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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.

Anonymous Referee #1

Received and published: 16 February 2018

The authors present oxygen stable isotope composition (δ18O and Δ17O) of atmospheric-derived nitrate (nitric acid (HNO3(g)) + particulate nitrate (p-NO3-) + wet-deposited nitrate (w-NO3-)) from serval locations in the Alberta, CA. The authors suggest that they have speciated HNO3(g) and p-NO3- utilizing a filter pack method, providing separate δ18O and Δ17O of these two nitrate phases in order to better understand their oxidation formation pathways. The authors find that the different sampled regions did not have an influence on Δ17O and δ18O of nitrate but this is an expected result since the authors collected nitrate downwind of emissions sources, allowing for NOx oxidation to have an influence on δ18O and Δ17O, rather than directly from emission plumes. One interesting point is that the authors think that lower than expected

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Discussion paper

Δ17O values during the summer may be explained due to non-equilibration of NOx with O3 during the summer, but this conclusion is not properly justified in text. This manuscript certainly has a lot of potential but there are major methodology and interruption flaws. Specifically, I have serious doubts that the authors truly achieved nitrate phase speciation due to the potential of p-NO3- volatilization. Additionally, I found the authors conclusion not often properly justified. It is also unclear whether the nitrate that was sampled from targeted emission sources was entirely derived from these targeted sources due to atmospheric lifetime and transit times, as suggested by the authors and explicitly in the title. It is my opinion that this manuscript does not expand upon the knowledge of atmospheric nitrate dynamics and/or its isotopic compositions, and that due to serious methodology concerns, their data should be interrupted as bulk nitrate (p-NO3- + HNO3(g)) rather than speciated, requiring significant reframing. For these reasons, I suggest that this manuscript should be rejected to ACP. My specific comments justifying this decision are listed below:

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.

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 δ18O and Δ17O 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.

Comment 3: Sampling Methodology: I think it would be useful to quantitatively demon-

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strate 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).

Comment 4 (MAJOR): Sampling Protocols: I'm not convinced that nitrate speciation (HNO3 and 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 δ18O 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

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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?

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 Δ17O of the interpreted HNO3(g) or p-NO3-. As an example, a 5% NO2- contribution would have lowered the Δ17O of the targeted nitrate (assuming Δ17O $\sim$ 30‰ by 1.5‰ and could be the primary driver behind the Δ17O 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 Δ17O definition (ln(1+d17O/1000)-0.516*ln(1+δ18O/1000)) impact the authors comparison to data using the more commonly used linear Δ17O definition (d17O-0.52*δ18O) (i.e. Table 4)?

Comment 6: Sections 3.2-3.3: I'm a little unsure as to why the authors are spending so much time on the δ18O + Δ17O "source effect". Their collections were from polluted air masses not direct stack emissions, such that δ18O and Δ17O 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 δ18O + Δ17O 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

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chemistries of the polluted air masses to understand how differences in NOx oxidation cycling and post NO2 reactions would have altered δ18O + Δ17O rather than a source-derived δ18O + Δ17O 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.

Comment 7 (MAJOR): Section 4.1: The Alberta nitrate δ18O and Δ17O 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? Much of the authors Δ17O 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"? Additionally, can the authors propagate the error made in the suggested Δ17O ranges? The authors indicate that the Δ17O range "shrinks" during winter but their calculations indicate a larger range during the winter (winter: 26 to 37‰ summer: 20 to 29‰. The authors conclusion that Δ17O 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 Δ17O of NO2. Also, could the authors compare their Δ17O in this region with the global Δ17O model? 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 δ18O and Δ17O 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 δ18O and Δ17O interruption should focus on total nitrate relative to wet-nitrate (which was hardly discussed in this manuscript!)

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

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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.

Comment 10: Overall, I'm not convinced that during the summer, source effects lowered the anthropogenic originating nitrate $\Delta 17O$ 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.

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