of HNO3 δ15N values with temperature. We therefore conclude that any dissociation of ammonium nitrate from the Teflon filter did not significantly alter the isotopic values in the samples. While we acknowledge that small part of the HNO3 is may derive from volatilized p-NO3, as discussed in the last paragraph of section 3.1 of the submitted article, 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 (Figure 3 of submitted article). In addition, this would be a mass-dependent process and therefore have no effect on the Δ17O signals.

To wrap up, both δ15N and δ18O values suggest that the data set is valid: dissociation of ammonium nitrate and volatilization are reduced to a minimum during winter (below 0°C), and these processes cannot create the δ18O trends observed during summer.

Comment 5: Analytical procedures: I also mind a general lack of information in the analytical procedures. First, how were concentrations measured? Importantly, was nitrite detected and removed from the samples? Even if NO2- was minor say 5% relative to NO3-, due to its rapid exchange with water below pH of 10, this could have artificially lowered the measured _17O of the interpreted HNO3(g) or p-NO3-. As an example, a 5% NO2- contribution would have lowered the _17O of the targeted nitrate (assuming _17O _ 30‰ by 1.5‰ and could be the primary driver behind the _17O difference in the “speciated” nitrate. Additionally, which chemical conversion method was used? Azide/Acetic Acid Buffer? If so, please cite the appropriate references (i.e. McIlvin and Altabet, 2005). How might using the long-form _17O definition (ln(1+d17O/1000)-0.516*ln(1+_18O/1000)) impact the authors comparison to data using the more commonly used linear _17O definition (d17O-0.52*_18O) (i.e. Table 4)?

REP – We can expand the analytical description as follows: We characterized the δ15N ratios of NH3, w-NH4, p-NH4 and NOx, and the triple isotopic ratios (δ15N, δ17O, δ18O) of w-NO3, HNO3 and p-NO3-. The present article deals solely with the δ18O values obtained for oxidized species. We treated the samples with the chemical conversion and thermal decomposition of N2O protocols, providing the ability to simultaneously analyze low-concentration N- and O-containing species (Smirnoff et al., 2012). The different preparation steps involved conversion of ammonium-containing and nitrate-containing samples into nitrite (NO2-), using sodium bromate and bromide, and a cadmium column, respectively. The final preparation step involved using sodium azide to ultimately produce N2O (Smirnoff et al., 2012). In addition to these procedures, which prepared samples for the NH3, NH4, NOx, p-NO3-, and precipitation NO3 isotopic analyses, HNO3 samples collected on nylon filters were treated as well. They were reduced to NO2- using the Cd-column before being converted into N2O.

NO2 resin cartridges and NO filters were sealed and shipped to Maxxam, along with field blanks, for extraction by a proprietary method. The resulting solutions of NO2- were converted into N2O using sodium azide (for details consult Smirnoff et al., 2012). All extracted N2O was analyzed with the pre-concentration/gold furnace-IRMS system developed at the Geological Survey of Canada (Smirnoff et al., 2012). This approach allows the spectrum of δ15N, δ17O and δ18O ratios from O-bearing N-species to be determined in samples containing as little as 37.5 nmol of N (15 mL final solution). The USGS-34, USGS-35, USGS-32 nitrate reference materials were used and processed exactly the same way as the samples, i.e., converted from nitrate to nitrite, then to N2O. The laboratory analytical precision (average of replicates) determined during the present study using the described analytical procedures was 0.6 ‰ for δ18O and δ17O values in gaseous (n=12) and solid nitrates (n=20). For w-NO3, analytical duplicates gave 0.6 and 0.5 ‰ for δ18O (n=3) and δ17O (n=4) values, respectively. The Δ17O values are defined as ln (1+δ17O/1000) − 0.516 x ln (1+δ18O/1000), relative to Vienna Standard Mean Ocean (VSMOW).

Comment 6: Sections 3.2-3.3: I’m a little unsure as to why the authors are spending so much time on the _18O + _17O “source effect”. Their collections were from polluted air masses not direct stack emissions, such that _18O and _17O should effectively be wiped of any “source effect” due to the rapid equilibration of NOx and its oxidants. The authors suggest in 3.2, that due to elevated _18O + _17O there isn’t a source effect (this is not surprising or a novel finding but expected), but extend the discussion of source effects in 3.3 despite ruling them out in 3.2. This seems a bit odd to me, and I think it would serve this manuscript better to simplify these sections into 1, removing source effect discussions. Instead the authors should focus on the unique oxidation chemistries of the polluted air masses to understand how differences in NOx oxidation cycling and post NO2 reactions would have altered _18O + _17O rather than a source derived _18O + _17O effect, but again this is complicated as previously mentioned because of the nitrate lifetime problem. We don’t know that the nitrate sampled is from the targeted source area.

REP – The final version of the article will show former Figure 1 in supplementary information (replaced in article by a location map), remove the emphasis previously put on the individual sources, and merge together sections 3.2 and former section 3.3 (for which the length is now much reduced).

Comment 7 (MAJOR): (a) Section 4.1: The Alberta nitrate _18O and _17O relationships appear linear despite the author's claim to the contrary. Can the authors include regression statistics so that their argument is supported quantitively rather than qualitatively?

REP – If the reviewer refers to Figure 2, data per seasons are not numerous enough to play with statistics. However this is a very minor point and the sentence can be erased without consequences.

(b) Much of the authors _17O range calculations and justifications are ad hoc. Can the authors properly justify their assumptions made in this calculation, specifically "50% contribution from each pathway for summer"?

REP – This assumption is just meant to help present alternatives. We do not claim that 50% is the proportion applicable for the collected samples.

(c) Additionally, can the authors propagate the error made in the suggested _17O ranges? The authors indicate that the _17O range "shrinks" during winter but their calculations indicate a larger range during the winter (winter: 26 to 37‰ summer: 20 to 29‰

REP – The "shrinks" referred to the wider range estimated from the extreme cases discussed earlier in the paragraph (100% from the OH pathway or 100% for the N2O5 pathway; 25-45 ‰ for winter samples). This can be clarified.

(d) The authors conclusion that _17O of NO2 is not equal to the asymmetrical O3 is not new but rather expected, due to VOC oxidation contributions that have an NO oxidation branching ratio of 70 to 80%. Perhaps the authors should retry their calculations

utilizing a more realistic approximated _17O of NO2. Also, could the authors compare their _17O in this region with the global _17O model?

REP – The goal of the calculation was to constrain the source NO2 Δ17O values based on those of nitrate, and it is not clear what the reviewer is suggesting. Use an approximate value of NO2 Δ17O to calculate the contributions from the different NO2 oxidation pathways in different samples? That would require assuming the NO2 Δ17O value was constant, which would also be unrealistic. The contribution of RO2 oxidation of NO is discussed in the paragraph following the calculation. The nitrate Δ17O are compared with the global model in section 4.4; NO2 Δ17O was not explicitly mapped in Alexander et al. (2009) for comparison.

(e) Again, the calculated transit times of 9 minutes to 4 hours, indicates that not all of the sampled nitrate is derived from the targeted upwind region due to the chemical lifetimes of NOx and atmospheric lifetime of nitrate. I find it hard to believe any of the interpretation on _18O and _17O differences between p-NO3- and HNO3(g) because this speciation was likely not truly achieved given the method concerns already raised in this review and others. I recommend that this speciation discussion should be removed and _18O and _17O interruption should focus on total nitrate relative to wet-nitrate (which was hardly discussed in this manuscript!)

REP – See reply to comment 4.

Comment 8: In general, I find the figures and tables difficult to read and interrupt (especially Figs. 3 and 4)

REP - We are planning to remove Figure 4 (see reply I to reviewer II) and willing to make the necessary changes to Figure 3 so it becomes easy to read.

Comment 9: The authors findings that meteorological parameters often correlate with HNO3, p-NO3- and their isotopic compositions isn't surprising (particularly phase separation) due to the well-established thermodynamic equilibrium of HNO3 and p-NO3-

that determines this phase separation. This point however, directly contradicts that authors claim that reaction pathways (i.e. NO2 + OH vs N2O5 heterogenous rxn) had a significant role on the observed speciation and isotopic composition in Section 4.1.

REP – Thermodynamic equilibrium will contribute to change the δ18O values, but not the Δ17O signals.

Comment 10: Overall, I'm not convinced that during the summer, source effects lowered the anthropogenic originating nitrate _17O values. The simplest explanation for this observation should be NO oxidation contributions from RO2. Until the authors can explicitly rule out the "oxidation chemistry effect" by modeling or empirical evidence, I don't think the authors suggested conclusion should be drawn.

REP – The RO2 oxidation contribution is not ruled out, but we believe it is valuable to raise an alternative hypothesis in order to spur further testing

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