Point-by-point REPLY to Anonymous Referee #1

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.

REPLY – We have modified the title.

Change in manuscript: “The Δ^{17}O and δ^{18}O values of atmospheric nitrates simultaneously collected downwind from anthropogenic sources – Implications for polluted air masses”

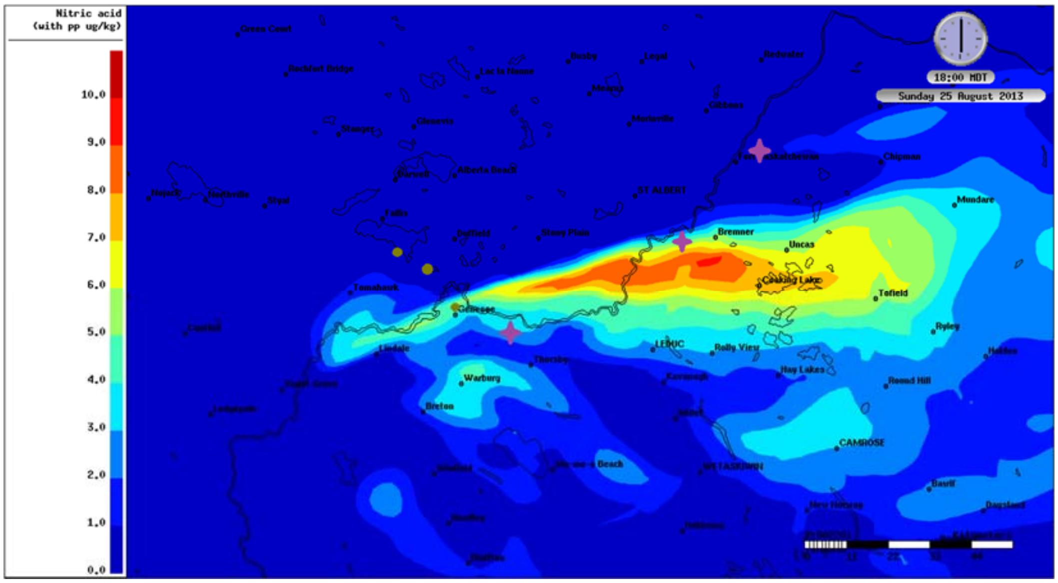
Comment 2: Intro: I think the introduction could use a better framework. If speciating HNO3(g) and p-NO3- is a main motivation of this study (however likely not achieved), then I think the introduction needs to have a better critical analysis of HNO3(g) and p-NO3- dynamics in the atmosphere. What might _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.

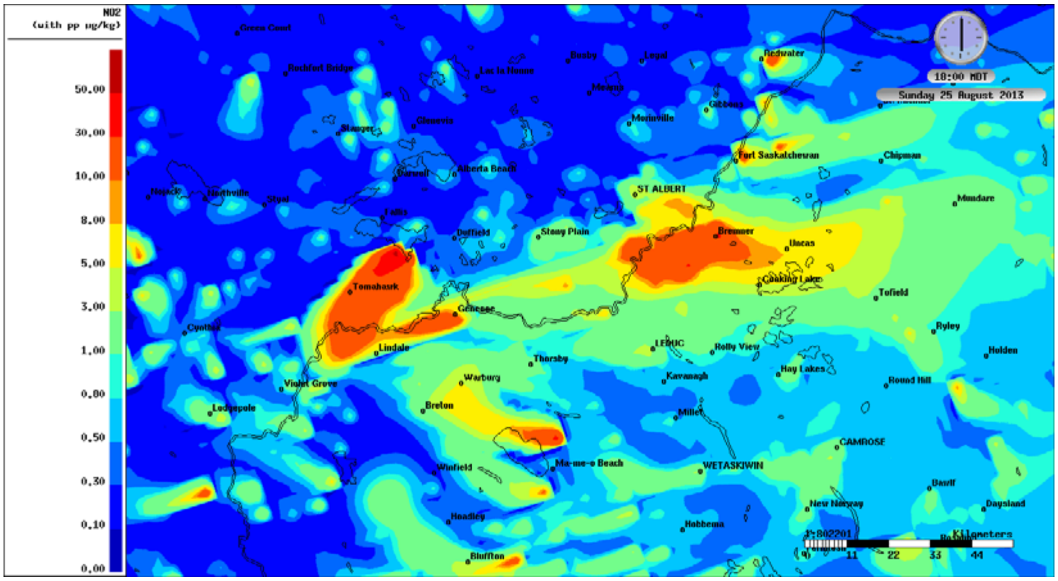
REPLY – We have modified the introduction to better illustrate the motivation for the research.

Change in manuscript: « In the past, due to sampling challenges, HNO_3 and p-NO_3^- were generally collected together (without differentiation). Therefore, no studies have separately and simultaneously collected and analyzed the HNO_3 and p-NO_3^- δ^{18}O and Δ^{17}O values, and discussed these isotopic characteristics of nitrate collected downwind of anthropogenic emitters. While HNO_3 and p-NO_3^- can be in equilibrium (e.g. if p-NO_3^- is in the form of solid NH_4NO_3), this is not always the case, for example, if nitrate is bonded to calcium or dissolved in liquid water on a wet particle (see section 3.3). They also have different lifetimes with respect to wet scavenging and dry deposition, and may differ in their formation pathways as well. Therefore, investigating the mass independent and dependent oxygen fractionations in nitrates separately collected may help identifying their respective formation and loss pathways, and provide additional constraints on processes controlling their distribution.»

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).

REPLY – 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. A few pieces of evidence support this. One is the low background concentrations; background particle nitrate and nitric acid concentrations at Wood Buffalo National Park in northern Alberta, where CAPMoN began sampling in 2014, averaged 0.016 and 0.020 µg N m^{-3}, respectively, for >2 years of monitoring. Concentrations from the conditional sampling at the sampling sites studied here were up to 20 times higher, suggesting that the collected samples have greater p-NO3 and HNO_3 concentrations than background. In addition, we obtained some model output from a 2-week simulation in 2013 (Makar et al., 2018) illustrating the significantly higher concentrations of nitric acid downwind of the coal-fired power plants near Genesee. In this snapshot, the three power plants are shown as brown dots and the three Edmonton-area sampling locations are shown as purple stars. The NO_2 plumes are shown as well to illustrate the change in direction of the plume. It is clear that at the Genesee site, the bulk of the nitric acid at this particular time resulted from the nearby power plants. Using the conditional sampling weighted the samples more heavily when this was the case.





Changes in manuscript:

Text added to section 3.2: *“Background sites for this region are sparse, but concentrations at Cree Lake in neighbouring Saskatchewan were the lowest in Canada reported up to 2011 (Cheng and Zhang, 2017), and 2014-2016 measurements at Wood Buffalo National Park on the northern Alberta border revealed similar average concentrations of 0.02* μg *N/*m^3 *for both* HNO_3 *and p-*NO_3^- *(preliminary internal data). Therefore, the lowest concentrations in our samples approached average background concentrations, while the highest were 20 or more times higher than regional background.”*

Text added to section 4.1: “*While the fraction of* NO_x *converted to nitrate in this transit time may be small, these are large sources of* NO_x *in an area with very low background nitrates. For example, a plume containing 10 ppb of* NO_2 *mixing with background air with 0.1 ppt of OH (Howell et al., 2014) would produce* HNO_3 *via R6 at a rate of 0.011*μg *N* m^{-3} min^{-1} *at T = 7 °C (Burkholder et al., 2015), or an equivalent amount of a typical sample in 10 minutes. Even if equilibration with* O_3 *is established within a few minutes, the nitrate produced in the interim can form a substantial fraction of the sample collected nearby*.”

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?

REPLY – A discussion of field tests and intercomparisons for the filter pack system has been added to section 2.2. Additional clarification of the isotopic evidence that volatilization was not the primary driver of the observed isotopic differences (i.e. that we assume that would be an equilibrium effect, and therefore the fractionation is not what would be expected) has also been provided. Finally, since much of the discussion hinges on $\Delta^{17}O$ values, this mass-dependent process would not create the observed HNO_3-pNO_3 differences.

Change in manuscript: Added to section 2.2: *"Ambient air was pulled through a three-stage filter pack system to collect, sequentially, particulate matter on a Teflon filter, gaseous nitric acid (*HNO_3*) on a Nylasorb nylon filter, and gaseous ammonia on a citric acid-coated Whatman 41 filter (all 47 mm). The Teflon-nylon filter method for p-*NO_3^-* and *HNO_3* has been extensively compared and evaluated, and is currently used by national monitoring networks targeting regional background sites, CAPMoN in Canada and CASTNet (Clean Air Status and Trends Network) in the United States. Previous testing showed negligible collection of *HNO_3* on the Teflon filter, <3% breakthrough of *HNO_3* from the nylon filter with loadings more than three times higher than reported here, and blanks for p-*NO_3^-* and *HNO_3* of approximately 0.2 μg N/filter (Anlauf et al., 1985; Anlauf et al., 1986). Intercomparisons with more labor-intensive methods, such as tunable diode laser absorption spectroscopy and annular denuder-filter pack systems, have shown evidence of some volatilization of ammonium nitrate from the Teflon filter leading to a negative bias in p-*NO_3^-* and positive bias in *HNO_3* under hot (> 25 °C) and dry conditions, particularly in high ambient concentrations (e.g., Appel et al., 1981). However, other field studies have shown no significant differences in *HNO_3* between filter packs and denuder and/or TDLAS systems (Anlauf et al., 1986; Sickles Ii et al., 1990) or mixed results (Spicer et al., 1982; Zhang et al., 2009). While those studies used short-duration sampling, a comparison for weekly samples at a lower-concentration site showed good agreement between filter pack and denuder values for most of the study but potential interference from *HNO_2* (nitrous acid) on the nylon filter in two samples(Sickles Ii et al., 1999). Based on the conditions in Alberta, we estimate that there is little or no volatilization of *NH_4NO_3* for samples with mean temperatures below 5 °C, but there is a possibility for nitrate loss of up to 30% in the warmest sampling periods. "*

More detail about poor flows have also been added to 2.2: "*Flow issues were primarily due to pump failure, likely due to cycling the pumps on and off frequently in early samples. Therefore, for later samples the protocol was changed such that the pumps remained on and valves were* *used to switch the pumps between sampling lines and non-sampling tubing based on the wind sector."*

The last paragraph of 3.1 has been edited as follows: *"…This could result in equilibrium isotopic fractionation between the particle and gaseous components, which would become artificially high and low, respectively, with more fractionation at higher temperatures (summer) relative to lower temperatures (winter) when volatilization is minimal (Keck and Wittmaack, 2005). We find the p-NO_3^- isotopic ratios ($\delta^{17}O$ and $\delta^{18}O$) to be generally higher during winter than during summer (see Section 3.4). Moreover, the p-NO_3^- minus HNO_3 isotopic differences are negative during summer, opposite to the expected isotopic artefact if particulate volatilization were the dominant factor in determining the particle-gas isotopic differences (the same was concluded for the $\delta^{15}N$ values in NH_3 and NH_4; Savard et al., 2017). We therefore conclude that, while volatilization may occur in the summer samples, other isotope effects must be larger in order to lead to the observed differences. In addition, volatilization would cause mass-dependent fractionation and would not affect the ^{17}O anomaly; therefore, $\Delta^{17}O$ values remain robust tracers in this situation…"*

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)?

REPLY – We have expanded the analytical description.

Change in manuscript; section 2.3: « Nitric acid from nylon filters were extracted using 10 mL of 0.01M solution of NaCl. Particulate-NO_3 from Teflon filters were extracted in two portions of 6 mL of ultrapure water (ELGA). To reduce possible evaporation, filters were placed in an ultrasonic bath with ice. The extractions were performed during one hour and samples were left for 48 hours in a fridge to insure the complete extractions. The solutions were decanted and a small portion (1-2 mL) was used to determine concentrations. The remaining extracts were stored in the fridge for subsequent isotope analysis. The blanks from both filters were treated the same way.

Concentration of nitrates in Teflon and Nylon filter extracts, and in precipitation samples were determined at the Institut national de la recherche scientifique – Eau, Terre, Environnement (INRS-ETE). The determinations used an automated QuikChem 8000 FIA+ analyzer (Lachat Instruments), equipped with an ASX-260 series autosampler. The detection limit for the method with sulfanilamide (# 31-107-04-1-A with sulfanilamide) was 2 ppb N-NO_3/L (0.03 N-NO_3 umol/L). Nitrite concentrations were also measured in the extracts. Nitrite concentrations above the detection limit (0.016 mg N/L) were found in a handful of samples at Terrace Heights. These samples were excluded from the reported data. »

« The preparation steps involved conversion of nitrate-containing samples into nitrite (NO_2^-) using a custom-made cadmium column. The final preparation step involved using sodium azide to ultimately produce N_2O (McIlvin and Altabet, 2005; Smirnoff et al., 2012). All extracted N_2O was analyzed using a pre-concentrator (PreCon, Thermo Finnigan MAT) including a furnace with 'gold' wires, online with an Isotope Ratio Mass Spectrometer (Delta V Plus, Thermo Electron; Kaiser et al., 2007; Smirnoff et al., 2012). The utilized approach… »

« Extracts from filter blanks were processed in the same way. The blanks from nylon filters were not integrated for the calculation of the results due to their negligible size. Peak heights from the blanks resulting from Teflon filters were always below 10% of sample peaks and were also neglected. »

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.

REPLY – Good piece of advice.

Change in manuscript: « We now show former Figure 1 in supplementary material (Fig. SM- 2). Figure 1 in the article now includes two location maps. We have removed the emphasis previously put on the individual sources by erasing former sub-section 3.3.

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?

REPLY – If the reviewer refers to Figure 2, data per seasons are not numerous enough to assess non-linearity with confidence. However, this is a very minor point.

Change in manuscript: The sentence was erased.

(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"?

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

Change in manuscript: none required.

(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‰.

REPLY – 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), however we realize the placement was misleading. We have clarified.

Change in manuscript in Subsection 4.1, end of first paragraph: «... the range is 26-37 ‰.»

(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?

REPLY – The goal of the calculation was to constrain the source NO_2 $\Delta^{17}O$ values based on those of nitrates, and it is not clear what the reviewer is suggesting. Use an approximate value of NO_2 $\Delta^{17}O$ to calculate the contributions from the different NO_2 oxidation pathways in different samples? That would require assuming the NO_2 $\Delta^{17}O$ value was constant, which would also be unrealistic. The contribution of RO_2 oxidation of NO is discussed in the paragraph following the calculation. The nitrate $\Delta^{17}O$ are compared with the global model in sub-section 3.5; NO_2 $\Delta^{17}O$ was not explicitly mapped in Alexander et al. (2009) for comparison.

Change in manuscript: the calculations and discussion of their implications are now presented in sub-section 4.1.

(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!)

REPLY – See reply to comment 4 for speciation. At section 3.2 second paragraph, we added: « Though the number of samples were limited, w-NO_3^- $\Delta^{17}O$ values were roughly correlated with the weighted average $\Delta^{17}O$ values of p-NO_3 and HNO_3 in samples covering the same time periods, consistent with scavenging of both HNO_3 and p-NO_3 by wet deposition. »

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

REP - We have modified caption of Figure 3 so the trends shown by the different symbols are easier to appreciate, and removed former Figure 4.

Change in manuscript, caption Figure 3: « Line-connected $\delta^{18}O$ and $\Delta^{17}O$ values (‰) for simultaneously collected HNO_3 (empty symbols) and p-NO_3^- (solid symbols) from cold (blue) and warm (red) sampling periods. » Figure 4 is now removed.

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.

REPLY – Actually the second point supports the first. Thermodynamic equilibrium will contribute to change the $\delta^{18}O$ values, but not the $\Delta^{17}O$ signals.

Change in manuscript: none really required, but we now present the comparison with other parameters in sub-section 3.4 and include the relevant data in Table SM-3.

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.

REPLY – We do not invoke a specific source effect, but sampling of p-NO_3 in early plumes characterized by $\Delta^{17}O$ values lower relative to those of HNO_3 due to differential depositional rates. The RO_2 oxidation contribution is not ruled out, but likely concomitant with differential deposition. We believe it is valuable to raise an alternative hypothesis in order to spur further testing of this common explanation.

Change in manuscript: Sub-section 4.2 has a new title and has been modified.

Point-by-point REPLY to Anonymous Referee #2

Received and published: 10 April 2018

1-The manuscript by Savard and colleagues presents interesting data worthy of publication. However, I found the results and discussion sections muddled and the important points worthy of highlighting buried. (A) The manuscript could be improved by a focus on key findings and condensing or eliminating repetitive sections. For example, page 10 lines 24-35 are potential explanations for low observed d18O, D17O values with important implications multiple communities. (B) Additionally, challenging the assumption of NOx isotopic steady state with O3 is a key takeaway (not mentioned until page 14). Why are these not highlighted more prominently in the abstract? The current conclusions in the Abstract and Conclusion by comparison are weak "isotopic signals of.... are not interchangeable", and "invariably interchangable".

Reply: (A) We have removed repetitive text parts, and after all changes we have reduced the overall text length by one page. We agree with the reviewer that our suggestion about NOx isotopes not at steady state with O_3 should be given more importance at the beginning of the article. NOTE that this is in total disagreement with the main concern of reviewer 3. Here we decide to keep our first suggestion on 'no steady state for some samples', as no other suggestion has been put forward to explain the low $\Delta^{17}O$ values in non-winter p-NO_3. We now explain better the rationale for studying the anthropogenic nitrate samples and highlight better the importance of studying separately nitric acid in the introduction (also briefly summarized in the abstract). (B) We have modified the content of the conclusion to better emphasize the implications of our results and interpretation.

<u>Changes in manuscript</u>: (A) in the abstract: « Recent laboratory experiments suggest that the isotopic equilibrium between NO_2 (the main precursor of NO_3^-) and O_3 may take long enough under certain field conditions that, nitrates may be formed near emission sources with lower isotopic values than those formed further downwind. Indeed, previously published field measurements of oxygen isotopes in w-NO_3^- and p-NO_3^- samples suggest that abnormally low isotopic values might characterize polluted air masses. However, none of the air studies have deployed systems allowing collection of samples specific to anthropogenic sources in order to avoid shifts in isotopic signature due to changing wind directions, or separately characterized HNO_3 with $\Delta^{17}O$ values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample HNO_3 and p-NO_3^-, and co-collect w-NO_3^-. The nitrates are from various distances (<1 to >125 km) downwind of different anthropogenic emitters, and consequently from varying time lapses after emission. »

(B) in the conclusion « The HNO_3, w-NO_3 and p-NO_3 from anthropogenic sources in central and southern Alberta, simultaneously collected with wind sector-based conditional sampling systems produced $\delta^{18}O$ and $\Delta^{17}O$ trends confirming the previous contention that regional ambient conditions (e.g., light intensity, oxidant concentrations, RH, temperature) dictate the triple isotopic characteristics and oxidation pathways of nitrates.

The gaseous form of nitrate (HNO_3) having distinct isotopic characteristics relative to the wet and particulate forms implies that understanding nitrate formation and loss requires characterizing the nitrate species individually. Particulate-NO_3^- in these samples generally shows higher $\delta^{18}O$ and $\Delta^{17}O$ values than HNO_3 in the fall-winter period as the heterogeneous N_2O_5 pathway favours the production of p-NO_3^-. In contrast, HNO_3 has higher $\delta^{18}O$ and $\Delta^{17}O$ values during warm periods, which we propose is due to faster dry deposition rates relative to p-NO_3^- in the event that low-$\Delta^{17}O$ NO_2 is oxidized in the plume. The mechanisms conferring nitrate with relatively low isotopic values, whether oxidation before NO_x-O_3 equilibrium is reached or higher contributions from RO_2, are likely to be observed in anthropogenic polluted air masses. »

2-The manuscript needs a map to put the respective sampling sites and the surround potential sources in a spatial context. Without this information, it is not possible to discern how far sites are from each other.

Reply: Positioning the sites was requested by reviewers 1 and 3. We have added two maps showing the various sites (new Fig. 1).

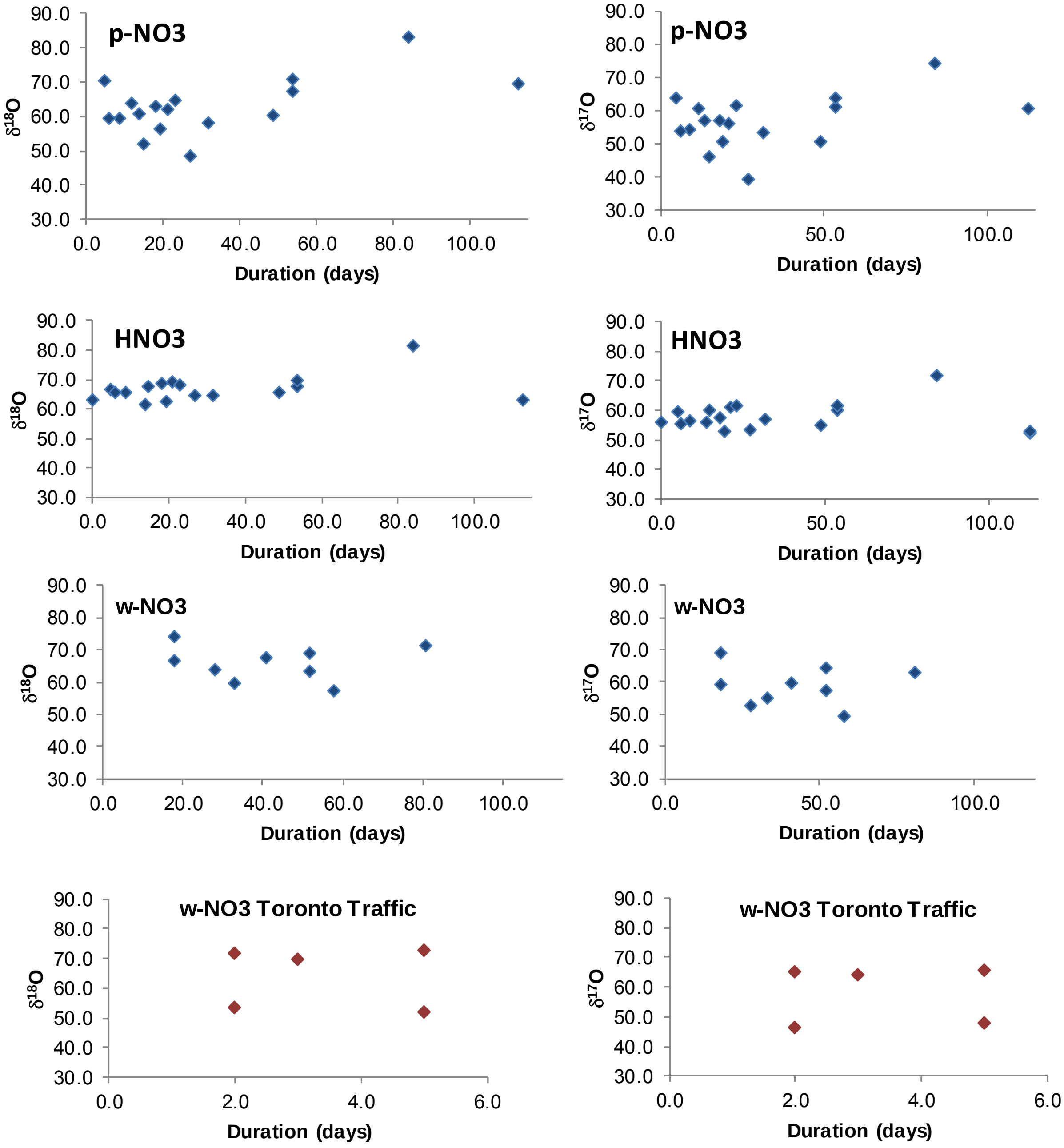
Change in manuscript: The location maps are now shown in Figure 1.

3-The authors points out "very few" air masses passed over other sources outside the targeted ones in the preceding 24 hours. For those that did, are they removed from the analysis? Why is this data not shown- as it seems relevant.
Reply: It's not possible to remove back trajectories from the integrated samples. This analysis was to determine if the conditional sampling method was indeed capturing air masses from the source region(s). Since we have de-emphasized the exact source types, the sentence has been revised to be more accurate.

Change in manuscript: Revised this sentence as follows: "*Back trajectories run using the HYSPLIT model (Stein et al., 2015; Rolph, 2017) for every hour of sampling verified that the conditional sampling approach collected air masses that had primarily passed over or near the targeted source (i.e. there was no landscape feature that decoupled wind direction from back trajectories). A sample plot of back trajectories from Genesee is show in Figure SM-2. A sample plot is now shown in Figure SM-2*"

4-The long variation in sampling times is concerning. For example, individual sample deployments ranged from 5 to 113 days. The authors should explore whether there is any evidence that the length of this sampling time caused any artifacts in their results.

Reply: If the sampling protocols had generated artefacts, they would be reflected in the isotopic difference between p-NO_3 and HNO_3: p-NO_3 would have higher $\delta^{18}O$ values than HNO_3 particularly during summer. But as explained in the article, the trends we observe are opposite to this prediction. Therefore, if there are effects due to sampling in our results, they perhaps minimize the ranges that lead to our conclusions. In other words, removing potential effects would just strengthen our conclusions. Additionally, if artefacts were created by the sampling procedure, the impact would increase with the duration of sampling. Now, we have plotted our $\delta^{18}O$ and $\delta^{17}O$ values against duration of sampling for nitrate types, and we find no systematic increase (or decrease) of values with duration. the Alberta data are shown below for all sampling periods in the 6 upper panels; the results previously obtained (Smirnoff et al., 2012) using the same sampling protocols for Highway 401 traffic are shown in the lower two panels.



Change in manuscript: no change required.

5- Page 5, line 10: What is "preconized"?

Reply: we have now clarified.

Change in manuscript: «… for the protocols used here.»

6- Page 5: line 33: Why was MAD scaled by 0.6745? Where did this number come from? Needs justification.

Reply: it is the normal divisor widely used for allowing the comparison of the mean absolute deviation (MAD) with the regular standard deviation (SD).

Change in manuscript: « Finally, for comparability with the more familiar standard deviation, the MAD was scaled using the standard 0.6745 divisor to give the modified median absolute deviation (M.MAD), which is consistent with the standard deviation in the event that the distribution is Gaussian… »

7-The authors conclude Elliott et al found minimal fractionation between d18O of pNO3- and HNO3. Figure 2 from that paper shows _10 permil differences during summer in the d18O values of these two components.

Reply: Good catch. This just not explained properly. We indeed know about figure 2 (see paragraph before last of section 3.5 in first manuscript submitted). We have now corrected.

Change in manuscript: «… minimal fractionation for p-NO_3^- and HNO_3…»

8-Page 1, line 19: Add distance to state how far collection sites are from major sources (i.e., from x to y km).

Reply: Done.

Change in manuscript: «…and co-collect w-NO_3^-, at various distances (<1 to >125 km) downwind from five different anthropogenic emitters.»

9-Figures 2a-c. Include 1:1 line to clarify your conclusion that data show a "vertical extent". More clarification needed here in this analysis/conclusion.

Reply: this part is removed to avoid confusion.

Change in manuscript: Sentence removed.

10-Discussion: Lines 18-35. This reads like intro text/results. Revise to lead off with a topic sentence that highlights your major finds and built supporting text around this.

Reply: Good point. This entire sub-section is now presented in the section 3.

Change in manuscript: See new sub-section 3.3.

11-Authors state that "Anthropogenic emitters involving combustion (O2) may generate primary NOx at or near sources that tend to carry low d18O and D17O values". It is not clear whether this is in reference to prior published studies, or whether this is one of their conclusions. Either way, it needs more justification.

Reply: Clearly not one of our interpretation, but a widely accepted information from the literature. The references solely appears in caption of Table 5 in the version the reviewer worked with. We now have removed that part of the text during the restructuration of the article.

Change in manuscript: sentence removed.

12-For the analysis on page 10 lines 7-22, it is not clear how the authors determined the relative proportion of R1, R2, R3 to calculate the influence of O3 on oxidation pathways from NO2 to HNO3 (R4, R7, R8).

Reply: These calculations did not make any assumptions about the relative contributions of R1, R2 and R3; rather, the purpose was to derive the possible range of $\Delta^{17}O$ values of NO_2 from which the observed HNO_3 and $p\text{-}NO_3^-$ could have been derived. We've added a topic sentence to this section (in 4.1) to make this more clear.

Change in manuscript: Text added in section 4.1: "*In the present sub-section, we estimate the $\Delta^{17}O$ values of NO_2 involved during the production of the Alberta nitrates based on the observed values and discuss the implications of these estimations.*"

13-I found the discussion on page 11 lines 13-25 very intriguing. How might seasonal differences in lifetimes affect how far different constituents travel? Is there any prior modeling work (e.g., GEOS-CHEM) that could support these ideas?

Reply: Longer lifetimes with respect to deposition would certainly allow for greater dispersal, depending on the wind speeds and chemical lifetimes (relatively long for nitrates). We note that dry deposition velocities are highly variable in space and time since they depend on both meteorological and detailed surface characteristics. These are quite challenging to model, and estimates from different models typically differ by at least a factor of 2 even with the same input data. Our main point is that HNO_3 has a deposition velocity consistently higher than that of $p\text{-}NO_3$ (though it depends on the size of the particle) as calculated using the multiple resistor model at numerous sites in Canada (Zhang et al., 2009).

Change in manuscript: none required

14-The authors refer to "seasonal changes in planetary boundary layer heights" but don't explicitly state what these changes are and how they could impact their results.

Reply: Seasonal changes in the planetary boundary layer height may also affect the impingement of emission plumes on the measurement sites, and thereby the relative amounts of fresh vs background nitrates. For example, winter boundary layer heights can be lower than the 138-155 m stacks at the three coal-fired power plants. During those periods, fresh plumes from those stacks may be emitted into the free troposphere where they are much less likely to mix back down to the surface where the samples are collected. This would be consistent with the observed higher $\Delta^{17}O$ values in winter, if the air masses reaching the sampling site are older than when the plume is emitted within the boundary layer. On the other hand, a relatively shallow boundary layer that DOES encompass the source stacks would concentrate the plume within the layer and lead to faster nitrate formation. Since we do not have data on the PBL height to determine which was most likely during our sampling periods, we decided to remove the sentence.

Change in manuscript: Sentence removed from manuscript.

15-Section 4.2 This reads as Results rather than Discussion.

Reply: We have now placed this part in the results.

Change in manuscript: See new sub-section 3.4.

16-Conclusions: What is “invariably interchangeable”?

Reply: The isotopic values of HNO_3 and p-NO_3.

Change in manuscript: «... and disavows the assumption that isotopic values of the dry nitrate phases are invariably interchangeable.»

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.

Reply: The option of adding this data set and interpretation to the AE paper on $\delta^{15}N$ values of all N-species investigated (NH_3/NH_4 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 $\delta^{15}N$ 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/HNO_3/p-NO_3 relationships.

Change in manuscript: not applicable.

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.

Reply: This article presents the first $\Delta^{17}O$ values in HNO_3, simultaneously sampled with p-NO_3. 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-O_3, suggested for the first time for field samples. For these reasons, we believe the article is worth publishing in ACP.

Change in manuscript: In this new version of the article, we have restructured the sequence of data presentation and interpretation: all results are in section 3 and all discussion and the main interpretations are in section4. We have also modified the introduction to better express the rationale: « While HNO_3 and p-NO_3^- can be in equilibrium (e.g. if p-NO_3^- is in the form of solid NH_4NO_3), this is not always the case, for example, if nitrate is bonded to calcium or dissolved in liquid water on a wet particle (see section 3.3). They also have different lifetimes with respect to wet scavenging and dry deposition, and may differ in their formation pathways as well. Therefore, investigating the mass independent and dependent oxygen fractionations in nitrates separately collected may help identifying their respective formation and loss pathways, and provide additional constraints on processes controlling their distribution. »

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).

The 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 sub-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: «In those studies, $\delta^{18}O$ and $\Delta^{17}O$ values were suggested to be useful to apportion the contribution of emission sources to regional atmospheric nitrate loads. However, the signals of precursor NO_x emitted from the same sources may quickly get modified through isotopic equilibration with O_3, so that the original source signals may be difficult to recognize.» In the new version of the article, we further explain the pertinence of evaluating source effects, not in terms of distinguishing the ultimate sources among themselves, but for assessing if low $\Delta^{17}O$ values previously suggested as indicative of anthropogenic emissions are characterizing anthropogenic emissions, generally speaking. Do low $\Delta^{17}O$ values reflect a larger role of RO_2 in the oxidation of anthropogenic NOx emissions in fresh plumes? This question is of interest to the scientific community as it is still debated in the literature (Proemse et al., 2013; Guha et al., 2017).

Change in manuscript: Introduction «. Triple oxygen isotope characterizations of field NO_3^- samples are not yet widespread. Also rare are the nitrate $\delta^{18}O$ and $\Delta^{17}O$ values of field samples downwind from NO_x-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). The few existing studies have chiefly characterized w-NO_3^- or the sum of p-NO_3^- and HNO_3 (Michalski et al., 2004; Morin et al., 2007; Morin et al., 2008; Alexander et al., 2009; Morin et al., 2009; Proemse et al., 2012; Guha et al., 2017), and suggested these indicators would be useful to trace atmospheric nitrate in water (Kendall et al., 2007; Tsunogai et al., 2010; Dahal and Hastings, 2016), or to apportion the contribution of anthropogenic emissions to regional atmospheric nitrate loads (Proemse et al., 2013). »

4- (A) The authors should have eliminated the source effect in one or two sentences (B) and concentrated on the oxidation mechanism by adding ancillary data such as NOx, O3 concentrations, photo-dissociation rates such JNO2 and/or modeling.

Reply: (A) We significantly shortened all text parts related to the individual anthropogenic emissions. We have used O_3 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 as a reasonable proxy for the amount of sample collected during active photochemistry. Detailed jNO_2 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).

Changes in manuscript: (A) not applicable.

(B) p. 6. First paragraph of 3.2. «As expected, there is no systematic tendency when looking at the samples collected from the anthropogenic sources: CFPP HNO_3 and p-NO_3^- have the highest $\delta^{18}O$ and $\Delta^{17}O$ averages, but not the highest w-NO_3^- values; chemical industries show the lowest $\delta^{18}O$ and $\Delta^{17}O$ averages for w- and p-NO_3, but not for HNO_3. This observation indicates that the oxygen isotopes in the three nitrate species are not predominantly source-dependent (see also Fig. SI-2), as previously suggested in the literature (Michalski et al., 2003).»

In addition, former sub-section 3.3 has been removed and part of the text merged with sub-section 3.2.

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.

Reply: 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-NO_3 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 HNO_3 is likely volatilized p-NO_3, as discussed in the last paragraph of sub-section 3.1, fractionation during this process would be negligible during winter sampling and bias the HNO_3 $\delta^{18}O$ values low relative to p-NO_3 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 $\Delta^{17}O$ signals, so it cannot explain the correlations between RH and $\Delta^{17}O$ values.

Changes in manuscript: A discussion of field tests and intercomparisons has been added to section 2.2: *"Ambient air was pulled through a three-stage filter pack system to collect, sequentially, particulate matter on a Teflon filter, gaseous nitric acid (HNO_3) on a Nylasorb nylon filter, and gaseous ammonia on a citric acid-coated Whatman 41 filter. The Teflon-nylon filter method for p-NO_3^- and HNO_3 has been extensively compared and evaluated, and is currently used by national monitoring networks targeting regional background sites, CAPMoN in Canada and CASTNet (Clean Air Status and Trends Network) in the United States. Previous testing by Anlauf et al. (1985, 1986) showed negligible collection of HNO_3 on the Teflon filter, <3% breakthrough of HNO_3 from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO_3^- and HNO_3 of approximately 0.2 μg N/filter. Intercomparisons with more labor-intensive methods, such as tunable diode laser absorption* *spectroscopy and annular denuder-filter pack systems, have shown evidence of some volatilization of ammonium nitrate from the Teflon filter leading to a negative bias in p-NO_3^- and positive bias in HNO_3 under hot (> 25 °C) and dry conditions, particularly in high ambient concentrations (e.g., Appel et al., 1981). However, other field studies have shown no significant differences in HNO_3 between filter packs and denuder and/or TDLAS systems (Anlauf et al., 1986; Sickles et al., 1990) or mixed results (Spicer et al., 1982; Zhang et al., 2009). While those studies used short-duration sampling, a comparison for weekly samples at a lower-concentration site showed good agreement between filter pack and denuder values for most of the study but potential interference from HNO_2 (nitrous acid) on the nylon filter in two samples (Sickles et al., 1999). Based on the conditions in Alberta, we estimate that there is little or no volatilization of NH_4NO_3 for samples with mean temperatures below 5 °C, but that there may be up to 30% nitrate loss in the warmest sampling periods."*

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.

Reply: We now present two location maps as Figure 1 and briefly describe the locations and contexts of sampling (not much added because we have removed the former emphasis that was placed on the various source types; see further).

We have explored the relationship between the isotopic results and daylight fraction and found a significant inverse correlation with isotopic values of p-NO_3, but not with HNO_3 (Table 6). We now provide all the data, including available O_3 and NO_x concentrations, in summary tables.

Changes in manuscript: New Figure 1 for locations and all data presented in Tables SM-1, 2 and 3 in the supplementary material.

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

Reply: 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 (Table 2), but in the end, the average values (Tables SM-1 and 2) were plotted. In brief, last paragraph of sub-section 2.2 of the submitted article clearly explains what the data represent.

Changes in manuscript: See Tables SM-1, 2 and 3 in Supplementary Material.

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".

Reply: We have now placed former Figure 1 in Supplementary Material, and replaced it in article by a location map (new Fig. 1), removed the emphasis previously put on the individual sources by eliminating sub-section 3.3.

Changes in manuscript: see new sub-section 3.2, Figure 1, and Figure SM-2.

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.

Reply: We specifically write in the article that the interpretation in terms of chemical pathways for cold and warm periods agree with former studies. We do no claim this is a novel interpretation. However, this aspect is crucial for estimating the isotopic signals of precursor NOx, and for further explaining the causes for the changes in isotopic differences between pNO_3 and HNO_3.

As mentioned in reply to point 5, as well as in the text, the mentioned sampling artefacts cannot cause the observed $\Delta^{17}O$ differences between pNO_3 and HNO_3. Additionally, if such effects had imprinted the isotopic results, the sampling duration would show a systematic influence on the results. We do not observe such an influence on our results (see reply to comment 4 of referee #2). Therefore, we maintain that our conclusions rely on high quality data.

Changes in manuscript: see sub-sections 4.1 and 4.2.

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).

Reply: The data on Fig. 3 show clearly both positive and negative values of $\Delta^{17}O_{(HNO3)}$-$\Delta^{17}O_{(pNO3)}$, with a somewhat positive trend with temperature. While we hypothesize that negative values may be due to the larger contribution of the N_2O_5+H_2O heterogeneous reaction to p-NO_3, 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 $\Delta^{17}O$ values in HNO_3 is that the deposition of HNO_3 is greater than the one of p-NO_3, a difference in rates that is much stronger during summer than winter. This mechanism combined with the NOx-O_3 isotopic equilibrium can explain our data set. If readers want to suggest different lines of interpretation, we will gladly receive them.

Changes in manuscript: see new caption of Figure 3 and new sub-section 4.2.

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.

The point is taken, though O_3 is at its peak in April/May in Alberta (NAPS), 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 NO_x sources (Table 1). We added Fig. 5 illustrating our examination of the relationship between the maturity of a plume relatively to the isotopic signal of the nitrates (graph of $\Delta^{17}O$ values (weighted average) as a function of NO_2 concentration divided by p-NO_3 plus HNO_3 concentrations). The relationship is strong (r^2=0.81) and supports our interpretation: the more mature is a plume (low NO_2 concentration), the higher are the $\Delta^{17}O$ values in the nitrates, i.e. the higher is the O_3-derived O content in the nitrates).

Changes in manuscript: in sub-section 4.1: « The fact that we find the lowest isotopic values in summer p-NO$_3^-$ samples collected from various anthropogenic sources at distance less than 16 km supports this suggestion (Table 1). Another argument supporting this interpretation is the strong correlation between Δ^{17}O values and the maturity of a plume as expressed by the NO$_2$ content divided by sum of dry nitrates (Fig. 6). The results reflect the higher content of O$_3$-derived O in dry nitrates from mature plumes, i.e., with relatively low NO$_2$ contents. »

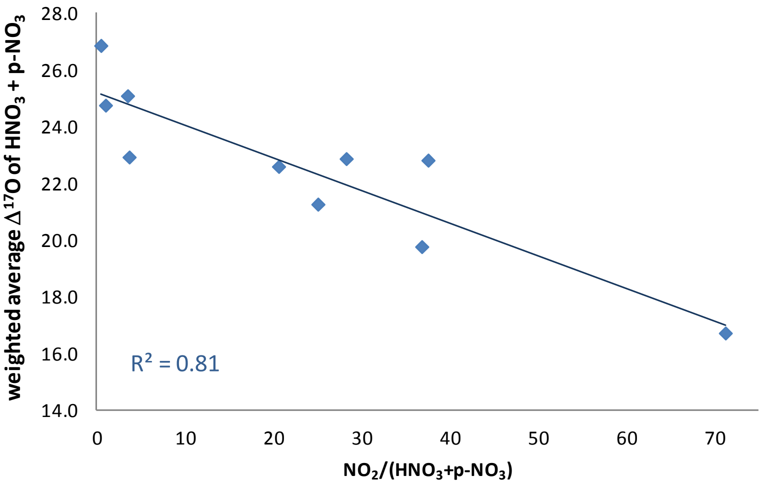


Figure 5: Weighted Δ^{17}O average (‰) for the sum of dry nitrates as a function of NO$_2$ concentration divided by p-NO$_3$ plus HNO$_3$ concentrations, a ratio indicative of the maturity of a plume.

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.

Reply: The reader should keep in mind that the main precursor of p-NO$_3$ is HNO$_3$. Additionally, we refer the reader again to the articles cited in the original manuscript showing higher dry deposition rates for HNO$_3$ (Zhang et al 2009; Benedict et al., 2013).

Changes in manuscript: none required.

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.

Reply: It is important to note here 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 NO_2. Therefore, their modeling results are not comparable with the nitrates collected within minutes to hours of fresh NO_x emissions. It would be interesting to see their spin-up period.

The field measurements reported here were not specifically designed to test Michalski's proposition on NOx-NO_3 isotopic disequilibrium (Michalski et al. 2014 paper), but they provide an opportunity to verify whether or not non steady-state is possible in the field by allowing examination of anthropogenic nitrates collected after various duration of sampling. The results are such that they suggest the nitrate loads are at least partly reflecting NOx-NO_3^-isotopic disequilibrium.

Considering that this article represents the first investigation of simultaneously sampled nitrates in precipitation, gas and particulate forms for their $\delta^{18}O$ and $\Delta^{17}O$ 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 by placing less emphasis on the types of sources from which the plumes were sampled, and by reworking the results and interpretation (section 3) and discussion (section 4).

Changes in manuscript: Former sub-sections 4.2 and 4.4 are now sub-sections 3.4 and 3.5, respectively; abstract lines 16-22, and new sub-section 3.2; new title and trimmed sub-section 4.2; new title for sub-section 4.3.

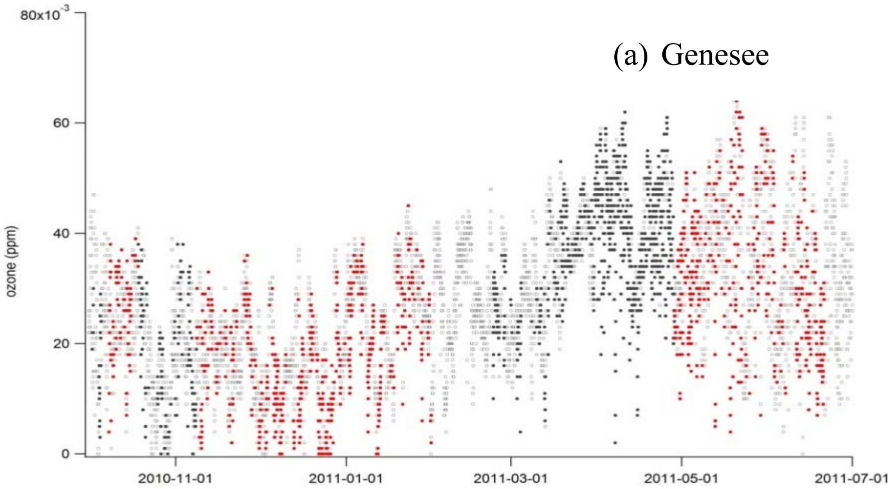
14- Explanation of correlations with meteorological parameters are ad hoc and rough with a weak constrain on possible mechanisms. For instance, correlations with RH and T can be the result of the winter/summer meteorology. Summer is more oxidant but also warmer, sunnier and lower RH. Should all correlations be interpreted, as much of them are not independently related?

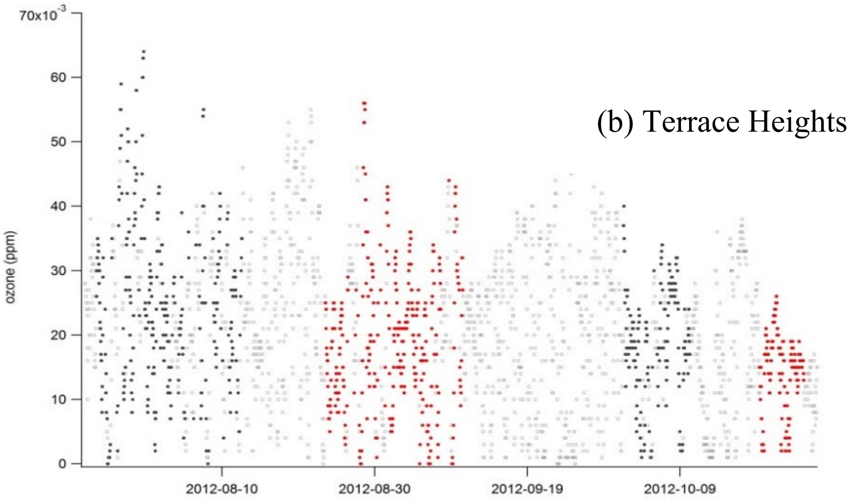
Reply: We judge pertinent suggesting an interpretation for these correlations as they relate to reactions summarized in Table 5. The text describing this interpretation is short, and it is now placed with the results and interpretation section (3), right after the interpretation in terms of oxidation pathways (sub-section 3.3).

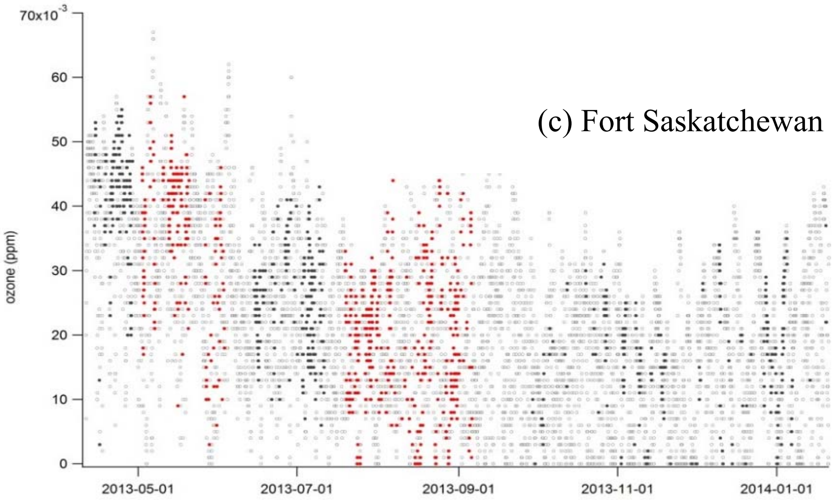
Changes in manuscript: see new section 3.4

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.

REPLY: We are not convinced that time series of O_3, NO_x and jNO_2 would be meaningful in interpreting these integrated and intermittent samples, which is why we used average values over the sampling times for O_3 and NO_x analysis. However, those average values are now reported in the new data table of the supplementary information. The use of daylight fraction rather than jNO_2 is discussed in point 4. Graphs of the O_3 time series at (a) Genesee, (b) Terrace Heights, and (c) Fort Saskatchewan, including during sampling periods, are below. Filled circles identify periods when nitrate sampling was taking place for at least half of the hour, with alternating black and red to indicate different samples. Due to expected large spatial gradients in NO_x, we decided the comparison with NO_x 5 km away was problematic and removed it. However, NO_2 data measured on-site now appear reported where available.







<u>Changes in manuscript</u>: average values are in Table SM-3.

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).

REPLY: Good point. The previous sentence was : « However, NO_2 not in isotopic equilibrium with O_3, and/or NO reacted with RO_2 significantly influenced the overall results.»

Changes in manuscript: sub-section 4.2, p. 12, line 25: *However, NO_2 not in isotopic equilibrium with O_3, and/or NO reacted with RO_2* may have *significantly influenced the overall results*.»

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.

REPLY: This is a good suggestion. A technique for actively sampling integrated NO_2 and NO concentrations was developed with some success through the course of the study, but since it was an evolving methodology, we have acceptable NO_2 concentrations only at 3 of the 4 sites, both in the Edmonton urban area.

We have plotted the $\Delta^{17}O$ values (weighed average) of p-NO_3 and HNO_3 as a function of NO_2 concentrations / (p-NO_3 plus HNO_3 concentrations), and there is clear inverse correlation. In other words, when NO_2 is high (low nitrates in early plume), the $\Delta^{17}O$ values are low, and when NO_2 is low (late plumes), the nitrates $\Delta^{17}O$ values are high. These NO_2 concentrations also appear in Table SM-1.

Changes in manuscript: See new Figure 5 and reply to comment 11.

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.

Point-by-point REPLY-II to Anonymous Referee #3

1-I maintain that this article should have been submitted to AE as a Part II for coherency but this is a minor comment
REPLY- We do not see the advantage for the readership in this proposition. Publishing two articles dealing with distinct issues of atmospheric science isotopic applications, with several months in between, is commonly done through different journals, even if reporting data from a single region.

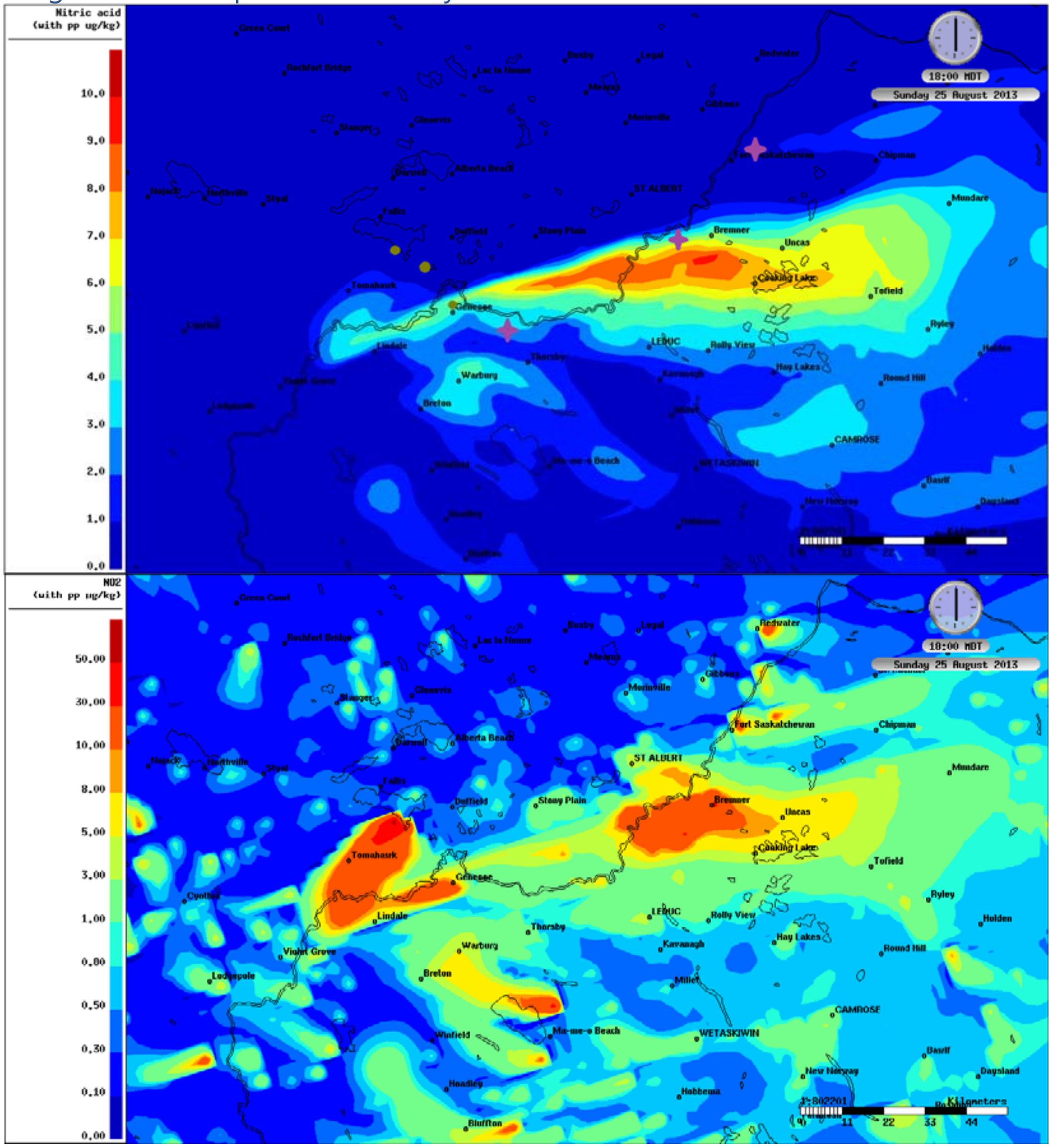
Change in manuscript: none required.

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)
REPLY- We mean 'New and novel' implying that the data is QA/QC checked, i.e., valid.

Change in manuscript: 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 NOx, nitrate (or any other tracers, CO, O3) 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.

REPLY- We did not claim a "permanent sampling" of plume emissions, as we agree that would be unrealistic. The goal was to isolate anthropogenic emissions at various locations (distances), downwind from the sources, with the emissions subject to field conditions and atmospheric processing (i.e. not stack sampling). By necessity, it is clear that background contributed to the sampled load, but not in significant proportions. A few pieces of evidence support this. One is the low background concentrations; background particle nitrate and nitric acid concentrations at Wood Buffalo National Park in northern Alberta, where CAPMoN began sampling in 2014, averaged 0.016 and 0.020 µg N m^{-3}, respectively, for >2 years of monitoring. Concentrations from the conditional sampling at the sampling sites studied here were up to 20 times higher, suggesting that the collected samples have greater p-NO_3 and HNO_3 concentrations than background. Second, back trajectories confirmed that the conditional sampling method sampled air masses that predominantly passed over or near the sources. In addition, we obtained some model output from a 2-week simulation in 2013 (Makar et al., 2018) illustrating the significantly higher concentrations of nitric acid downwind of the coal-fired power plants near Genesee. In this snapshot, the three power plants are shown as brown dots and the three Edmonton-area sampling locations are shown as purple stars. The NO2 plumes are shown as well to illustrate the change in direction of the plume. It is clear that at the Genesee site, the bulk of the nitric acid at this particular time resulted from the nearby power plants. Using the conditional sampling weighted the samples more heavily when this was the case.



<u>Changes in manuscript</u>: The title is changed to “The δ^{17}O and δ^{18}O values of atmospheric nitrates simultaneously collected *downwind of* anthropogenic sources – Implications for polluted air masses.”

Text edited in section 2.2: *“Back trajectories run using the HYSPLIT model (Stein et al., 2015; Rolph, 2017) for every hour of sampling verified that the conditional sampling approach collected air masses that had primarily passed over or near the targeted source (i.e. there was no landscape feature that decoupled wind direction from back trajectories). A sample plot of back trajectories from Genesee is show in Figure SM-2.”*

Text added to section 3.2: *"Background sites for this region are sparse, but concentrations at Cree Lake in neighbouring Saskatchewan were the lowest in Canada reported up to 2011 (Cheng and Zhang, 2017), and 2014-2016 measurements at Wood Buffalo National Park on the northern Alberta border revealed similar average concentrations of 0.02 µg N/m^3 for both HNO_3 and p-NO_3^- (preliminary internal data). Therefore, the lowest concentrations in our samples approached average background concentrations, while the highest were 20 or more times higher than regional background."*

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.

REP- It is unclear to us how informative it will be to see hourly time series, which must then be compared with an integrated sample, however, in the interests of fulfilling the request we have added the plots for O3.

Change in manuscript: The data for each sampling period are now reported in Tables SM-1 through SM-3. In addition, plots to show the O_3 measured at nearby stations including during sampling periods are shown in reply I to reviewer 3, comment 15. Due to expected large spatial gradients in NO_x, we decided the comparison with NO_x 5 km away was problematic and removed it. However, NO_2 measured on-site is now reported where available.

5 (merged with 9; see below) -It is wrong to think that denuders are best used in urban area. Denuders to collect HNO3 are used in the most remote regions of world (eg Antarctica, Jourdain and Legrand, 2002, Legrand et al., 2017). Denuders that are operational at 1m3/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-NO3 and 2nd nylon filter for HNO3) is not the reference set up used to separate p-NO3 and HNO3. It is a set up used mainly to collect total nitrate. The difference in 17O between p-NO3 and HNO3 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 HNO3 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, 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, NorwayEMEP/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.

9- I will give one example where 17O 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 HNO3 and H2O 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 17O 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 17O HNO3 and p-NO3 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.
REPLY- We have responded to points 2, 5 and 9 together since we interpreted them as raising closely-related issues.
We acknowledge that it is possible to use denuders in remote areas, our point was that there are specific and well-regarded networks of rural and remote stations that continue to use filter-based sampling. Since our system was using the established methods of one of those networks (CAPMoN), and evaluation of the method blanks, collection efficiencies and interferences have been previously reported, it seems excessive to us to require repetition of these tests in every report using the same method. Where we developed a new method (for NO and NO$_2$ active sampling, not reported here), blanks and breakthrough tests were done and evaluated before reporting results. Again, denuders were considered, but we chose not to use them for several reasons: (1) we were not certain of the denuder capacity or the ambient levels of HNO$_3$ in this region prior to the study; (2) given the potential for long periods without flow in the conditional sampling setup, denuders open to the atmosphere would be likely to passively sample during non-pumped periods; while (3) denuders with size-selective impactors at the inlets would result in screening out nitrate on some particles, with the size cutoff varying as the pumps cycled on and off in (sometimes) 5-minutes periods. Note that isotopic results based on collection with filter packs are not new. For instance, isotopic values for dry deposition (p-NO$_3$ and HNO$_3$) actively collected with filter packs over a week have previously been validated in eastern USA (Elliott et al., JGR, vol 114, 2009).

Our primary concern with this system was the volatilization that is well documented, and that would affect both the O and N isotopes in a mass dependent and highly temperature dependent way. Therefore, as we stated, we evaluated the relative HNO$_3$ and p-NO$_3$ δ^{18}O and δ^{15}N values (as well as δ^{15}N in NH$_3$ and p-NH$_4$), and their pattern with temperature, to judge whether this was strongly affecting the results. We did not draw conclusions about the artifact based on Δ^{17}O values, just stated that mass-dependent volatilization would not affect the Δ^{17}O value, which is correct. While the reviewer does suggest a possible mechanism that would affect Δ^{17}O values (exchange with H$_2$O due to highly acidic particles), this scenario is unlikely in the studied region. Where we analyzed a complete suite of major ion data from the particle filter (2 of the 4 sites), the charge balance was always positive due to both relatively high Ca^{2+} and NH$_4^+$. In any case, this scenario would similarly influence p-NO$_3$ collected in a denuder-filter pack sampling system.

Change in manuscript: A discussion of field tests and intercomparisons has been added to section 2.2: *"Ambient air was pulled through a three-stage filter pack system to collect, sequentially, particulate matter on a Teflon filter, gaseous nitric acid (HNO_3) on a Nylasorb nylon filter, and gaseous ammonia on a citric acid-coated Whatman 41 filter. The Teflon-nylon filter method for p-NO_3^- and HNO_3 has been extensively compared and evaluated, and is currently used by national monitoring networks targeting regional background sites, CAPMoN in Canada and CASTNet (Clean Air Status and Trends Network) in the United States. Previous testing by Anlauf et al. (1985, 1986) showed negligible collection of HNO_3 on the Teflon filter, <3% breakthrough of HNO_3 from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO_3^- and HNO_3 of approximately 0.2 µg N/filter. Intercomparisons with more labor-intensive methods, such as tunable diode laser absorption spectroscopy and annular denuder-filter pack systems, have shown evidence of some volatilization of ammonium nitrate from the Teflon filter leading to a negative bias in p-NO_3^- and positive bias in HNO_3 under hot (> 25 °C) and dry conditions, particularly in high ambient concentrations (e.g., Appel et al., 1981). However, other field studies have shown no significant differences in HNO_3 between filter packs and denuder and/or TDLAS systems (Anlauf et al., 1986; Sickles et al., 1990) or mixed results (Spicer et al., 1982; Zhang et al., 2009). While those studies used short-duration sampling, a comparison for weekly samples at a lower-concentration site showed good agreement between filter pack and denuder values for most of the study but potential interference from HNO_2 (nitrous acid) on the nylon filter in two samples (Sickles et al., 1999). Based on the conditions in Alberta, we estimate that there is little or no volatilization of NH_4NO_3 for samples with mean temperatures below 5 °C, but that there may be up to 30% nitrate loss in the warmest sampling periods."*

Revised text end of section 3.1: "*We therefore conclude that, while volatilization may occur in the summer samples, other isotope effects must be larger in order to lead to the observed differences. In addition, volatilization would cause mass-dependent fractionation and would not affect the ^{17}O anomaly; therefore, $\Delta^{17}O$ values remain robust tracers in this situation."*

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
REPLY- The main point of the article is not to address differences between various anthropogenic sources, but to examine isotopic trends in anthropogenic plumes sampled at different periods (various distances from sources, i.e., various delays after emissions), with the specific objective of verifying if low $\Delta^{17}O$ values exist in some contexts. The results clearly show that they do. This finding has implications for interpreting isotopic data collected downwind from anthropogenic sources in general. The title refers to this aspect, which the article largely discusses.

Change in manuscript: title reworded « The $\Delta^{17}O$ and $\delta^{18}O$ values of atmospheric nitrates simultaneously collected downwind of anthropogenic sources – Implications for polluted air masses »

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.

REPLY- Merged parallel samples (Genesee and Vauxhall) constitutes a physical average of atmospheric characteristics at a given area. This operation can be compared with the calculated average through 4 parallel samples (4 other sites), which only aimed at determining the reproducibility of our sampling and analytical protocols. We have judged this type of care determinant and crucial in guaranteeing the quality of the data. Not clear what the reviewer means in the second point. There is no other way to plot the data since each sample is integrated over a variety of conditions. We would agree that higher-frequency field measurements would add to our understanding of the processes, though it would be challenging to collect enough material for isotopic analysis as methods currently stand.

Change in manuscript: additional details for each sample (air volumes, daylight fraction, etc.) are included in Tables SM-1 to SM-3.

10- Again I do not see any systematic trend in 17O difference between p-NO3 and HNO3 with season (fig3). In summer, two out of four have 17O nitrate > 17O HNO3 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- HNO3 is formed from non-equilibrated NOx/O3 system and 2- HNO3 is faster scavenged. I can propose the formation of lower 17O p-NO3 by the heterogeneous reaction 2NO2 + H2O(s) –> HNO3(ads) + HONO (Finlayson-Pitts, 2009), or higher 17O HNO3 by NO3 + RH –> HNO3 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.

REPLY- The trends are various and each deserves attention. We discuss all of them in the article.

Change in manuscript: none required.

13- Well, I disagree again with the authors. One of the strongest argument used in this paper is to claim that NOx-O3 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 O3 vs NOx). Yet ozone formation is the only reaction creating 17O-excess, and since chemical steady state is quickly reached, equilibrium of 17O among all species can't be reached faster than O3 own equilibrium time in Michalski's model. Clearly, the limiting step in Michalski's model to propagate 17O is ozone formation and not NOx/O3 interaction. If ozone is in isotopic equilibrium, any new population of NO2 formed by O3+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 NO2 versus flux of NO2 to reach equilibrium. Isotopic abundance has nothing to do here. Let's imagine that O3 is already in isotopic equilibrium, further formation/destruction have no effect on ozone 17O. Let's imagine further that NOx and O3 are in chemical/isotopic equilibrium (new O3 formed has the same isotopic composition than consumed O3 as O3 isotope is controlled by pressure and temperature only). Suddenly, a new pool of NO is emitted. NO will be converted to NO2 by O3 contained in the surrounding atmosphere upon mixing and thus NO2 will be formed at the rate of the Leighton cycle in this system. The characteristic time of the isotopic transfer from O3 to NO2 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 O3 so that O3 stays constant. The characteristic time, Tau, at which the non-equilibrated isotopic NOx reservoir is replaced by the isotopic equilibrated NO2 is simply twice the size of NO2 reservoir divided by the speed of Leighton cycle, either NO+O3 reaction or JNO2 depending on the chemistry context, as one of these reactions is the limiting step. Using Michalski first simulations, NO = 23 ppbv (assumed NO2/NOx = 0.3 for fresh plume), NO2 = 10 ppbv, O3 = 50 ppbv and k = 2e-14 molecules cm-3 s-1, J = 0,007 s; then Tau = 2/J = 4,8 min. In 20 min NO2 is at 98 % in isotopic equilibrium. Using Michalski second simulations NO2= 0,03ppb, NO=0,003 ppb (assumed NO2/NOx = 0.9 for remote place), O3 = 5 ppb, Tau = 2 [NO2]/(k[NO][O3]) = 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 NOx are recycled through the BrO + NO and not NO+O3 reaction. In a more rural situation (Rohrer et al., 1998), NO2 = 1,4 ppb, NO = 0,3 ppb, O3 = 25 ppb, Tau = 11 min Rohrer, F., Brüning, D., Grobler, E. S., Weber, M., Ehhalt, D. H., Neubert, R., Schüßler, W., and Levin, I.: Mixing Ratios and Photostationary State of NO and NO2 Observed During the POPCORN Field Campaign at a Rural Site in Germany, Journal of Atmospheric Chemistry, 31, 119-137, 10.1023/a:1006166116242, 1998.

REPLY- We do not want to discuss the fundamentals of Michalski et al.'s paper here, this is not the place. However, we trust that the conclusion of Michalski's experiments open up the possibility of seeing isotopic disequilibrium in natural samples under certain conditions. In fact, given the unknowns, the back-of-envelope calculations above (20 min and 8 h to 98% of equilibrium in the two scenarios) are roughly in agreement with the timescales shown in Michalski et al. (Fig. 8). Therefore, it is not clear why the reviewer is not comfortable with the results of their simulations. Given that transit times from the closest point sources to our measurement sites averaged 25 minutes (range 9-55), and that we were sampling the fraction of NO_x that had been converted to nitrate and therefore "frozen" in $\Delta^{17}O$ at the point of conversion, contributions from unequilibrated NO_x are not ruled out by the tau of 11 minutes suggested by the reviewer for similar conditions.

Based on this discussion and comments from another reviewer, we have realized that the salient point is whether the amount of nitrate formed shortly after emission (before the NO_2-O_3

isotopic equilibration) is enough to contribute significantly to the samples. Our calculations indicate that it is feasible, and we've updated the manuscript to include those results.

We would like to be clear that we are not claiming to present definitive evidence of this phenomenon in the atmosphere. Indeed, we do suggest in the manuscript that the contribution from enhanced RO_2 could also give a similar result, as has been previously hypothesized. However, since the possibility of incomplete NO_x equilibration retained in nitrate field samples was a new idea supported by winter data when RO2 cannot play significantly, NOx-O3 disequilibrium was also highlighted. We have carefully reviewed the wording of the document to be sure not to overstate our confidence in the mechanism, as was suggested in the earlier comments.

Change in manuscript:.

Text added to section 4.1: "*While the fraction of NO_x converted to nitrate in this transit time may be small, these are large sources of NO_x in an area with very low background nitrates. For example, a plume containing 10 ppb of NO_2 mixing with background air with 0.1 ppt of OH (Howell et al., 2014) would produce HNO_3 via R6 at a rate of 0.011µg N m^{-3} min^{-1} at T = 7 °C (Burkholder et al., 2015), or an equivalent amount of a typical sample in 10 minutes. Even if equilibration with O_3 is established within a few minutes, the nitrate produced in the interim can constitute a substantial fraction of the sample collected nearby*."

Subsection 4.3; first paragraph: « As expected, the measured oxygen isotopes of the various nitrate groups are consistent with exchange with O_3 and oxidation through the well-known OH and N_2O_5 oxidation paths. However, NO_2 not in isotopic equilibrium with O_3, and/or NO reacted with RO_2 may have significantly influenced the overall results. »

Subsection 4.3; end of first paragraph: «Meanwhile, our results raise the question: are these overall effects observable in triple oxygen isotopes of nitrates from other polluted sites?»

In summary, authors' reply did not change my position and did not convince me. Because the idea that 1- HNO3 has a different 17O composition than p-NO2 and 2- NOx 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.

REPLY- Point 1 refers to measurements; the difference in isotopic signals is an observation, it is not an idea inferred through an interpretation. We have shown that the data are valid. Point 2 is a suggestion for which all arguments are exposed in the article; the reader gets substantial information allowing for a personal opinion to be made; this suggestion may create a debate (indeed, it already has) and spur further testing of the hypothesis through additional measurements and plume modelling, a healthy outcome in science.

The $\Delta^{17}O$ and $\delta^{18}O$ values of atmospheric nitrates simultaneously collected downwind of anthropogenic sources – Implications for polluted air masses

Martine M. Savard[1*], Amanda Cole[2], Robert Vet[2], Anna Smirnoff[1]

[1] Geological Survey of Canada (Natural Resources Canada), 490 de la Couronne, Québec (QC), G1K 9A9, Canada
[2] Air Quality Research Division, Environment and Climate Change Canada, 4905 Dufferin St., Toronto (ON), M3H 5T4, Canada

Correspondence to: Martine M. Savard (martinem.savard@canada.ca)

Abstract. There are clear motivations for better understanding the atmospheric processes that transform nitrogen (N) oxides (NO_x) emitted from anthropogenic sources into nitrates (NO_3^-), two of them being that NO_3^- contributes to acidification and eutrophication of terrestrial and aquatic ecosystems, and particulate nitrate may play a role in climate dynamics. For these reasons, oxygen isotope ratios ($\delta^{18}O$, $\Delta^{17}O$) are frequently applied to infer the chemical pathways leading to the observed mass independent isotopic anomalies from interaction with ^{17}O-rich ozone (O_3). Recent laboratory experiments suggest that the isotopic equilibrium between NO_2 (the main precursor of NO_3^-) and O_3 may take long enough under certain field conditions that nitrates may be formed near emission sources with lower isotopic values than those formed further downwind. Indeed, previously published field measurements of oxygen isotopes in NO_3^- in precipitation (w-NO_3^-) and in particulate (p-NO_3^-) samples suggest that abnormally low isotopic values might characterize polluted air masses. However, none of the air studies have deployed systems allowing collection of samples specific to anthropogenic sources in order to avoid shifts in isotopic signature due to changing wind directions, or separately characterized gaseous HNO_3 with $\Delta^{17}O$ values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample HNO_3 and p-NO_3^-, and co-collect w-NO_3^-. The nitrates are from various distances (<1 to >125 km) downwind of different anthropogenic emitters, and consequently from varying time lapses after emission.

The separate collection of nitrates shows that the HNO_3 $\delta^{18}O$ ranges are distinct from those of w- and p-NO_3^-. Interestingly, the $\Delta^{17}O$ differences between p-NO_3^- and HNO_3 shift from positive during cold sampling periods to negative during warm periods. The low p-NO_3^- $\Delta^{17}O$ values observed during warm periods may partly derive from the involvement of ^{17}O-depleted peroxy radicals (RO_2) oxidizing NO during that season. Another possibility is that nitrates derive from NO_x that has not yet reached isotopic equilibrium with O_3. However, these mechanisms, individually or together, cannot explain the observed p-NO_3 minus HNO_3 isotopic changes. We propose differences in dry depositional rates, faster for HNO_3, as a mechanism for the observed shifts. Larger proportions of p-NO_3^- formed *via* the N_2O_5 pathway would explain the opposite fall-winter patterns. Our results show that the separate HNO_3, w-NO_3^- and p-NO_3^- isotopic signals can be used to further our understanding of NO_x oxidation and deposition. Future research should investigate all tropospheric nitrate species as well as NO_x to refine our understanding of nitrate distribution worldwide and to develop effective emission reduction strategies.

Supprimé: **simultaneously collected**

Supprimé: typically

Supprimé: distribution of wet (w-NO_3^-), particulate (p- NO_3^-), and the sum of p-NO_3^- and gaseous HNO_3,

Supprimé: Importantly,

Supprimé: while the gaseous form (HNO_3) has never been separately characterized for ^{17}O.

Supprimé: r…ecent laboratory experiments suggest that the reveal time lapses between emission of NOx…sotopic equilibrium between NO_2 (the main precursors…of NO_3^-) and its isotopic equilibrium with O_3 may take long enough under certain field conditions that , even if photochemical steady-state is reached. This mechanism if occurring under field conditions could lead to …itrates may be formed near emission sources with lower isotopic values than those at equilibrium…ormed further downwind. Equally important, Previous research studies have investigatedcharacterization of f…ndeed, previously published field measurements of oxygen isotopes in NO_3^- in precipitation (w-NO_3^- … and in particulate (p-NO_3^- ... [1]

Supprimé: or p-NO_3^- + HNO_3 from non-polluted or polluted air masses, and inferred seasonal changes in the dominance of oxidation pathways to account for higher $\delta^{18}O$ and $\Delta^{17}O$ values in winter relative to summer.

Supprimé: pathways related to

Supprimé: polluted …ir studies have deployed systems allowing collection ofed…samples specific to targeted emission ... [2]

Supprimé: pathways…sotopic signature due to moving…hanging wind directions, or separately characterized gaseous HNO_3 with $\Delta^{17}O$ values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample HNO_3 and p-NO_3^-, and co-collect w-NO_3^-. The nitrates are from various distances (<1 to >125 km) downwind from …f five ... [3]

Supprimé: five different …nthropogenic sources ... [4]

Supprimé: Overall, the w- and p-NO_3 $\delta^{18}O$ and $\Delta^{17}O$ values show expected differences between cold and warm seasons, but only the $\Delta^{17}O$ values of HNO_3 follow this pattern.

Supprimé: the …hose of w- and p-NO_3^- patterns… Interestingly, the $\Delta^{17}O$ differences between p-NO_3^- and HNO_3 shifts…from positive during cold sampling periods to negative during warm periods. The very ... [5]

Supprimé: The summer pattern …ay be …artly derive ue to…rom the …nvolvement of ^{17}O-depleted peroxy radicals (RO_2) oxidizing NO during that season. Another possibility is that the presence of nitrates derived…from NO_x that has not yet reached isotopic equilibrium with O_3 … However, these mechanisms, individually or together, cannot explain the observed p-NO_3 minus HNO_3 isotopic changes. We propose and subsequent ... [6]

Supprimé: valid …echanism for the observed shifts. Subsequent increased renewal of HNO_3 in the plume, with higher $\Delta^{17}O$ values in newly formed HNO_3 as NOx-O_3 equilibrate with time. ... [7]

Supprimé: while the l…arger proportions of p-NO_3^- formed *via* the N_2O_5 pathway would can …xplain the opposite fall-winter patterns. Very low p-NO_3^- $\Delta^{17}O$ values observed during warm months may be due to this non-equilibrated NO_x, though contribution from RO_2 oxidation remains a possibility. …ur results show that the separate HNO_3, w-NO_3^- and p-NO_3^- isotopic signals of HNO_3, w-NO_3^- and p-NO_3^- are not interchangeable and that their differences …an be used to further our understanding of NO_x oxidation and deposition. Future research should investigate all tropospheric nitrate species as well as NO_x to refine our understanding of nitrate distribution worldwide and to develop effective emission reduction strategies.¶ ... [8]

1 Introduction

Anthropogenic NO_x (NO and NO_2) emissions are oxidized to nitrate in the atmosphere in the form of gaseous, wet or particulate forms, HNO_3 being one of the main precursors of p-NO_3^-. All these species may have detrimental effects on human health and aquatic and terrestrial ecosystems through inhalation, acidification and excess nitrogen deposition. In addition, aerosols may play a significant role in regional climate dynamics as they interact with clouds and solar radiation (e.g., IPCC, 2013). For these reasons, understanding the chemical processes controlling the transport and fate of atmospheric reactive N is required to help develop effective emission reduction strategies and drive climate models (in the present article, we use *nitrates* to collectively refer to p-NO_3, HNO_3 and w-NO_3).

Triple oxygen isotopes ($\delta^{18}O$ and $\delta^{17}O$) have been used to decipher atmospheric oxidation pathways of NO_x leading to ambient nitrate. Michalski et al. (2003) performed the first measurement of $\delta^{17}O$ values in atmospheric nitrate. The authors found nitrate highly enriched in ^{18}O and ^{17}O, likely due to the transfer of anomalous oxygen atoms from ozone (O_3) via the NO_x-ozone photochemical cycle and oxidation to nitrate. During its formation, O_3 inherits abnormally high $\delta^{18}O$ and $\delta^{17}O$ values through mass independent fractionation. The specific $\delta^{17}O$ departure from the terrestrial mass dependent fractionation line, named the ^{17}O anomaly, is often expressed as $\Delta^{17}O = \delta^{17}O - 0.517 \times \delta^{18}O$ (Thiemens, 1999). Further investigations suggested that the $\delta^{18}O$ and $\delta^{17}O$ values of w-NO_3^- and p-NO_3^- reflect several reactions taking place after the atmospheric emission of NO_x, *i.e.*, atmospheric oxidation pathways transforming NO_x into secondary products (Hastings et al., 2003; Michalski et al., 2003; Michalski et al., 2004; Morin et al., 2007; Savarino et al., 2007; Alexander et al., 2009). Seasonal $\delta^{18}O$ differences in w-NO_3^- samples (less variable and lower values during summer) have been interpreted to be due to changes in these chemical pathways (Hastings et al., 2003). Modeling and validation based on sparse existing data provide hope regarding a global understanding of atmospheric nitrate (Alexander et al., 2009), however, further measurements need to be done on the ground, particularly at mid-latitudes.

Additional studies dealing with triple oxygen isotope characterizations have addressed questions of methodology (Kaiser et al., 2007; Smirnoff et al., 2012), transfer of the ozone ^{17}O anomaly to atmospheric nitrate (Liang and Yung, 2007; Savarino et al., 2008; Michalski et al., 2014), or sources and chemical pathways of high (Arctic) and low (Taiwan) latitude nitrate (Morin et al., 2008; Guha et al., 2017, respectively). Triple oxygen isotope characterizations of field NO_3^- samples are not yet widespread. Also rare are the nitrate $\delta^{18}O$ and $\Delta^{17}O$ values of field samples downwind from NO_x-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). The few existing studies have chiefly characterized w-NO_3^- or the sum of p-NO_3^- and HNO_3 (Michalski et al., 2004; Morin et al., 2007; Morin et al., 2008; Alexander et al., 2009; Morin et al., 2009; Proemse et al., 2012; Guha et al., 2017), and suggested these indicators would be useful to trace atmospheric nitrate in water (Kendall et al., 2007; Tsunogai et al., 2010; Dahal and Hastings, 2016), or to apportion the contribution of anthropogenic emissions to regional atmospheric nitrate loads (Proemse et al., 2013).

In the past, due to sampling challenges, HNO_3 and p-NO_3^- were generally collected together (without differentiation). Therefore, no studies have separately and simultaneously collected and analyzed the HNO_3 and p-NO_3^- $\delta^{18}O$ and $\Delta^{17}O$ values, and discussed these isotopic characteristics of nitrate collected downwind of anthropogenic emitters. While HNO_3 and p-NO_3^- can be in equilibrium (e.g. if p-NO_3^- is in the form of solid NH_4NO_3), this is not always the case, for example, if nitrate is

Supprimé: (HNO_3)

Supprimé: (precipitation or w-NO_3^-)

Supprimé: (p-NO_3^-)

Supprimé: together

Supprimé: may serve for

Supprimé: ing

Supprimé: that atmospheric

Supprimé: is

Supprimé: and

Supprimé: . Elliott et al. (2009) measured $\delta^{18}O$, but not $\Delta^{17}O$, in United States CASTNET (Clean Air Status and Trends Network) samples of simultaneously-collected p-NO_3^- and HNO_3 as well as in nearby NTN (National Trends Network) precipitation samples.

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (Canada)

Supprimé: (Proemse et al., 2013)Even rarer are the nitrate $\delta^{18}O$ and $\Delta^{17}O$ values of field samples downwind from NO_x-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). In those studies, $\delta^{18}O$ and $\Delta^{17}O$ values were suggested to be useful to apportion the contribution of emission sources to regional atmospheric nitrate loads.

Mis en forme : Anglais (Canada)

Supprimé: However, the signals of precursor NO_x emitted from the same sources may quickly get modified through isotopic equilibration with O_3, so that the original source signals may be difficult to recognize.

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (Canada)

Mis en forme : Anglais (États-Unis)

Mis en forme : Anglais (États-Unis)

Mis en forme : Anglais (États-Unis)

Supprimé: at mid-latitudes

bonded to calcium or dissolved in liquid water on a wet particle (see section 3.3). They have different lifetimes with respect to wet scavenging (Cheng and Zhang, 2017) and dry deposition velocities (Zhang et al., 2009), and may differ in their formation pathways as well. Therefore, investigating the mass independent and dependent oxygen fractionations in nitrates separately collected may help identifying their respective formation and loss pathways, and provide additional constraints on processes controlling their distribution.

Here we have characterized nitrate collected downwind of five emission sources in central and southern Alberta, Canada, namely: (1) coal-fired power plants, (2) city traffic, (3) chemical industries and metal refining, (4) fertilizer plant and oil refinery, and (5) gas compressors plus cattle and swine feedlots. To this end, we employed wind-sector-based active samplers to collect HNO_3 and p-NO_3^- as well as w-NO_3^- downwind of the source types. The objective of this work was to assess the atmospheric NO_x reaction pathways and determine processes responsible for the distribution of HNO_3, and w- and p-NO_3^- in a mid-latitudinal region.

2 Methodology

2.1 Regional context

While national reported NO_x emissions in Canada declined steadily from 2000 to 2015, emissions in the Province of Alberta have remained relatively constant since 2004 (Environment and Climate Change Canada, 2016). Pioneering work was accomplished measuring nitrate on emitted PM2.5 (particulate matter less than 2.5 µm) and in bulk and throughfall precipitation samples (wet and some dry deposition on ion exchange resin collectors) collected at or downwind of the Athabasca oil-sands mining operations in northern Alberta (Proemse et al., 2012; Proemse et al., 2013). However, the Edmonton area in central Alberta, known to generate the highest NO_x emissions in Canada, and the area of southern Alberta, characterized by dense gas compressor station and agricultural emissions, have never been investigated.

This research project investigated nitrates (p-NO_3^-, HNO_3 and w-NO_3^-) from two main emission source areas: the Genesee and Edmonton areas of central Alberta, and the Vauxhall area of southern Alberta (Fig. 1A). These areas experience a continental climate, but the mean annual temperature at Vauxhall is slightly higher (5.6 °C) and total annual precipitation lower (320 mm) than in central Alberta (3.9°C; 537 mm; Fig. SM-1). Autumn is generally the wettest season and winter the driest. The sampling sites were at altitudes between 645 and 820 m (altitude above sea level), and in continental regions devoid of the influence of marine air masses (negligible halogen oxides).

The rural Vauxhall area was selected for collecting nitrates emitted from multiple small gas compressor stations scattered throughout southern Alberta and reduced N from cattle and swine feedlots. The other anthropogenic emissions are from three sites in central Alberta (Fig. 1B): coal-fired power plants (CFPP) at the Genesee site, 55 km southwest of Edmonton; traffic-dominated emissions at Terrace Heights, a residential area near downtown Edmonton; and an industrial area in Fort Saskatchewan, northeast of Edmonton, where sampling two different wind sectors allowed separating different industries. In

Supprimé: (Cheng and Zhang, 2017)

Supprimé: (Zhang et al., 2009)

Mis en forme : Anglais (États-Unis)

Supprimé:

Mis en forme : Anglais (États-Unis)

Mis en forme : Anglais (États-Unis)

Supprimé: Importantly, the rate of HNO_3 production depends on the atmospheric NOx amounts and production rates of oxidizing agents (e.g., O_3, OH, RO_x; see section 3.3), and further down the chain of reactions, atmospheric HNO_3 participates in forming p-NO_3^- by reacting with ammonia or other base cations . Hence, *a priori*,

Supprimé: the gaseous and particulate nitrate forms carry different isotopic characteristics likely to reflect their formation conditions, and if nitrates are sampled quickly after their emission, they may record NOx-O_3 isotopic disequilibrium. It is clearOur working hypothesis is that

Supprimé: causes of isotopic fractionation

Supprimé: of

Supprimé: these

Supprimé: specie

Supprimé: and

Supprimé: reaction

Supprimé: responsible for their transformation would contribute to our understanding of

Supprimé: nitrogen

Supprimé: worldwide

Déplacé vers le bas [2]: ¶
While national reported NO_x emissions in Canada declined steadily from 2000 to 2015, emissions in the Province of Alberta have remained relatively constant since 2004 (Environment and Climate Change Canada, 2016). Pioneering work was accomplished measuring nitrate on emitted PM2.5 (particulate matter less than 2.5 µm) and in bulk and throughfall precipitation samples (wet and some dry deposition on ion exchange resin collectors) collected at or downwind of the Athabasca oil-sands mining operations in Alberta (Proemse et al., 2012; Proemse et al., 2013). However, the Edmonton area in Central Alberta, known to generate the highest NO_x emissions in Canada, and the area of southern Alberta, characterized by dense gas compressor station and agricultural emissions, have never been investigated. ¶

Supprimé: targeted

Supprimé: s

Déplacé (insertion) [2]

Code de champ modifié

Supprimé: C

Supprimé: three

Supprimé: (Fig. 1)

Supprimé: (Fig. 1).

Fort Saskatchewan, sampling in the northwest sector targeted emissions from a mixture of sources of which the largest were a chemical plant and metal refinery (referred to as chemical plus metal industries; distance to sources of 3 to 7 km), while the north sector point emissions were dominated by a fertilizer plant and an oil refinery (referred to as fertilizers plus oil; distance to sources from 9 to 14 km). The NO$_x$ emissions reported to the National Pollutant Release Inventory (Environment and Climate Change Canada, 2018b) for 2013 from all Alberta sources are also shown in Fig. 1.

2.2 Sampling protocols

Collection of nitrate samples took place between 30 September 2010 and 20 January 2014. Active air sampling was carried out using a modified version of Environment Canada's CAPMoN (Canadian Air and Precipitation Monitoring Network) sampling protocol, which is described in detail elsewhere (Sirois and Fricke, 1992). Precipitation sampling also followed CAPMoN wet-only protocols as described in the literature (Sirois and Vet, 1999). A 'conditional sampling' method was employed to maximize the collection of nitrogen compounds from the anthropogenic sources, in which the sampling pumps and precipitation collector were activated when the site wind vane registered winds faster than 0.55 m/s (2 km/h) from the direction of the targeted sources. The CAPMoN sampling system was installed and operated at different sites, each at varying distances from the targeted point (<1 to 35 km), and diffuse sources (3 to >125 km; Table 1). Back trajectories run using the HYSPLIT model (Stein et al., 2015; Rolph, 2017) for every hour of sampling verified that the conditional sampling approach collected air masses that had primarily passed over or near the targeted source (i.e., there was no landscape feature that decoupled wind direction from back trajectories; see sample plot of back trajectories from Genesee in Fig. SM-2).

Ambient air was pulled through a three-stage filter pack system to collect, sequentially, particulate matter on a Teflon filter, gaseous nitric acid (HNO$_3$) on a Nylasorb nylon filter, and gaseous ammonia on a citric acid-coated Whatman 41 filter (all 47 mm). The Teflon-nylon filter method for p-NO$_3^-$ and HNO$_3$ has been extensively compared and evaluated, and is currently used by national monitoring networks targeting regional background sites, CAPMoN in Canada and CASTNet (Clean Air Status and Trends Network) in the United States. Previous testing showed negligible collection of HNO$_3$ on the Teflon filter, <3% breakthrough of HNO$_3$ from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO$_3^-$ and HNO$_3$ of approximately 0.2 µg N/filter (Anlauf et al., 1985; Anlauf et al., 1986). Intercomparisons with more labor-intensive methods, such as tunable diode laser absorption spectroscopy and annular denuder-filter pack systems, have shown evidence of some volatilization of ammonium nitrate from the Teflon filter leading to a negative bias in p-NO$_3^-$ and positive bias in HNO$_3$ under hot (> 25 °C) and dry conditions, particularly in high ambient concentrations (e.g., Appel et al., 1981). However, other field studies have shown no significant differences in HNO$_3$ between filter packs and denuder and/or TDLAS systems (Anlauf et al., 1986; Sickles Ii et al., 1990) or mixed results (Spicer et al., 1982; Zhang et al., 2009). While those studies used short-duration sampling, a comparison for weekly samples at a lower-concentration site showed good agreement between filter pack and denuder values for most of the study but potential interference from HNO$_2$ (nitrous acid) on the nylon filter in two samples (Sickles Ii et al., 1999). Based on the conditions in Alberta, we estimate that there is little or no volatilization of NH$_4$NO$_3$ for samples with mean temperatures below 5 °C, but there is a possibility for nitrate loss of up to 30% in the warmest sampling periods.

Supprimé: 4

Supprimé: 7

Supprimé: 9

Supprimé: standard

Supprimé: (Sirois and Fricke, 1992)

Mis en forme : Surlignage

Supprimé: recognized and used worldwide to measure ambient NO$_3^-$ (HNO$_3$ and p-NO$_3^-$)

Supprimé: A description of the samplers and sample handling protocols is available in the literature

Supprimé: of interest

Supprimé: 25

Mis en forme : Non Surlignage

Mis en forme : Non Surlignage

Mis en forme : Non Surlignage

Supprimé: verified that very few air masses within the sampling sector passed over other sources outside of the targeted ones in the preceding 24 hours

Mis en forme : Non Surlignage

Supprimé:). A

Mis en forme : Non Surlignage

Supprimé: is show

Mis en forme : Couleur de police : Accent 6

Supprimé: ure

Supprimé:

Déplacé vers le bas [3]: (Anlauf et al., 1985; Anlauf et al., 1986)

Supprimé: by Anlauf et al. (1985, 1986)

Mis en forme : Surlignage

Déplacé (insertion) [3]

Code de champ modifié

Mis en forme : Non Surlignage

Supprimé: (Anlauf et al., 1986; Sickles et al., 1990)

Mis en forme : Surlignage

Supprimé:

Supprimé: (Spicer et al., 1982; Zhang et al., 2009)

Mis en forme : Non Surlignage

Supprimé:

Supprimé: (Sickles et al., 1999)

Supprimé: that

Supprimé: may be

Supprimé: nitrate loss

After the first five sample periods, an experimental active sampling system for NO_2 and NO_x was added downstream of the three-stage filter pack. This system consisted of one or two custom cartridges packed with Maxxam Analytics' resin to selectively collect NO_2, and one- or two-stage filter pack containing two identical Maxxam Analytics' impregnated filters designed to collect NO_x (mostly NO due to upstream collection of NO_2). Oxygen isotopes in NO_2 and NO_x were not measured since we could not rule out oxygen isotope exchange during the extraction process, however, concentrations meeting the QC criteria (Savard et al., 2017) are presented for reference in Table SM-1.

Supprimé: a

Supprimé: .

Supprimé: (NH_3; see Savard et al., 2017 for exact location of sampling sites and $\delta^{15}N$ values of reduced and oxidized atmospheric N species)

Code de champ modifié

Supprimé: repor

Here we report on oxygen isotopes in the simultaneously sampled HNO_3 and p-NO_3^-, along with co-sampled w-NO_3^- in rain and snow samples. Note that precipitation events did not occur regularly (see Fig. SM-1), so that the number of aqueous samples collected was fewer than the gas and particulate samples. Both the air and precipitation samplers were only active when the wind direction was from the desired source sector and the wind speed was greater than 0.55 m/s (2 km/h). Four identical air-sampling systems operated simultaneously at each site, with samples pooled when necessary to provide sufficient filter loadings for isotope analysis and, when possible, measured separately to estimate sampling precision. In contrast to the four gas-and-particle sampling systems, there was a single precipitation collector at each site, and therefore external precision was not determined for precipitation samples. Individual sample deployment times ranged from 5 to 113 days, and total air sampling time within the wind-direction sectors ranged from 21 to 360 hours (Table SM-1). The variable cumulative periods reflected the frequency of the wind flow from the targeted source sectors and the amount of time required to obtain sufficient mass loadings on the filters.

Supprimé: collected in CAPMoN wet-only precipitation samplers

Two or three replicate samples for most species were pooled at Genesee and Vauxhall, the first two sampling sites, subject to the requirement that sampled air volumes be within 15 % of each other, thereby eliminating samples that experienced flow problems. Flow issues were primarily due to pump failure, likely caused by cycling the pumps on and off frequently in early samples. Therefore, for later samples the protocol was changed such that the pumps remained on and valves were used to switch the pumps between sampling lines and non-sampling tubing based on the wind sector. At the sites sampled later in the Edmonton area, improvements to the laboratory analytical procedure allowed for smaller sample amounts and eliminated the need for sample pooling.

Supprimé: due to

Supprimé:

Supprimé: Replicate isotopic values at these sites could be determined by analyzing each of the four samples individually.

2.3 Analytical procedures

Nitric acid from nylon filters were extracted using 10 mL of 0.01M solution of NaCl. Particulate-NO_3 from Teflon filters were extracted in two portions of 6 mL of ultrapure water (ELGA). To reduce possible evaporation, filters were placed in an ultrasonic bath with ice. The extractions were performed during one hour and samples were left for 48 hours in a fridge to insure the complete extractions. The solutions were decanted and a small portion (1-2 mL) was used to determine concentrations. The remaining extracts were stored in the fridge for subsequent isotope analysis. The blanks from both filters were treated the same way.

Concentration of nitrates in Teflon and Nylon filter extracts, and in precipitation samples were determined at the Institut national de la recherche scientifique – Eau, Terre, Environnement (INRS-ETE). The determinations used an automated QuikChem 8000 FIA+ analyzer (Lachat Instruments), equipped with an ASX-260 series autosampler. The detection limit for the method with sulfanilamide (# 31-107-04-1-A) was 2 ppb N-NO_3/L (0.03 N-NO_3 umol/L). Nitrite concentrations were also measured in the extracts. Nitrite concentrations above the detection limit (0.016 mg N/L) were found in a handful of samples at Terrace Heights. These samples were excluded from the reported data.

We characterized the $\delta^{17}O$, $\delta^{18}O$ and $\delta^{15}N$ ratios of HNO_3, w-NO_3^-, and p-NO_3^-, along with the $\delta^{15}N$ values of NH_3, w-NH_4, p-NH_4 and NO_x (all N isotopic results are in Savard et al., 2017). The present article deals solely with the $\delta^{18}O$ and $\Delta^{17}O$ values obtained for the three nitrate species. We treated the samples using the chemical conversion and thermal decomposition of N_2O protocols, providing the ability to simultaneously analyze low-concentration N- and O-containing species (Smirnoff et al., 2012).

A notable challenge in the analysis of the filter-based atmospheric samples is their small extraction volumes. Only 10-12 mL of extract solution were normally available for the measurement of concentrations and isotopic analysis. In addition, the concentrations of these low volume samples were also low (7.1-21.4 µmol NO_3/L). Therefore, not all samples could be diluted to produce volumes sufficient for reduction of NO_3^- to NO_2 and subsequent conversion to N_2O, the final product before isotope analysis. Samples with an initial concentration below 2.3 µmol/L could not be treated individually and were combined to produce volumes sufficient for analyses (same sampling period but combination of collected parallel samples).

The preparation steps involved conversion of nitrate-containing samples into nitrite (NO_2^-) using a custom-made cadmium column. The final preparation step involved using sodium azide to ultimately produce N_2O (McIlvin and Altabet, 2005; Smirnoff et al., 2012). All extracted N_2O was analyzed using a pre-concentrator (PreCon, Thermo Finnigan MAT) including a furnace with 'gold' wires, online with an Isotope Ratio Mass Spectrometer (Delta V Plus, Thermo Electron; Kaiser et al., 2007; Smirnoff et al., 2012). The utilized approach allows the spectrum of $\delta^{15}N$, $\delta^{17}O$ and $\delta^{18}O$ ratios from O-bearing N-species to be determined in samples containing as little as 37.5 nmol of N (15 mL final solution). Extracts from filter blanks were processed in the same way. The blanks from nylon filters were not detectable. Peak heights from the blanks resulting from Teflon filters were detected and always below 10% of sample peaks, having a negligible effect (within the analytical precision). 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 N_2O. The laboratory analytical precision (average of replicates) determined during the present study was 0.6 ‰ for $\delta^{18}O$ and $\delta^{17}O$ values in gaseous (n=12) and solid nitrates (n=20). For w-NO_3, analytical replicates gave 0.6 and 0.5 ‰, for $\delta^{18}O$ (n=3) and $\delta^{17}O$ (n=4) values, respectively. The $\Delta^{17}O$ values are defined as $\ln(1+\delta^{17}O/1000) - 0.516 \times \ln(1+\delta^{18}O/1000)$, relative to Vienna Standard Mean Ocean Water (VSMOW).

Supprimé: Concentration of nitrates on Teflon and Nylon filters, and in rain collectors were determined at Institut national de la recherche scientifique–Eau, Terre, Environnement (INRS-ETE). The determinations used an automated QuikChem 8000 FIA+ analyzer (Lachat Instruments), equipped with an ASX-260 series autosampler. The detection limit for the used method (# 31-107-04-1-A with sulfanilamide) was 2 ppb N-NO_3/L (0.03 N-NO_3 umol/L). The concentration for NO and NO_2 collected with samplers of Maxxam Analytics were determined by Maxxam Analytics using an ion chromatograph.¶
¶

Supprimé: triple oxygen isotopic ratios (

Supprimé: and,

Supprimé:)

Supprimé: their

Supprimé: , and those

Supprimé: $\delta^{17}O$ (

Supprimé:)

Supprimé: with

Supprimé: ¶
¶
Concentration of nitrates on Teflon and Nylon filter extracts, and in precipitation samples were determined at Institut national de la recherche scientifique–Eau, Terre, Environnement (INRS-ETE). The determinations used an automated QuikChem 8000 FIA+ analyzer (Lachat Instruments), equipped with an ASX-260 series autosampler. The detection limit for the method (# 31-107-04-1-A with sulfanilamide) was 2 ppb N-NO_3/L (0.03 N-NO_3 umol/L). The ... [9]

Supprimé: ;

Supprimé: o

Supprimé: 6-

Supprimé: was

Supprimé: generally

Supprimé: µmol

Supprimé: for the protocols preconized here

Supprimé: ,

Supprimé: some

Supprimé: several

Supprimé: (for details consult Smirnoff et al., 2012)

Supprimé: with

Supprimé: the

Supprimé: concentration

Supprimé: /

Supprimé: furnace-

Supprimé: system

Mis en forme : Couleur de police : Automatique

Supprimé: developed at the Geological Survey of Canada

Supprimé: This

Supprimé: duplicates

Supprimé:

Supprimé: ¶

3 Results and interpretation

3.1 Isotopic reproducibility when using the CAPMoN filterpack sampling system

Data obtained from at least two of the four identical CAPMoN sample collection streams at each sampling site were used to calculate the reproducibility of each isotopic value measured. With four or fewer samples collected during each sampling period, a non-parametric approach was deemed most appropriate. Therefore, for each of the 18 sampling periods, a median isotopic value was calculated, then the two to four absolute deviations from this median were calculated (Table 2; Table SM-1). Although there were four replicates in 18 periods, the pooling of simultaneously collected samples and the QC steps described earlier reduced the total number of replicates for each compound (Table 3). The median absolute deviation (MAD) for each compound was then calculated from the 15-38 absolute deviations. Finally, for comparability with the more familiar standard deviation, the MAD was scaled using the standard 0.6745 divisor to give the modified median absolute deviation (M.MAD), a scaled parameter that will be equal to the standard deviation in the event that the distribution is Gaussian (Randles and Wolfe, 1979; Sirois and Vet, 1999). This suite of parallel tests indicates that all measured species show coherent and reproducible $\delta^{17}O$ and $\delta^{18}O$ results, with the M.MAD varying between 0.7 and 2 ‰ (Table 2). These estimations encompass the precision of the entire method, including errors due to sampling, chemical treatments and instrumental analysis.

A potential complication of the air sampling method can arise if there was significant volatilization of NH_4NO_3 on the particle filter into HNO_3 and NH_3, with subsequent collection on the downstream gas filters. This could result in equilibrium isotopic fractionation between the particle and gaseous components, which would become artificially high and low, respectively, with more fractionation at higher temperatures (summer) relative to lower temperatures (winter) when volatilization is minimal (Keck and Wittmaack, 2005). We find the p-NO_3^- isotopic ratios ($\delta^{17}O$ and $\delta^{18}O$) to be generally higher during winter than during summer (see Section 3.4). Moreover, the p-NO_3^- minus HNO_3 isotopic differences are negative during summer, opposite to the expected isotopic artefact if particulate volatilization were the dominant factor in determining the particle-gas isotopic differences (the same was concluded for the $\delta^{15}N$ values in NH_3 and NH_4; Savard et al., 2017). We therefore conclude that, while volatilization may occur in the summer samples, other isotope effects must be larger in order to lead to the observed differences. In addition, volatilization would cause mass-dependent fractionation and would not affect the ^{17}O anomaly; therefore, $\Delta^{17}O$ values remain robust indicators of chemical pathways in this situation. Finding that the sampling protocols are adequate for isotopic work is in agreement with a previous study using a comparable method that found minimal fractionation for p-NO_3^- and HNO_3 (Elliott et al., 2009).

3.2 Concentrations and isotopic ratios of nitrates in Alberta samples

The range of HNO_3 concentrations measured by the filters (from 0.01 to 0.15 µg N/m^3; average of 0.06) are slightly lower than those of p-NO_3^- (from 0.02 to 0.35 µg N/m^3; average of 0.12). For context, the median concentrations at all CAPMoN sites, which represent non-urban areas across Canada, range from 0.02 to 0.25 µg N/m^3 for HNO_3 and from 0.007 to 0.45 µg N/m^3 for p-NO_3^- (Cheng and Zhang, 2017), with the higher values at sites affected by regional and transboundary pollution. Background sites for this region are sparse, but concentrations at Cree Lake in neighbouring Saskatchewan were the lowest in Canada reported up to 2011 (Cheng and Zhang, 2017), and 2014-2016 measurements at Wood Buffalo National Park on the

Supprimé: using

Supprimé: in which multiple (2-4) values were obtained,

Supprimé: This operation was repeated for each of the 18 sampling periods in which multiple measurements were obtained.

Supprimé:). This scaling factor ensures that the M.MAD will be

Supprimé: consistent

Supprimé: with

Supprimé: stronger effects

Mis en forme : Non Surlignage

Supprimé: overall

Supprimé: is

Supprimé: influencing the final signal of the samples

Supprimé: d

Supprimé: is likely to

Supprimé: collecting particles and gaseous components simultaneously provides the best information for understanding atmospheric reactive nitrogen

Supprimé: trace

Supprimé: between

Supprimé: **compositions**

Supprimé: **Averages and ranges of triple oxygen isotopic results in Alberta**

northern Alberta border revealed similar average concentrations of 0.02 µg N/m^3 for both HNO_3 and p-NO_3^- (preliminary internal data). Therefore, the lowest concentrations in our samples approached average background concentrations, while the highest were 20 or more times higher than regional background. The range of concentrations of the w-NO_3^- samples was 0.15 – 0.48 mg N/L. For comparison, volume-weighted mean annual concentrations of nitrate at the remote CAPMoN site to the north (Snare Rapids) for 2011-2014 were approximately 0.07 mg N/L, while at the most polluted site in southern Ontario (Longwoods) the volume-weighted mean concentration was approximately 0.3 mg N/L (Environment and Climate Change Canada, 2018a). It should be pointed out that precipitation ion concentrations vary significantly with precipitation amount, so the short samples collected here are not necessarily representative of annual volume-weighted means.

The average $\delta^{18}O$ and $\Delta^{17}O$ values of HNO_3 (gas), w- and p-NO_3^- show no apparent systematic ordering (Table 3; Tables SM-1 and 2), in contrast to what was found for $\delta^{15}N$ values in the same samples (Savard et al., 2017). As expected, there is no systematic tendency when looking at the samples collected from the anthropogenic sources: CFPP HNO_3 and p-NO_3^- have the highest $\delta^{18}O$ and $\Delta^{17}O$ averages, but not the highest w-NO_3^- values; chemical industries show the lowest $\delta^{18}O$ and $\Delta^{17}O$ averages for w- and p-NO_3, but not for HNO_3. Though the number of samples were limited, w-NO_3^- $\Delta^{17}O$ values were roughly correlated with the weighted average $\Delta^{17}O$ values of p-NO_3 and HNO_3 in samples covering the same time periods, consistent with scavenging of both HNO_3 and p-NO_3 by wet deposition. This observation indicates that the oxygen isotopes in the three nitrate species are not predominantly source dependent (see also Fig. SM-3), as previously suggested in the literature (Michalski et al., 2003).

Considering all nitrate species, the Alberta $\delta^{18}O$ and $\Delta^{17}O$ values range between +48.4 and +83.2 ‰, and between 13.8 and 30.5 ‰, respectively (Table 4; Table SM-1, Fig. SM-4). These ranges indicate that ozone partly transferred its isotopic anomaly to nitrates during NOx cycling and oxidation (nitrate derived through combustion in O_2 would show $\delta^{18}O$ and $\Delta^{17}O$ values of 23.5 and 0 ‰, respectively). When examining the existing $\delta^{18}O$ and $\Delta^{17}O$ data for w- and p-NO_3^- in the literature, the ranges for our mid-latitude samples are within those previously reported (Table 4). The worldwide compilation of documented data is broadening the $\delta^{18}O$ range of atmospheric NO_3^- previously suggested to be between 60 and 95 ‰ (Hastings et al., 2003; Kendall et al., 2007).

Previous studies that report triple isotope oxygen results in atmospheric NO_3 samples are scarce (Table 4). The HNO_3 range documented here is within the broad spectrum of p-NO_3^- values compiled for remote to contaminated sites. Elliott et al. (2009) reported HNO_3 oxygen results for $\delta^{18}O$ values only, with a range of +51.6 to +94.0 ‰ (mean of 77.4), with simultaneously-sampled p-NO_3^- $\delta^{18}O$ values between +45.2 and +92.7 ‰ (mean of 75.2). Those ranges are broader than the HNO_3 and p-NO_3^- values obtained in the present study.

3.3 The $\delta^{18}O$ and $\Delta^{17}O$ trends in nitrates from cold and warm sampling periods

The $\delta^{18}O$ and $\Delta^{17}O$ ranges for HNO_3 identified by sampling period are narrower than those of the simultaneously collected p-NO_3^- (Fig. 2; Table SM-1), suggesting that there are additional mechanisms affecting HNO_3, or that p-NO_3 is derived from different pathways with more variation in isotopic signatures. Overall, the $\Delta^{17}O$ and $\delta^{18}O$ results for HNO_3, w-NO_3^- and p-NO_3^-

Supprimé: In addition

Supprimé: At first sight, t

Supprimé: suggests

Supprimé: 2

Supprimé: (see Section 3.3)

Supprimé: 3

Supprimé: oxidation

Supprimé: To our knowledge, triple oxygen isotopic characterization specific to HNO_3 has never been documented before; previous studies only reported values for the sum of HNO_3 and p-NO_3^- (Table 4).

Supprimé: have

Déplacé vers le bas [1]: The $\delta^{18}O$ and $\Delta^{17}O$ ranges we document here for HNO_3 in Alberta are narrower than those of the simultaneously collected p-NO_3^- (Fig. 1), suggesting that there are additional isotopic fractionation processes when HNO_3 is transformed to p-NO_3^-, or that p-NO_3 is derived from different pathways with more variation in isotopic signatures.

Supprimé: **3.3 Covariations of $\Delta^{17}O$ and $\delta^{18}O$ values in nitrates from individual sources¶**
The p-NO_3^-, w-NO_3^- and HNO_3 values co-vary when identified by source type in the $\delta^{18}O$ and $\Delta^{17}O$ space (Fig. 1). The isotopic range for a single source can be as large as 6 ‰ for $\Delta^{17}O$ values and 19 ‰ for $\delta^{18}O$ values in HNO_3, 12 and 17 ‰ in w-NO_3^-, and 7 and 21 ‰ in p-NO_3. Each source type clearly exhibits nitrate $\Delta^{17}O$ and $\delta^{18}O$ with a specific grouping. The CFPP w-NO_3^- results show a range similar to the HNO_3 results, but lower $\delta^{18}O$ values than the HNO_3 and p-NO_3^- groups. The few other precipitation samples show $\delta^{18}O$ and $\Delta^{17}O$ values generally higher than the p-NO_3^- and HNO_3 samples, again with exception of the chemical and metal industries. ¶
¶
The HNO_3 samples from a given source type tend to have a higher $\delta^{18}O$ value for a given $\Delta^{17}O$ value than p-NO_3^- (or *vice versa*; Fig. 1). These observations suggest that the contribution of oxidation pathways leading to HNO_3 and p-NO_3^- are not identical, or that there is an isotope fractionation in the conversion of HNO_3 to p-NO_3^-. ¶
¶
Regarding the potential for identifying nitrate sources, it appears that using $\delta^{18}O$ and $\Delta^{17}O$ values for such a task is not feasible, as previously suggested in the literature (Michalski et al., 2003). This interpretation stems from the fact that nitrate species show either continuous trends regardless of their sources (p- and w- NO_3) or overlapping source results (HNO_3; Fig. 1).¶
¶
The individual range of points identified by source may partly reflect different initial ambient conditions and rates of changes in ambient conditions during NO_x oxidation (Fig. 1; see Section 3.5). Specifically, each isotopic range may depict the progressively changing influence of ozone due to ambient conditions through time. Indeed, the atmospheric samples were collected repeatedly over several weeks or months at a given site (near a given source), and consecutively from one site to the other over more than three ... [10]

Supprimé: **Seasonal**

Déplacé (insertion) [1]

Supprimé: we document here for HNO_3 in Alberta

Supprimé: isotopic fractionation processes when

Supprimé: is transformed to p-NO_3^-

Supprimé: from all sources combined and identified by sampling period clearly show higher $\delta^{18}O$ and $\Delta^{17}O$ values during cold periods relative to warm periods (Fig. 2), with the exception of HNO_3 $\delta^{18}O$ values, which were similar in cold and warm periods. The collection of several samples lasted over periods overlapping fall and winter and, in such cases, the results are labelled as covering the two seasons; note that for many fall cases, the average sampling temperatures were below 0ºC (Table SM-3). Nevertheless, plotting by sampling period can be regarded as a general repartition of results between warm and cold months, which show lower and higher isotopic values, respectively, in both the w- and p-NO_3^-.

A series of reactions listed in Table 5 summarizes the main atmospheric processes taking place during the production of nitrates in contaminated air masses. First, during anthropogenic combustion of fossil fuels, NO_x (NO and NO_2) is produced through reactions of air N_2 with atmospheric O_2 at high temperatures (reactions R1; Table 5). Then, NO_x cycles between NO and NO_2 through a series of reactions involving sunlight (R5), O_3 (R2, R4), and peroxy (HO_2) or alkyl peroxy (RO_2) radicals (R3; Morin et al., 2007; Fang et al., 2011; Michalski et al., 2014; here we use RO_2 to refer collectively to HO_2 and RO_2).

The oxidation of NO_x (specifically NO_2) to HNO_3 further incorporates additional O atoms from different oxidants (R6-R8; Table 5). Production of nitrate via R6 is restricted to daytime (since OH is generated through photochemistry), whereas production through reactions R4, R7 and R8 dominates at night. In addition, N_2O_5 is thermally unstable, so the contribution of the R4-R7-R8 pathway is larger during winter than during summer. Additionally, in the heterogeneous hydrolysis of N_2O_5 (R8), HNO_3 is likely to be retained on the reaction particle as p-NO_3^- due to its hygroscopicity (Seinfeld and Pandis, 2006). We have neglected contributions from BrO cycling due to the location far from the coast, and from reactions of NO_3^- with hydrocarbons (R12) since they are predicted to have a minimal contribution to nitrate formation in this region (Alexander et al., 2009). Finally, HNO_3 in the gas phase can be irreversibly scavenged by wet surfaces or precipitation (R9) and calcium carbonate on particles (R11), and can equilibrate with solid ammonium nitrate where there is excess ammonia available (R10).

It has been previously suggested that the $\delta^{18}O$ and $\Delta^{17}O$ values of w- and p-NO_3^- formed during summer are lower than those during winter due to higher contribution from the N_2O_5 path (R4, R7-R8) during that season (e.g., Hastings et al., 2003; Morin et al., 2008). As an early take on the data identified by sampling periods, the w- and p-NO_3^- $\delta^{18}O$ and $\Delta^{17}O$ data presented here follow the same patterns for warm and cold months (Fig. 2). In contrast, the less commonly studied HNO_3 shows similar $\delta^{18}O$ values during warm and cold seasons, but summer $\Delta^{17}O$ values mostly lower than the fall-winter, fall and spring ones.

3.4 Correlations with meteorological parameters and co-pollutants

The distribution and proportion of HNO_3 and p-NO_3^- in polluted air masses can vary daily and seasonally with temperature, relative humidity (RH) and concentration of co-contaminants (Morino et al., 2006). For that reason, we compared the isotopic ratios of the HNO_3 and p-NO_3 samples (n of w-NO_3 too low) with meteorological and air quality parameters measured routinely at nearby monitoring stations where available (Table SM-3). We found that the p-NO_3^- and HNO_3 $\delta^{18}O$ and $\Delta^{17}O$ values correlate with RH, with p-NO_3 values showing stronger statistical links than HNO_3 (Table 6). The N_2O_5 hydrolysis reaction (R8) rate increases with humidity (Kane et al., 2001), which may explain this positive correlation. Significant inverse relationships exist between temperature and p-NO_3^- $\delta^{18}O$, p-NO_3^- $\Delta^{17}O$, and HNO_3 $\Delta^{17}O$. These negative links likely arise since

Supprimé: As

Supprimé: mentioned above,

Supprimé: t

Supprimé: periods

Supprimé: [supp info]

Supprimé: p-NO_3^-

Supprimé: s

Supprimé: I

Supprimé: [REF Seinfeld and Pandis?]

Supprimé: it seems that all the studied

Supprimé: trends

Supprimé: expected

Supprimé: In the case of

Supprimé: with,

Supprimé: the

Supprimé: are

Supprimé: , suggesting that the processes leading to the summer isotopic ratios perhaps include O_3 contributions similar to winter ones, but with lower $\Delta^{17}O$ values (see section 4.1).

N_2O_5 is more stable under cold conditions, leading to a higher contribution of R8. The stronger links with p-NO_3^- may be due to R8 taking place on surfaces (such as particles) with liquid water, which is likely to retain the HNO_3 as p-NO_3^- rather than release it to the gas phase. Therefore, in winter, R8 may contribute more to p-NO_3^- than to HNO_3(g). Moreover, the highest $\delta^{18}O$ and $\Delta^{17}O$ values for both p-NO_3^- and HNO_3 were found for fall-winter samples collected at high RH (76 %) and low temperature (-10ºC). In contrast, the lowest p-NO_3^- isotopic values were found for samples with similar proportions of HNO_3 and p-NO_3^-, and sampled during moderately humid (60-63 %) and warm (8-20ºC) periods. The accompanying shift in isotopic differences between p-NO_3 and HNO_3, will help infer the mechanisms dominating during the cold and warm periods (Section 4.2).

Concentrations of oxidants, co-contaminants (e.g., SO_4^- aerosols) and NO_x influence the dominance and rates of the discussed reactions (Brown et al., 2006; Michalski et al., 2014). However, while temperature, RH and O_3 are well captured within a 5 km radius, other pollutant measurements like continuous SO_2, $PM_{2.5}$ and NO_x can have large gradients near sources, therefore it is not surprising that no correlations were found with SO_2 or $PM_{2.5}$ measured at sites 4-5 km away (Table 6). Surprisingly, only the p-NO_3^- $\Delta^{17}O$ and $\delta^{18}O$ values correlated with the fraction of each sample collected during daylight hours (i.e., between the sunrise and sunset times on the day at the middle of each sampling period, either at Edmonton or Lethbridge), which was expected for HNO_3 as well due to the daytime-only OH pathway. However, daylight hours do not take into account light intensity, which can influence significantly the oxidation rate through this pathway, and consequently both the $\delta^{18}O$ and $\Delta^{17}O$ values.

3.5 Comparison with high-latitude p-NO_3^-

An interesting aspect of the Alberta p-NO_3^- cold-period $\Delta^{17}O$ ranges is that they compare relatively well with the range obtained for the Canadian Arctic (Fig. 4), during winter, when nighttime conditions and the N_2O_5 pathway prevail without interruption (Morin et al., 2008; for comparison with HNO_3 values see Fig. SM-4). This observation supports the suggestion that the N_2O_5 pathway produces around 90 % of nitrates during mid-latitudinal cold months (Michalski et al., 2003; Section 4.1). The $\delta^{18}O$ ranges of cold months are similar in Alberta and in the Arctic. This similarity goes against previous suggestions that at higher latitudes, nitrate $\delta^{18}O$ annual means should be higher than at mid-latitudes due to local ambient conditions and atmospheric chemistry affecting the proportions of species involved in producing nitrate (Morin et al., 2009), namely, the sole influence of the N_2O_5 pathway during the Arctic winter (Fang et al., 2011).

The $\Delta^{17}O$ departure between the Alberta and Arctic winter parallel lines is about 3 ‰. Such difference is slightly larger than the one calculated for winter NO_3^- at 80 and 40º N latitudes (about 2 ‰; Morin et al., 2008). In contrast, the warm-months and summer data sets for Alberta and the Arctic, respectively, show different isotopic ranges (Fig. 5), possibly due to the plume effects described later (sub-section 4.3). Moreover, contrary to a previous suggestion, the winter-summer difference in nitrate $\Delta^{17}O$ values is similar at the mid- and high-latitudinal sites (about 6 ‰ here, and 5 ‰ in Morin et al., 2008). This similarity is likely coincidental as it may reflect the fact that within-plume chemistry may lower the $\Delta^{17}O$ values of NO_x in the sampled anthropogenic plumes in Alberta (see sub-section 4.3 for details), whereas the seasonal departure in Arctic samples comes from the oxidation to nitrate through the dominant OH and N_2O_5 pathways during summer and winter, respectively. Finally, the

Supprimé: p-NO_3

Supprimé: p-NO_3

Supprimé: 66 %

Supprimé: For instance, high NOx/O_3 ratios do not favor NO oxidation by peroxy radicals (RO_2 family) with typically low isotopic values, explaining the positive link between $\delta^{18}O$ and $\Delta^{17}O$ values with NOx/O_3 ratios (Table 6).

Mis en forme : Indice

Supprimé: contrast

Supprimé: during warm months active reactions and mechanisms

$\Delta^{17}O$ averages for the Alberta summer and winter results approximately fits within ranges predicted for the studied area by global modeling (Alexander et al., 2009), suggesting that global modeling of nitrate distribution worldwide is promising.

3.6 Isotopic differences between HNO_3 and p-NO_3^-

As far as the isotopic characteristics are concerned, an important feature to keep in mind is that the HNO_3 of central and southern Alberta has distinct properties relative to simultaneously sampled p-NO_3^-. In practical terms, the relationships between the simultaneously sampled HNO_3 and p-NO_3^- are of four types (Fig. 3): (i) HNO_3 $\delta^{18}O$ and $\Delta^{17}O$ are both lower than p-NO_3^-; (ii) HNO_3 has lower $\Delta^{17}O$ but higher $\delta^{18}O$ values than p-NO_3^-; (iii) HNO_3 has higher $\delta^{18}O$ values and similar $\Delta^{17}O$ ones relative to p-NO_3^-; and (iv) HNO_3 has higher $\delta^{18}O$ and $\Delta^{17}O$ values than p-NO_3^- (Fig. 3).

The fall-winter isotopic results belong to group (i), fall results, to groups (i), (ii) and (iii), and the spring and summer results, to groups (ii), (iii) and (iv) (Fig. 3). Elliott et al. (2009) reported simultaneously sampled p-NO_3^- and HNO_3 in northeastern USA with similar seasonal changes of $\delta^{18}O$ differences (no $\Delta^{17}O$ measurement). The HNO_3 $\delta^{18}O$ were generally similar or lower than the p-NO_3^- values during winter and fall, and slightly to much higher during spring and summer, with the spring and autumn p-NO_3^--HNO_3 relationships being roughly intermediate between the winter and summer ones. The average $\delta^{18}O$ difference of p-NO_3^- minus HNO_3 reported between winter and summer (15 ‰) by Elliott et al. (2009) agrees with the difference for fall-winter and summer obtained here (12 ‰).

The marked shifts in isotopic differences between the separately analyzed HNO_3 and p-NO_3^- reported here likely reflect changes in the dominant reactions and processes leading to the production of the two nitrates (see sub-section 4 2). Analyzing them separately provides additional granularity that may be used to elucidate further details of the production and loss of nitrate species downwind from a NO_x source.

4 Discussion

4.1 Estimation of $\Delta^{17}O$ values of NOx precursor to the studied nitrates- Highlighting oxidation mechanisms

In the present sub-section, we estimate the $\Delta^{17}O$ values of NO_2 involved during the production of the Alberta nitrates based on the observed nitrate values and discuss the implications of these estimations. Generally, winter to summer isotopic differences are thought to be due to the high oxygen isotopic values of N_2O_5 due to interaction with O_3 (Johnston and Thiemens, 1997; Michalski et al., 2003; Morin et al., 2008; Vicars et al., 2012) and low values of OH in isotopic equilibrium with atmospheric H_2O (Dubey et al., 1997). According to Table 5, the first reaction pathway produces nitrates via R4-R7-R8 with 2/3 of the O atoms coming from NO_2, 1/6 from O_3 and 1/6 from H_2O, while the second produces nitrates via R6 with 2 out of 3 O atoms coming from NO_2 and 1/3 from OH (e.g., Michalski et al., 2003). Using these proportions with the Alberta $\Delta^{17}O$ values of p-NO_3^- and HNO_3 in weighted averages allows us to make a rough estimation of the maximum and minimum $\Delta^{17}O$ values of NO_2 oxidized to nitrates in the air masses sampled. The calculations assume the O from O_3 contributes a signal of ~39 ‰ as was recently measured (Vicars et al., 2014) and that $\Delta^{17}O$ of OH and H_2O are zero. The estimated NO_2 $\Delta^{17}O$ values for fall-

Supprimé: ¶

Supprimé: Regarding the specific forms of dry nitrates, it is pertinent to mention that the HNO_3 concentrations (from 0.01 to 0.15 µg N/m^3; average of 0.06) are slightly lower than those of p-NO_3^- (from 0.02 to 0.35 µg N/m^3; average of 0.12). For context, the median concentrations at all CAPMoN sites, which represent non-urban areas across Canada, range from 0.07 to 1.1 µg N/m^3 for HNO_3 and from 0.03 to 2 µg N/m^3 for p-NO_3^- (Cheng and Zhang, 2017).

Supprimé: In the Alberta samples, HNO_3 is present at such significant proportions, that if they had not been differentiated, the low end of the isotopic range obtained for p-NO_3^- would have been significantly higher in both $\delta^{18}O$ and $\Delta^{17}O$ (Table 4, see undifferentiated category). Hence, a

Supprimé: and co-sampled w-NO_3^-

Supprimé: (and w-NO_3)

Supprimé: The isotopic signals from NO_x to the final nitrate species follow the isotopic trajectory of the dominant reactions, so we conceive the final oxidation trends as lines resulting from adding vectors that represent these main trajectories (Fig. 4).¶
¶

Supprimé: different sampled dry

Supprimé: forms

Supprimé: Section

Supprimé: 1

Supprimé: In the Alberta samples, HNO_3 is present at such significant proportions, that if it had not been differentiated, the low end of the isotopic range obtained for p-NO_3^- would have been missed, and the HNO_3 plus p-NO_3^- mixture would have shown significantly higher $\delta^{18}O$ and $\Delta^{17}O$ values (Table 4, see undifferentiated category). These isotopic differences also imply that: (1) the analysis of samples that combine p-NO_3^- and HNO_3 can mislead when attempting to understand in detail the chemical pathwaysreactions involved in a specific region where HNO_3 is significantly present; and that (2) the isotopic signals of HNO_3 and p-NO_3^- are not interchangeable in such cases (REF to support; WHO WROTE THEY WERE???).

Supprimé: Sub-sections 3.3 to 3.6 determined the main ... [11]

Supprimé: **stimation**

Supprimé: **producing**

Supprimé: **HNO_3, w-NO_3^- and p-NO_3**

Supprimé: The Alberta nitrate values do not fall on a singl ... [12]

Supprimé: Considering the relevant oxidation reactions sh ... [13]

Supprimé: want to

Supprimé: to help interpret

Supprimé: trends

Supprimé: the

Supprimé: these two

Supprimé: s

Supprimé: O

Supprimé: O

Supprimé: O

Supprimé: and

Supprimé: added O

winter (34-45 ‰ daytime, 25-36 ‰ nighttime) and for summer (25-34 ‰ for daytime; 15-24 ‰ for nighttime) represent the extremes assuming daytime oxidation takes place 100 % through the OH pathway and nighttime oxidation takes place entirely through the N_2O_5 pathway. One should keep in mind that the Alberta results are for nitrates collected during multi-week sampling periods. Each nitrate sample therefore contains *a priori* a mixture of O from the pathways operating during daytime (R6) and nighttime (R4-R7-R8). Assuming a 50 % contribution from each pathway for summer, we generate values ranging from 20 to 29 ‰. Alternatively, assuming domination of the N_2O_5 pathway during winter (90 %; Michalski et al., 2014), the range is 26-37 ‰. Fall and spring values should fit between these summer and winter estimated ranges. The estimated NO_2 $\Delta^{17}O$ ranges indicate that the potential parent NO_2 had a smaller ^{17}O anomaly than O_3 (39 ‰; Vicars and Savarino, 2014) or NO_2 in isotopic equilibrium with O_3 alone (45 ‰; Michalski et al., 2014) in all possible scenarios.

Two mechanisms could be responsible for the $\Delta^{17}O$ differences between these estimates and NO_2 in isotopic equilibrium with O_3. One is the competition of R3 with R2 in oxidizing NO to NO_2, since RO_2 will decrease the $\Delta^{17}O$ values relative to an ozone-only equilibrium. The relative reaction rates of R2 and R3 have previously been presumed to control the NO_2 isotopic composition (e.g., Alexander et al., 2009) based on the assumption of isotopic steady state. A larger contribution of RO_2 is expected in the NO_2 precursors for summer relative to winter, since biogenic VOCs that are major sources of RO_2 radicals are much higher in the summer (e.g., Fuentes and Wang, 1999). This suggestion is consistent with the lower $\Delta^{17}O$ ranges in summer reported here. A second possibility is that the nitrates were formed from some NO_x that did not reach isotopic steady state with O_3, retaining some of its original signature (assumed to be $\Delta^{17}O=0$ ‰). Most studies have assumed that isotopic steady state is established between O_3 and NO_2 within a few minutes after emission of NO_x from a combustion source – or at least, that nitrate formation is negligible before NO_x isotopic equilibrium is reached. However, recent modeling by Michalski et al. (2014) suggests that isotopic equilibration of NO_x with O_3 could take several minutes up to a few hours at the relatively low O_3 concentrations in rural Alberta. At the measured average wind speeds on site of 8-19 km hr^{-1}, transit times from the nearest sources to observation sites are estimated to be 9-55 minutes. While the fraction of NO_x converted to nitrate in this transit time may be small, these are large sources of NO_x in an area with very low background nitrates. For example, a plume containing 10 ppb of NO_2 mixing with background air with 0.1 ppt of OH (Howell et al., 2014) would produce HNO_3 via R6 at a rate of 0.011 µg N m^{-3} min^{-1} at T = 7 °C (Burkholder et al., 2015), or an equivalent amount of a typical nitrate sample in 10 minutes (Table SM-1). Even if equilibration with O_3 is established within a few minutes, the nitrate produced in the interim can constitute a substantial fraction of the sample collected nearby. Therefore, the nitrates measured at our sites may partly derive from NO_x that had not yet reached isotopic steady state with O_3. These two mechanisms are not exclusive and could both contribute to lower NO_x, and therefore nitrate, $\Delta^{17}O$ values.

An additional piece of evidence suggests that the NO_x plumes themselves, rather than ambient conditions, are the source of low-$\Delta^{17}O$ nitrates in these samples. There is a strong correlation between the total nitrate $\Delta^{17}O$ values and the maturity of the plume as expressed by the NO_2 concentration divided by sum of HNO_3 and p-NO_3^- concentrations (Fig. 5). This observation is consistent with the unequilibrated NO_2 hypothesis. However, it does not rule out the possible contribution of RO_2, since VOC releases from the NO_x sources could lead to elevated RO_2 concentrations in the plume.

Supprimé: sets

Supprimé: the

Supprimé: shrinks

Supprimé: to

Supprimé: generally

Supprimé:

Supprimé: nitrates measured with and the latternitrate derived from

Supprimé: $_x$

Mis en forme : Indice

Supprimé: at

Supprimé: dilute

Supprimé: assumed

Supprimé: $_2$

Supprimé: and RO_2

Supprimé: since photochemical

Supprimé: is established

Supprimé: exists

Mis en forme : Non Surlignage

Supprimé: , isotopic steady state is also reached occurs quickly

Supprimé: NO_x and

Supprimé: could be

Supprimé: to almost 4 hours

Mis en forme : Non Surlignage

Mis en forme : Non Surlignage

Mis en forme : Non Surlignage

Mis en forme : Non Surlignage

Mis en forme : Indice

Mis en forme : Non Surlignage

Supprimé: (and RO_2)

Supprimé: TThe extent of the $\Delta^{17}O$ difference between the spring-summer and fall-winter HNO_3 clusters (Fig. 2B) likely reflects various combinations degrees of involvement of the invoked se two mechanisms. (Myrick et al., 1994) $\Delta^{17}O$ reaching the sampling site older than when the plume is emitted within the boundary layer¶

Mis en forme : Surlignage

Mis en forme : Non Surlignage

Mis en forme : Non Surlignage

Mis en forme : Non Surlignage

Mis en forme : Non Surlignage

Supprimé: 6

4.2 Causes of shifts in HNO_3 to p-NO_3^- isotopic differences

A challenging question is why do the HNO_3 to p-NO_3^- isotopic differences shift seasonally (Fig. 3)? One factor that may influence the relationship between HNO_3 and p-NO_3^- is mass-dependent isotopic equilibrium between NH_4NO_3 and HNO_3 (R10); however, this mechanism would result in higher $\delta^{18}O$ in p-NO_3^- and unchanged $\Delta^{17}O$ values and, therefore, cannot be solely responsible for any of the observed patterns (Fig. 3). Alternately, the trend for cold months (trend *i*) could be due to the fact that the heterogeneous N_2O_5 pathway is likely to produce more p-NO_3^- than HNO_3(g), which would result in a higher contribution from ozone and explain why $\delta^{18}O$ and $\Delta^{17}O$ values are both higher in p-NO_3^-. A previous study addressing why p-NO_3^- on coarse particles is more enriched than on fine particles invoked a similar explanation (Patris et al., 2007).

For some of the spring and summer samples, both $\delta^{18}O$ and $\Delta^{17}O$ values were lower in p-NO_3^- than in HNO_3 (trend *iv*), therefore the mechanism above cannot dominate the fractionation; nor can a mass-dependent process be responsible. We suggest a different fractionation process because HNO_3 dry deposits to surfaces more rapidly than p-NO_3^- (Zhang et al., 2009; Benedict et al., 2013), which would create the discussed isotopic shifts in the situation where NO_2 has low $\Delta^{17}O$ values in a fresh plume. The first nitrates formed in the plume shortly after emission from the NO_x source have low $\delta^{18}O$ and $\Delta^{17}O$ values, either because NO_x has not yet reached isotopic steady state with O_3 or because it reacted with ^{17}O-poor RO_2 present in the plume due to VOC emissions. Those nitrates that form as p-NO_3^- or that partition to p-NO_3^- remain in the plume for longer than HNO_3, which is removed from the plume rapidly upon contact with vegetation or other surfaces. As the plume travels, the NO_x becomes more enriched, and the newly formed nitrates take on higher $\delta^{18}O$ and $\Delta^{17}O$ values. However, p-NO_3^- collected further downwind will derive from a mixture of low-$\delta^{18}O$ and -$\Delta^{17}O$ p-NO_3^- formed earlier, plus high-$\delta^{18}O$ and -$\Delta^{17}O$ p-NO_3^- formed more recently, while HNO_3 will have a larger proportion formed more recently and will therefore have higher $\delta^{18}O$ and $\Delta^{17}O$ values. The fact that we find the lowest isotopic values in summer p-NO_3^- samples collected from various anthropogenic sources at distances less than 16 km supports this suggestion (Table 1).

The above two mechanisms that we propose to explain the shifts in HNO_3 to p-NO_3- isotopic differences between cold and warm sampling periods – differential N_2O_5 contribution resulting in higher $\Delta^{17}O$ values in p-NO_3^- than in HNO_3, and differential deposition resulting in lower $\Delta^{17}O$ values in p-NO_3 – would essentially compete against each other, with local conditions and chemistry influencing the results. In winter, when the N_2O_5 pathway is most important, the first mechanism dominates, as supported by the observation that p-NO_3^- concentrations are higher during that season (trend *i*). Conversely, in summer, when the N_2O_5 pathway is less important and dry deposition is likely faster due to absence of snow cover, higher surface wetness and high leaf areas, the second mechanism is more important (trend *iv*). The local reactant concentrations, wind speeds and radiative fluxes (which control the time to reach isotopic equilibrium) would also be factors in the second mechanism. We find intermediate trends (*ii, iii*) in the transitional seasons, as expected. In addition to these non-mass-dependent fractionation processes, mass-dependent fractionation in formation and loss of nitrate likely contributes to the observed $\delta^{18}O$ differences. For instance, kinetic fractionation may be involved in the production of trend *iii*.

Supprimé: **– Complexity of nitrate production processes**
Supprimé: s
Supprimé: , 4)
Supprimé: R4, R7-R8 and R9-
Supprimé: contribute
Supprimé: to
Supprimé: to
Supprimé: only apply
Supprimé: is
Supprimé: not in isotopic equilibrium with O_3
Supprimé: in
Supprimé: since
Supprimé: (and
Supprimé: of additional
Supprimé:)
Supprimé: deposits
Supprimé: more
Supprimé: be a
Supprimé: of
Supprimé: the
Supprimé: nitrate
Supprimé: NO_2
Supprimé: and
Supprimé: with
Supprimé: and
Supprimé: the
Supprimé:
Supprimé: nitrate
Supprimé: NO_2
Supprimé: dominatly from late oxidation
Supprimé: less of from the low-
Supprimé: -
Supprimé: NO_2
Supprimé: nitrate
Supprimé: Another argument supporting this interpretation is the strong correlation between $\Delta^{17}O$ values and the maturity of a plume as expressed by the NO_2 content divided by sum of dry nitrat ... [14]
Supprimé: have
Supprimé: d
Supprimé: minimal
Supprimé: Therefore,
Supprimé: w
Supprimé: would
Supprimé: expect
Supprimé: other

In summary, examining the isotopic relationship of HNO_3 to p-NO_3^- (Fig. 3), reveals the complexity of anthropogenic NOx oxidation mechanisms. The negative isotopic differences between p-NO_3^- and HNO_3 during warm months may reflect differential removal rates from plumes containing NO_2 temporarily low in ^{17}O.

4.3 - Low $\delta^{18}O$ and $\Delta^{17}O$ trends in global w- and p-NO_3^- - Implications for polluted air masses

Atmospheric nitrates measured in central and southern Alberta were sampled downwind of well-identified anthropogenic sources to verify the potential role of emitted NO_x isotopic signals through to final nitrate isotopic ratios (primarily N isotopes; see Savard et al., 2017). As expected, the measured oxygen isotopes of the various nitrate groups are consistent with exchange with O_3 and oxidation through the well-known OH and N_2O_5 oxidation paths. However, NO_2 not in isotopic equilibrium with O_3, and/or NO reacted with RO_2 may have significantly influenced the overall results. Co-contaminants in the emissions and sampling plumes at short distances from the sources may have favoured these two mechanisms, and quantifying RO_2 and/or HO_2 would help distinguish between the two mechanisms. Meanwhile, our results raise the question: are these overall effects observable in triple oxygen isotopes of nitrates from other polluted sites?

The full $\Delta^{17}O$ and $\delta^{18}O$ ranges for p-NO_3^-, w-NO_3^- and HNO_3 (between 13.8 and 20.5 ‰, 48.4 and 83.2 ‰; Table 4) compare well with the isotopic ranges obtained for bulk deposition NO_3^- samples collected downwind from oil sands mining operations in the lower Athabasca region farther north in Alberta (Proemse et al., 2013). Moreover, the isotopic values in cold and warm months delineated here essentially overlap with the data sets of winter and summer from the lower Athabasca region (Fig. 6). This correspondence exists despite the slightly different climatic conditions (Fig. SM-1), and very different sampling methods (bulk/throughfall deposition samples using open ion exchange resin collectors, vs. wind sector-specific active sampling on filters and precipitation-only collectors). Notably, many points carry relatively low $\delta^{18}O$ and $\Delta^{17}O$ values.

Previous work in the Athabasca region reported very low $\delta^{18}O$ and near-zero $\Delta^{17}O$ values for p-NO_3^- sampled directly within oil-sands industrial stacks, i.e., in the emissions measured in-stack and diluted with ambient air (Proemse et al., 2012). These values are very close to those of O_2. Similar isotopic signatures are very likely produced in source emissions of NO_x in the studied Edmonton and Vauxhall areas (e.g., CFPP, gas compressors, industries). This source signature may persist into p-NO_3 collected close to the sources. Within the first few hours in the atmosphere (less, in polluted areas), the NO_x $\delta^{18}O$ and $\Delta^{17}O$ values rapidly increase due to isotope exchange with O_3 (R2, R3, R5 and O_3 formation, Table 5; Michalski et al., 2014) and reach isotopic equilibrium. Though the e-folding lifetime for NO_x oxidation to nitrates may be longer than these few hours, depending on the NO_x/VOC ratio, only a fraction of the oxidized source NO_x will create a measureable contribution to the ambient nitrate where the background air is very low in nitrate. This is likely the case in the oil sands region, where Proemse et al. (2013) reported the lowest $\Delta^{17}O$ values within 12 km of the emission sites, and where direct stack emissions of p-NO_3^- were ~5000 times lower than NO_x emissions (Wang et al., 2012).

In a methodological test study, we obtained low values for w-NO_3^- sampled near a high traffic volume highway in Ontario, Canada (Smirnoff et al., 2012). Low $\delta^{18}O$ and $\Delta^{17}O$ values in atmospheric nitrates during warm months (65 and 20 ‰ or less,

Supprimé: the $\delta^{18}O$ and $\Delta^{17}O$ patterns of the measured nitrates follow the generally described seasonal isotopic trend from high, during cold periods, to low, during warm periods. However,

Supprimé: and by extension w-NO_3^-,

Supprimé: The final isotopic values are derived from the O_3-NO_x (Leighton) cycle and competing oxidation by RO_2 possibly not yet at isotopic steady state - followed by the OH and N_2O_5 (O_3) oxidation pathways in proportions that vary with the periods of sampling (Fig. 4).

Supprimé: likely

Supprimé: s

Supprimé: NO_x

Supprimé: Δ

Supprimé: at disequilibrium with O_3. ¶

Supprimé: 3

Supprimé: world

Supprimé: rom

Supprimé: areas

Supprimé: show no source-specific isotopic characteristics, but instead

Supprimé: sampled

Supprimé: The

Supprimé: remains

Supprimé: clusters

Supprimé: 5

Supprimé: SI-

Supprimé: different source types,

Supprimé: appear near the O_2-end of the O_2-O_3-NO_x line (Fig. 46)

Supprimé:

Supprimé: or

Supprimé: more

Supprimé: severely

Supprimé: via many iterations of the photochemical NO_x-O_2-O_3 cycle respectively) have been reported for other parts of the world as well (Table 4). Authors of these studies have invoked peroxy radicals to account for low δ^{18}O values in w-NO$_3^-$ from a polluted city (Fang et al., 2011), in p-NO$_3^-$ from Taiwan collected partly from air masses influenced by pollutants (Guha et al., 2017) and from a polluted coastal site in California (Michalski et al., 2004; Patris et al., 2007; Table 4). However, sampling in these three other regions did not use collection restricted to air masses transported from targeted anthropogenic sources. So uncertainties persist regarding the ultimate sources of nitrates with low isotopic values.

Although a few low values are also reported for seemingly non-polluted areas of the Arctic and Antarctic regions (unknown cause; Morin et al., 2008; Morin et al., 2009) and of coastal California (Patris et al., 2007), the information from the literature integrated with the interpretation proposed for the Alberta low δ^{18}O and Δ^{17}O values in summer nitrates may reflect the involvement of air masses that include nitrates from oxidation of NO$_2$ with light isotopes in plumes. In such cases, while not ruling out a higher contribution from RO$_2$ oxidation of NO, it is also possible that significant portions of the collected nitrate were formed before the NO$_x$-O$_3$ isotopic equilibrium was reached (see Section 4.1). Keeping in mind that other hydrocarbon and halogen pathways may play a role in determining the isotopic nitrate characteristics in other parts of the world, we propose that, in general, the warm-periods isotopic ranges appear to be lower in polluted areas. Given these points, our nitrate δ^{18}O and Δ^{17}O may reflect relative proximity to anthropogenic N emitters in general. Further research work on plume NO$_x$ to nitrates chemical mechanisms may help to validate this suggestion. In the future, the assumption of NO$_x$ isotopic steady state with O$_3$ should be explored, given recent findings (Michalski et al., 2014), the critical importance of NO$_x$ isotope characteristics on resulting nitrate isotopic values (Alexander et al., 2009), and the suggestion regarding the evolution of NO$_x$-NO$_3^-$ signals in fresh anthropogenic plumes (present study).

Supprimé: favour RO$_2$ reactions and/or

Supprimé: NO$_x$

Supprimé: we hypothesize

Supprimé: not

Supprimé: , regardless of the anthropogenic source types

Supprimé: values do not represent indicators of specific sources but, more likely, in the case of summer solid phases, they

Supprimé: nitrates

Supprimé: early

5 Conclusion

The HNO$_3$, w-NO$_3$ and p-NO$_3$ from anthropogenic sources in central and southern Alberta, simultaneously collected with wind sector-based conditional sampling systems produced δ^{18}O and Δ^{17}O trends confirming the previous contention that regional ambient conditions (e.g., light intensity, oxidant concentrations, RH, temperature) dictate the triple isotopic characteristics and oxidation pathways of nitrates.

Supprimé: five different

Supprimé: similar

Supprimé: , regardless of their sources types (CFPP, various industries, city traffic, and gas compressors).

Supprimé: This

Supprimé: s

Supprimé: observations

The gaseous form of nitrate (HNO$_3$) having distinct isotopic characteristics relative to the wet and particulate forms implies that understanding nitrate formation and loss requires characterizing the nitrate species individually. Particulate-NO$_3^-$ in these samples generally shows higher δ^{18}O and Δ^{17}O values than HNO$_3$ in the fall-winter period as the heterogeneous N$_2$O$_5$ pathway favours the production of p-NO$_3^-$. In contrast, HNO$_3$ has higher δ^{18}O and Δ^{17}O values during warm periods, which we propose is due to faster dry deposition rates relative to p-NO$_3^-$ in the event that low-Δ^{17}O NO$_2$ is oxidized in the plume. The mechanisms conferring nitrate with relatively low isotopic values, whether oxidation before NO$_x$-O$_3$ equilibrium is reached or higher contributions from RO$_2$, are likely to be observed in anthropogenic polluted air masses. An interesting deduction arising from this interpretation and from a comparison with nitrate isotopes from other polluted areas of the world is that relatively low δ^{18}O and Δ^{17}O values may reflect nitrates produced from undifferentiated anthropogenic NO$_x$ emissions.

Supprimé: y

Supprimé: , and disavows the assumption that isotopic values of the dry nitrate phases are invariably interchangeablesimilar

Supprimé: The Albertan nitrate production operated mostly through the well-known OH and N$_2$O$_5$ oxidation pathways, possibly prior to their reaching isotopic equilibrium with O$_3$ in some samples, though we also suggest contributions from RO$_2$ oxidation of NO, as well leading to low oxygen isotopic values.

Supprimé: Moreover

Supprimé: NO$_x$

Supprimé: before reaching isotopic steady state with O$_3$

Supprimé: se

Supprimé: p-NO$_3^-$

Supprimé: prone

Supprimé: happen

Future research should explore the assumption of NO_x isotopic equilibration with O_3, given the critical importance of NO_x isotopes on resulting nitrate isotopic values. More field sampling, including additional on-site oxidant data, and state-of-the-art isotopic analyses of all tropospheric nitrate species as well as NO_x are required for refining our understanding of atmospheric nitrate worldwide. This endeavour is fundamental for developing effective emission-reduction strategies towards improving future air quality.

Supprimé: needs to

Supprimé: ,

Supprimé: ,

Acknowledgements. The authors are grateful for the technical support provided by Marie-Christine Simard and Jade Bergeron of the Geological Survey of Canada, and by Syed Iqbal, Rachel Mintz, Daniel McLennan, Matthew Parsons, Mike Shaw Amy Hou of Environment and Climate Change Canada; and for the constructive pre-submission review by Drs. Geneviève Bordeleau from the Geological Survey of Canada, and Felix Vogel and Jason O'Brien from ECCC. This research has been financially supported by the Clean Air Regulatory Agenda of Environment and Climate Change Canada, and the Environmental Geoscience program of Natural Resources Canada (NRCan contribution number: 20170310). The first author dedicates this research article to Pauline Durand for her support.

References

Alexander, B., Hastings, M. G., Allman, D. J., Dachs, J., Thornton, J. A., and Kunasek, S. A.: Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition (δ17O) of atmospheric nitrate, Atmospheric Chemistry and Physics, 9, 5043-5056, 2009.

Anlauf, K. G., Fellin, P., Wiebe, H. A., Schiff, H. I., Mackay, G. I., Braman, R. S., and Gilbert, R.: A comparison of three methods for measurement of atmospheric nitric acid and aerosol nitrate and ammonium, Atmospheric Environment (1967), 19, 325-333, 10.1016/0004-6981(85)90100-3, 1985.

Anlauf, K. G., Wiebe, H. A., and Fellin, P.: Characterization of Several Integrative Sampling Methods for Nitric Acid, Sulphur Dioxide and Atmospheric Particles, Journal of the Air Pollution Control Association, 36, 715-723, 10.1080/00022470.1986.10466107, 1986.

Appel, B. R., Tokiwa, Y., and Haik, M.: Sampling of nitrates in ambient air, Atmospheric Environment (1967), 15, 283-289, 10.1016/0004-6981(81)90029-9, 1981.

Benedict, K. B., Carrico, C. M., Kreidenweis, S. M., Schichtel, B., Malm, W. C., and Collett Jr, J. L.: A seasonal nitrogen deposition budget for Rocky Mountain National Park, Ecological Applications, 23, 1156-1169, 10.1890/12-1624.1, 2013.

Brown, S. S., Ryerson, T. B., Wollny, A. G., Brock, C. A., Peltier, R., Sullivan, A. P., Weber, R. J., Dubé, W. P., Trainer, M., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.: Variability in nocturnal nitrogen oxide processing and its role in regional air quality, Science, 311, 67-70, 10.1126/science.1120120, 2006.

Cheng, I., and Zhang, L.: Long-term air concentrations, wet deposition, and scavenging ratios of inorganic ions, HNO3, and SO2 and assessment of aerosol and precipitation acidity at Canadian rural locations, Atmospheric Chemistry and Physics, 17, 4711-4730, 10.5194/acp-17-4711-2017, 2017.

Coplen, T. B., Böhlke, J. K., and Casciotti, K.: Rapid Commun. Mass Spectrom., 18, 245, 2004.

Dahal, B., and Hastings, M. G.: Technical considerations for the use of passive samplers to quantify the isotopic composition of NO x and NO 2 using the denitrifier method, Atmospheric Environment, 143, 60-66, 2016.

Dubey, M. K., Mohrschladt, R., Donahue, N. M., and Anderson, J. G.: Isotope specific kinetics of hydroxyl radical (OH) with water (H2O): Testing models of reactivity and atmospheric fractionation, Journal of Physical Chemistry A, 101, 1494-1500, 1997.

Elliott, E. M., Kendall, C., Boyer, E. W., Burns, D. A., Lear, G. G., Golden, H. E., Harlin, K., Bytnerowicz, A., Butler, T. J., and Glatz, R.: Dual nitrate isotopes in dry deposition: Utility for partitioning NO x source contributions to landscape nitrogen deposition, Journal of Geophysical Research: Biogeosciences, 114, 10.1029/2008JG000889, 2009.

Environment and Climate Change Canada; Air Pollutant Emission Inventory Online Data Query: http://www.ec.gc.ca/inrp-npri/donnees-data/ap/index.cfm?lang=En, access: accessed 2016/12/15, 2016.

Environment and Climate Change Canada; Canadian Air and Precipitation Monitoring Network (CAPMoN): http://donnees.ec.gc.ca/data/air/monitor/monitoring-of-atmospheric-precipitation-chemistry/major-ions/, 2018a.

Environment and Climate Change Canada; National Pollutant Release Inventory: https://www.canada.ca/en/environment-climate-change/services/national-pollutant-release-inventory/tools-resources-data.html, 2018b.

Erisman, J. W., and Fowler, D.: Oxidized and reduced nitrogen in the atmosphere, Knowledge for Sustainable Development, An Insight into the Encyclopedia of Life Support Systems, Volumes I, II, III, UNESCO Publishing-Eolss Publishers, Oxford, UK, 2003.

Fang, Y. T., Koba, K., Wang, X. M., Wen, D. Z., Li, J., Takebayashi, Y., Liu, X. Y., and Yoh, M.: Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China, Atmospheric Chemistry and Physics, 11, 1313-1325, 10.5194/acp-11-1313-2011, 2011.

Fuentes, J. D., and Wang, D.: On the seasonality of isoprene emissions from a mixed temperate forest, Ecological Applications, 9, 1118-1131, 10.1890/1051-0761(1999)009[1118:OTSOIE]2.0.CO;2, 1999.

Guha, T., Lin, C. T., Bhattacharya, S. K., Mahajan, A. S., Ou-Yang, C. F., Lan, Y. P., Hsu, S. C., and Liang, M. C.: Isotopic ratios of nitrate in aerosol samples from Mt. Lulin, a high-altitude station in Central Taiwan, Atmospheric Environment, 154, 53-69, 10.1016/j.atmosenv.2017.01.036, 2017.

Hastings, M. G., Sigman, D. M., and Lipschultz, F.: Isotopic evidence for source changes of nitrate in rain at Bermuda, Journal of Geophysical Research D: Atmospheres, 108, ACH 22-21 - ACH 22-12, 2003.

IPCC; Fifth Assessment Report (AR5): https://www.ipcc.ch/report/ar5/, access: September 2017, 2013.

Johnston, J. C., and Thiemens, M. H.: The isotopic composition of tropospheric ozone in three environments, Journal of Geophysical Research Atmospheres, 102, 25395-25404, 1997.

Kaiser, J., Hastings, M. G., Houlton, B. Z., Röckmann, T., and Sigman, D. M.: Triple oxygen isotope analysis of nitrate using the denitrifier method and thermal decomposition of N2O, Analytical Chemistry, 79, 599-607, 10.1021/ac061022s, 2007.

Kane, S. M., Caloz, F., and Leu, M. T.: Heterogeneous uptake of gaseous N2O5 by (NH4)2SO4, NH4HSO4, and H2SO4 aerosols, Journal of Physical Chemistry A, 105, 6465-6470, 10.1021/jp010490x, 2001.

Keck, L., and Wittmaack, K.: Effect of filter type and temperature on volatilisation losses from ammonium salts in aerosol matter, Atmospheric Environment, 39, 4093-4100, 10.1016/j.atmosenv.2005.03.029, 2005.

Kendall, C., Elliott, E. M., and Wankel, S. D.: Tracing Anthropogenic Inputs of Nitrogen to Ecosystems, in: Stable Isotopes in Ecology and Environmental Science: Second Edition, 375-449, 2007.

Lavoie, G. A., Heywood, J. B., and Keck, J. C.: EXPERIMENTAL AND THEORETICAL STUDY OF NITRIC OXIDE FORMATION IN INTERNAL COMBUSTION ENGINES, M, I.T.-Dept Mech Eng-Fluid Mechanics Laboratory Publ 69-10, 1969.

Liang, M. C., and Yung, Y. L.: Sources of the oxygen isotopic anomaly in atmospheric N<inf>2</inf>O, Journal of Geophysical Research Atmospheres, 112, 10.1029/2006JD007876, 2007.

McIlvin, M. R., and Altabet, M. A.: Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater, Analytical Chemistry, 77, 5589-5595, 2005.

Michalski, G., Scott, Z., Kabiling, M., and Thiemens, M. H.: First measurements and modeling of Δ17O in atmospheric nitrate, Geophysical Research Letters, 30, 14-11, 2003.

Michalski, G., Meixner, T., Fenn, M., Hernandez, L., Sirulnik, A., Allen, E., and Thiemens, M.: Tracing Atmospheric Nitrate Deposition in a Complex Semiarid Ecosystem Using Δ17O, Environmental Science and Technology, 38, 2175-2181, 10.1021/es034980+, 2004.

Michalski, G., Bhattacharya, S. K., and Girsch, G.: NOx cycle and the tropospheric ozone isotope anomaly: An experimental investigation, Atmospheric Chemistry and Physics, 14, 4935-4953, 10.5194/acp-14-4935-2014, 2014.

Morin, S., Savarino, J., Bekki, S., Gong, S., and Bottenheim, J. W.: Signature of Arctic surface ozone depletion events in the isotope anomaly (Δ17O) of atmospheric nitrate, Atmospheric Chemistry and Physics, 7, 1451-1469, 2007.

Morin, S., Savarino, J., Frey, M. M., Yan, N., Bekki, S., Bottenheim, J. W., and Martins, J. M. F.: Tracing the origin and fate of NOx in the arctic atmosphere using stable isotopes in nitrate, Science, 322, 730-732, 10.1126/science.1161910, 2008.

Morin, S., Savarino, J., Frey, M. M., Domine, F., Jacobi, H. W., Kaleschke, L., and Martins, J. M. F.: Comprehensive isotopic composition of atmospheric nitrate in the Atlantic Ocean boundary layer from 65°S to 79°N, Journal of Geophysical Research Atmospheres, 114, 10.1029/2008JD010696, 2009.

Morino, Y., Kondo, Y., Takegawa, N., Miyazaki, Y., Kita, K., Komazaki, Y., Fukuda, M., Miyakawa, T., Moteki, N., and Worsnop, D. R.: Partitioning of HNO<inf>3</inf> and particulate nitrate over Tokyo: Effect of vertical mixing, Journal of Geophysical Research Atmospheres, 111, 10.1029/2005JD006887, 2006.

Patris, N., Cliff, S. S., Quinn, P. K., Kasem, M., and Thiemens, M. H.: Isotopic analysis of aerosol sulfate and nitrate during ITCT-2k2: Determination of different formation pathways as a function of particle size, Journal of Geophysical Research Atmospheres, 112, 10.1029/2005JD006214, 2007.

Proemse, B. C., Mayer, B., Chow, J. C., and Watson, J. G.: Isotopic characterization of nitrate, ammonium and sulfate in stack PM 2.5 emissions in the Athabasca Oil Sands Region, Alberta, Canada, Atmospheric Environment, 60, 555-563, 10.1016/j.atmosenv.2012.06.046, 2012.

Proemse, B. C., Mayer, B., Fenn, M. E., and Ross, C. S.: A multi-isotope approach for estimating industrial contributions to atmospheric nitrogen deposition in the Athabasca oil sands region in Alberta, Canada, Environmental Pollution, 182, 80-91, 10.1016/j.envpol.2013.07.004, 2013.

Randles, R. H., and Wolfe, D. A.: Introduction to the theory of nonparametric statistics, Wiley New York, 1979.

Rolph, G. D.; Real-time Environmental Applications and Display sYstem (READY): http://www.ready.noaa.gov, access: January, 2017.

Savard, M. M., Cole, A., Smirnoff, A., and Vet, R.: δ15N values of atmospheric N species simultaneously collected using sector-based samplers distant from sources – Isotopic inheritance and fractionation, Atmospheric Environment, 162, 11-22, 10.1016/j.atmosenv.2017.05.010, 2017.

Savarino, J., Kaiser, J., Morin, S., Sigman, D. M., and Thiemens, M. H.: Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica, Atmospheric Chemistry and Physics, 7, 1925-1945, 2007.

Savarino, J., Bhattacharya, S. K., Morin, S., Baroni, M., and Doussin, J. F.: The NO+ O3 reaction: A triple oxygen isotope perspective on the reaction dynamics and atmospheric implications for the transfer of the ozone isotope anomaly, Journal of Chemical Physics, 128, 10.1063/1.2917581, 2008.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics. Hoboken, NJ: Wiley, 2006.

Sickles Ii, J. E., Hodson, L. L., McClenny, W. A., Paur, R. J., Ellestad, T. G., Mulik, J. D., Anlauf, K. G., Wiebe, H. A., Mackay, G. I., Schiff, H. I., and Bubacz, D. K.: Field comparison of methods for the measurement of gaseous and particulate contributors to acidic dry deposition, Atmospheric Environment Part A, General Topics, 24, 155-165, 10.1016/0960-1686(90)90451-R, 1990.

Sickles Ii, J. E., Hodson, L. L., and Vorburger, L. M.: Evaluation of the filter pack for long-duration sampling of ambient air, Atmospheric Environment, 33, 2187-2202, 10.1016/S1352-2310(98)00425-7, 1999.

Sirois, A., and Fricke, W.: Regionally representative daily air concentrations of acid-related substances in Canada; 1983-1987, Atmospheric Environment Part A, General Topics, 26, 593-607, 10.1016/0960-1686(92)90172-H, 1992.

Sirois, A., and Vet, R.: The Precision of Precipitation Chemistry Measurements in the Canadian Air and Precipitation Monitoring Network (CAPMoN), Environmental Monitoring and Assessment, 57, 301-329, 10.1023/a:1006035129393, 1999.

Smirnoff, A., Savard, M. M., Vet, R., and Simard, M. C.: Nitrogen and triple oxygen isotopes in near-road air samples using chemical conversion and thermal decomposition, Rapid Communications in Mass Spectrometry, 26, 2791-2804, 10.1002/rcm.6406, 2012.

Spicer, C. W., Howes Jr, J. E., Bishop, T. A., Arnold, L. H., and Stevens, R. K.: Nitric acid measurement methods: An intercomparison, Atmospheric Environment (1967), 16, 1487-1500, 10.1016/0004-6981(82)90071-3, 1982.

Stein, A., Draxler, R., Rolph, G., Stunder, B., Cohen, M., and Ngan, F.: NOAA's HYSPLIT atmospheric transport and dispersion modeling system, Bulletin of the American Meteorological Society, 96, 2059-2077, 2015.

Stroud, C. A., Jonathan; Leiming, Zhang; Flagg, David; Makar, Paul: Atmospheric processes, Chapitre 2 - Draft version, in, Canadian smow Science Assessment, 2008.

Thiemens, M. H.: Mass-independent isotope effects in planetary atmospheres and the early solar system, Science, 283, 341-345, 10.1126/science.283.5400.341, 1999.

Tsunogai, U., Komatsu, D. D., Daita, S., Kazemi, G. A., Nakagawa, F., Noguchi, I., and Zhang, J.: Tracing the fate of atmospheric nitrate deposited onto a forest ecosystem in Eastern Asia using Δ17O, Atmospheric Chemistry and Physics, 10, 1809-1820, 2010.

Vicars, W. C., Bhattacharya, S. K., Erbland, J., and Savarino, J.: Measurement of the 17O-excess (δ 17O) of tropospheric ozone using a nitrite-coated filter, Rapid Communications in Mass Spectrometry, 26, 1219-1231, 10.1002/rcm.6218, 2012.

Vicars, W. C., Morin, S., Savarino, J., Wagner, N. L., Erbland, J., Vince, E., Martins, J. M. F., Lerner, B. M., Quinn, P. K., Coffman, D. J., Williams, E. J., and Brown, S. S.: Spatial and diurnal variability in reactive nitrogen oxide chemistry as reflected in the isotopic composition of atmospheric nitrate: Results from the CalNex 2010 field study, Journal of Geophysical Research Atmospheres, 118, 10567-10588, 10.1002/jgrd.50680, 2013.

Vicars, W. C., and Savarino, J.: Quantitative constraints on the 17O-excess (δ17O) signature of surface ozone: Ambient measurements from 50°N to 50°S using the nitrite-coated filter technique, Geochimica et Cosmochimica Acta, 135, 270-287, 10.1016/j.gca.2014.03.023, 2014.

Wang, X. L., Watson, J. G., Chow, J. C., Kohl, S. D., Chen, L. W. A., Sodeman, D. A., Legge, A. H., and Percy, K. E.: Measurement of Real-World Stack Emissions with a Dilution Sampling System, in: Developments in Environmental Science, 171-192, 2012.

Zel'dovich, Y. B.: The Oxidation of Nitrogen in Combustion and Explosions, Acta Physicochimica, 21, 577-628, 1946.

Zhang, L., Vet, R., O'Brien, J. M., Mihele, C., Liang, Z., and Wiebe, A.: Dry deposition of individual nitrogen species at eight Canadian rural sites, Journal of Geophysical Research Atmospheres, 114, 10.1029/2008JD010640, 2009.

Table 1. Settings and conditions for wind sector-based simultaneous sampling of atmospheric nitrates.

Site (coordinates)	**Sources**	**Distance** Km (mean)	**Sector** direction; opening	**Sampling** period;	**n**	**Avg T** (°C)	**Context**
Genesee (114.14° W, 53.31° N)	Coal-fired power plants	7-35	NW, 35°	30/09/2010 – 21/06/2011	6	11.7, 12.2, 5.5, -9.8, -0.9, 12.2	3 plants
Vauxhall (112.11° W, 50.06° N)	Gas compressors and cattle and swine feedlots	12-125+; 7.5-45+	W, 65°	25/10/2011 – 13/12/2011	3	2.6, 0.7,-3.5	65+ compressors; 200+ feedlots
Terrace Heights (113.44° W, 53.54° N)	Urban traffic	<1-15 (4)	W, 150°	24/07/2012 – 25/10/2012	4	20.3, 15.6, 7.9, -1.8	Park in residential area, 3.5 km east of downtown core
Fort Saskatchewan (113.14° W, 53.72° N)	Chemical industries and metal refining	3-7 (4)	NW, 88°	12/04/2013 – 06/09/2013	4	4.3, 15.7, 16.3, 17.7	Chemical plant and metal refinery largest NO_x sources; fertilizer plant largest NH_3 source
Fort Saskatchewan (113.14° W, 53.72° N)	Fertilizers plant and oil refinery	9-14 (11)	N, 27°	20/09/2013 – 20/01/2014	1	-8.1	Fertilizer plant largest NH_3 and NO_x source, oil refinery major NO_x source

N: number of sampling sessions. Avg T: average temperature during each of the consecutives sampling sessions.

Supprimé: 25

Table 2. Isotopic reproducibility (modified median absolute deviation) established using 2 to 4 parallel active CAPMoN sampling setups in seven separate sampling periods, resulting in (n) total samples.

N compound (n)	**$\delta^{18}O$**	**$\delta^{17}O$**
Teflon filters p-NO_3^- (19)	2	1
Nylon filters HNO_3 (18)	1	0.7

Table 3. Average oxygen isotopic ratios (‰) for NO_3^- sampled as gas (HNO_3), w (precipitation) and p (particulate matter) relative to VSMOW.

Matrix	Gas	w	p	Gas	..w	..p
Source	**$\delta^{18}O$**			**$\Delta^{17}O$**		
Coal-fired power plants	69.7 (5)	66.1 (4)	70.7 (4)	25.1 (5)	25.4 (4)	26.6 (4)
Fertilizers plant & oil refinery	63.2 (1)	71.4 (1)	69.5 (1)	19.3 (1)	26.0 (1)	23.8 (1)
Chemical industries & metal refining	65.7 (4)	61.9 (2)	54.6 (4)	21.8 (4)	21.4 (2)	18.5 (4)
Gas compressors	65.0 (2)	-	63.1 (3)	24.5 (2)	-	26.4 (3)
City traffic	65.7 (3)	67.2 (2)	59.6 (3)	21.2 (3)	24.4 (2)	22.5 (3)
Mean	**66.8**	**66.0**	**62.6**	**23.0**	**24.3**	**23.4**

(n): number of sampling periods characterized

Table 4. Compilation of triple oxygen isotopic ranges obtained for atmospheric and emitted nitrates.

$\delta^{18}O$ (‰)	$\Delta^{17}O$ (‰)	Regional context	Location	Authors
HNO_3				
62.4-81.7	19.3-29.0	Various contaminated sites	Alberta, Canada	*This study*
p-NO_3^-				
43-62	20-27	Coast, Trinidad Head	California, USA	Patris et al. (2007)
78-92	29.8-35.0	High Arctic (Alert, Ellesmere Is.)	Nunavut, Canada	Morin et al. (2007)
62-112	19-43	Coast	Antarctica	Savarino et al. (2007)
15.6-36.0	-0.2 to 1.8	Oil-sands mining stacks, PM 2.5	Alberta, Canada	Proemse et al. (2012)
49-86	19-27	Coast (onboard sampling)	California, USA	Vicars et al. (2013)
10.8-92.4	2.7-31.4	Mt. Lulin, partly polluted air masses	Central Taiwan	Guha et al. (2017)
48.4-83.2	13.8-30.5	Various contaminated sites	Alberta, Canada	*This study*
w-NO_3^-				
66.3-84.0	20.2-36.0	Shenandoah National Park	Virginia, USA	Coplen et al. (2004)
70-90	20-30	Bi-monthly sampling across state	New England, USA	Kendall et al. (2007)
68-101	20.8-34.5	Rishiri Island, polluted air masses	Northern Japan	Tsunogai et al. (2010)
51.7-72.8	18.9-28.1	Highway traffic emissions	Ontario, Canada	Smirnoff et al. (2012)
35.0-80.7	15.7-32.0	Oil-sands mining (with some dry dep)	Alberta, Canada	Proemse et al. (2013)
57.4-74.4	19.2-30.1	Various contaminated sites	Alberta, Canada	*This study*
Undifferentiated and Bulk NO_3^-				
60-95	21-29	Polluted coastal area & Remote land	California, USA	Michalski et al. (2004)
57-79	22-32	High Arctic	Nunavut, Canada	Morin et al. (2008)
36-105	13-37	Marine boundary layer	65S to 79N Atlantic	Morin et al. (2009)
56.6-82.3*	16.7-30.2*	Various contaminated sites	Alberta, Canada	*This study*

Note: isotopic values rounded at unit are from published graphs (except for O values with actual precision at unit in Morin et al., 2007). *Calculated using weighted averages of HNO_3 and p-NO_3 isotopic results.

Table 5. Main reactions producing atmospheric nitrates (Zel'dovich, 1946; Lavoie et al., 1969; Erisman and Fowler, 2003; Michalski et al., 2003; Morino et al., 2006; Morin et al., 2007; Stroud, 2008; Michalski et al., 2014) Reactions 1, 9-12 can occur any time.

Daytime - Summer	Nighttime - Winter
(R1) $O_2 + Q \rightarrow O + O + Q$; $N_2 + O \rightarrow NO + N$; $N + O_2 \rightarrow NO + O$	
(R2) $O + O_2 + M \rightarrow O_3$; $NO + O_3 \rightarrow NO_2 + O_2$	
(R3) $NO + RO_2 \rightarrow NO_2 + RO$	
	(R4) $NO_2 + O_3 \rightarrow NO_3 + O_2$
(R5) $NO_2 + hv$ (sunlight) $\rightarrow NO + O$	
(R6) $NO_2 + OH + M \rightarrow HNO_3 + M$	(R7) $NO_2 + NO_3^- \Leftrightarrow N_2O_5$ (R8) $N_2O_5 + H_2O(surface) \rightarrow 2HNO_3\ (aq)^*$
(R9) $HNO_3(g) \Leftrightarrow HNO_3(aq)^* \rightarrow NO_3^-(aq)^* + H^+(aq)$	
(R10) $HNO_3(g) + NH_3(g) \Leftrightarrow NH_4NO_3(s)$	
(R11) $HNO_3(g) + CaCO_3(s) \rightarrow Ca(NO_3)_2(s) + HCO_3$	
(R12) $NO_3^- + HC;(CH_3)_2S \rightarrow HNO_3$ + products	

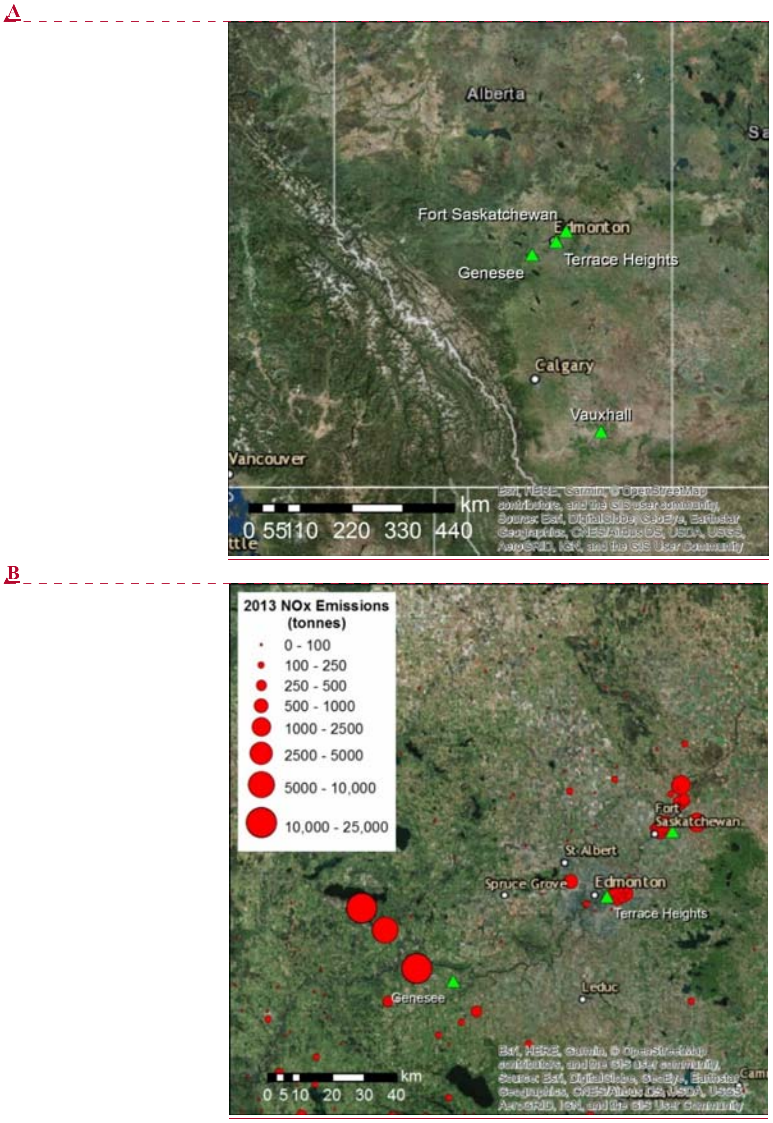
*Q is a stable molecule of high energy; M is either O_2 or N_2; RO_2 stands for both HO_2 and alkyl peroxy. HC stand for hydrocarbons. *This aqueous nitrate may be on a particle.*

Table 6. Correlations of NO_3^- isotopic results (‰) with meteorological parameters and concentration (or ratio) of co-contaminants.

	Relative Humidity		Temperature		Daylight (fraction)		PM	SO_2	O_3	
	r	R^2	r	R^2	r	R^2	r	r	r	R^2
HNO_3										
$\delta^{18}O$	**0.8**	0.59	-0.4		-0.3		0.1	0.0	-0.29	
n	8		15		15		13	13	13	
$\Delta^{17}O$	0.6		**-0.5**	0.24	-0.4		0.4	0.3	-0.03	
n	8		15		15		13	13	13	
p-NO_3^-										
$\delta^{18}O$	**0.9**	0.79	**-0.6**	0.34	**-0.6**	0.35	0.1	0.5	**-0.61**	0.38
n	7		15		15		12	12	12	
$\Delta^{17}O$	**0.9**	0.73	**-0.6**	0.34	**-0.7**	0.44	0.0	0.5	-0.47	
n	7		15		15		12	12	12	

In **bold** are the significant correlation coefficients, equal or above the 95 % significance value

Tableau mis en forme



Mis en forme : Police :Gras

Mis en forme : Centré

Mis en forme : Police :Gras

Mis en forme : Centré

Figure 1. Aerial images showing sampling sites (green triangles) in central and southern Alberta (A), and in the greater Edmonton area (B), along with emissions of NO$_x$ as tonnes of NO$_2$ reported to the National Pollutant Release Inventory for 2013 (Environment and Climate Change Canada, 2018b).

Supprimé: photographs

Supprimé: (NPRI, 2018)

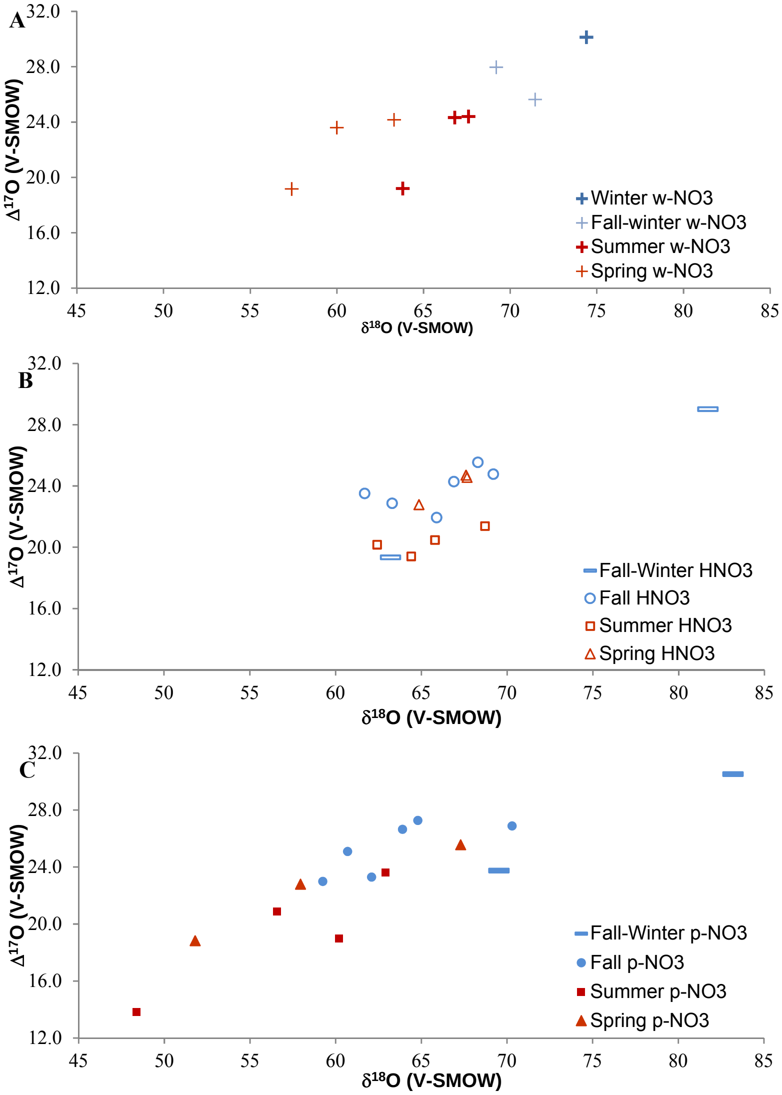


Figure 2: Triple O isotopic results (‰) obtained for simultaneously collected atmospheric HNO_3 (A), w-NO_3^- (B) and p-NO_3^- (C), in Alberta, identified by sampling periods (cold months - blue; warm months - red).

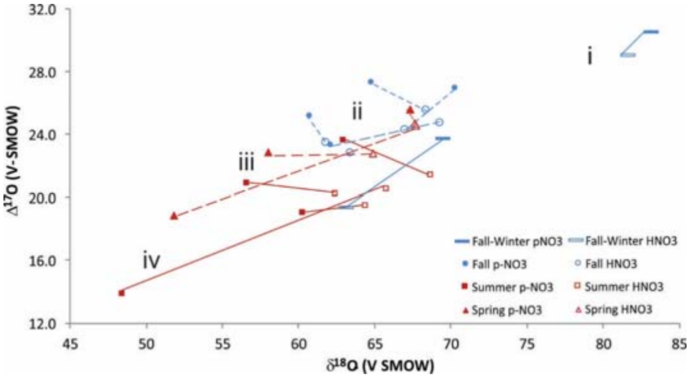


Figure 3: Line-connected $\delta^{18}O$ and $\Delta^{17}O$ values (‰) for simultaneously collected HNO_3 (empty symbols) and p-NO_3^- (solid symbols) from cold (blue) and warm (red) sampling periods.

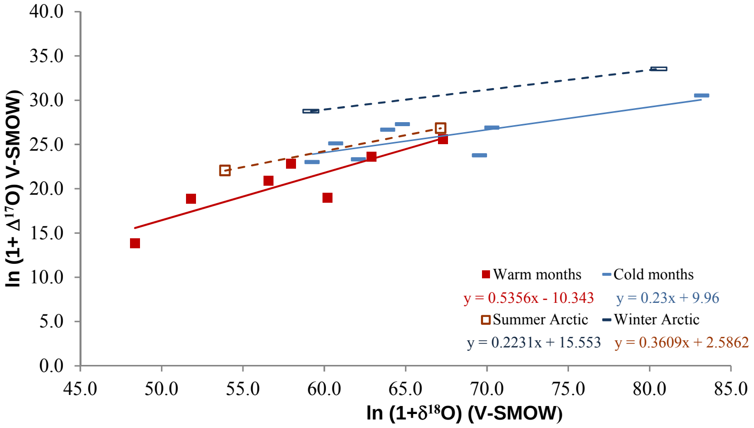
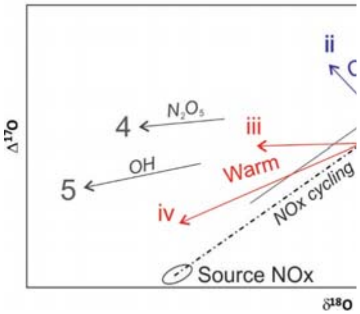


Figure 4: Isotopic results (‰) for p-NO_3^- identified by sampling periods (solid lines), compared with summer and winter trends obtained for Arctic sites (dashed lines; derived from ln (1+ δ) in Morin et al., 2008).



Supprimé:

Figure 4: Schematic outline of main steps in the production of Alberta nitrates: NO_x-O_2-O_3 photochemical cycle (1) and reaction with RO_2 (2) modify NO_x source signals (R2, R3, R9); oxidation of NO_x produces HNO_3 along the N_2O_5 (4) or OH (5) pathways. The grey line represents NO_x from photochemical cycling with O_2 and O_3 (Michalski et al., 2014). The direction of arrows 1 to 5 indicates how the isotopic values would evolve along the different chemical reactions; the positions of these arrows are arbitrary.¶

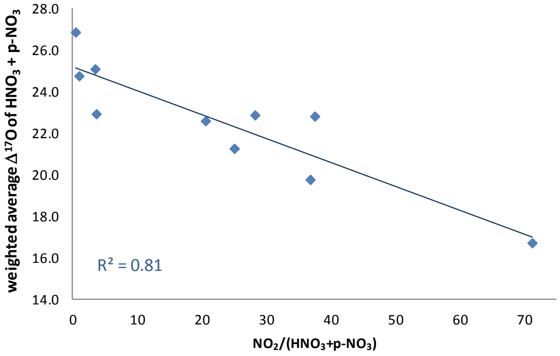


Figure 5: Weighted average $\Delta^{17}O$ (‰) for the sum of dry nitrates as a function of NO_2 concentration divided by p-NO_3 plus HNO_3 concentrations, a ratio indicative of the maturity of a plume.

Supprimé: average

Mis en forme : Non Surlignage

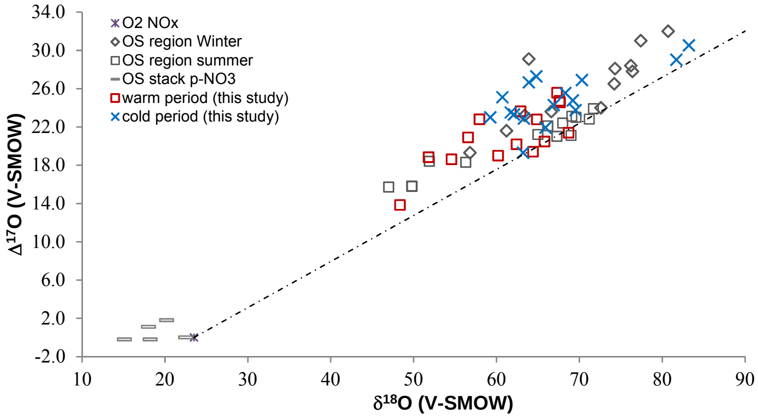


Figure 6: Isotopic ratios (‰) for atmospheric p-NO_3^-, w-NO_3^- and HNO_3 samples in cold and warm periods from central and southern Alberta (this study), compared with previously published winter and summer bulk and throughfall deposition samples from the oil sands (OS) region from northern Alberta (Proemse et al., 2013), and p-NO_3^- in-stack emissions data for an OS upgrader located in the same region (Proemse et al., 2012). The grey dotted line connects NO_x from theoretical combustion with O_2 isotopic composition and at isotopic equilibrium with tropospheric O_3 (Michalski et al., 2014).

Supprimé: 5

Supprimé: ¶

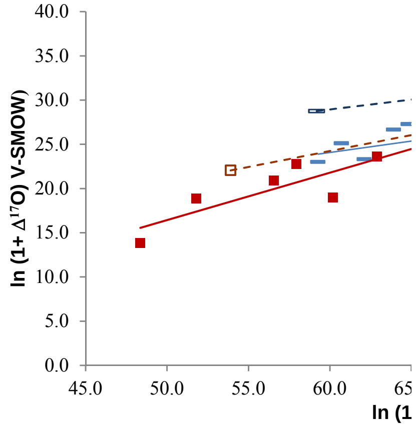


Figure 6: Isotopic results (‰) for p-NO_3^- identified by sampling periods (solid lines), compared with summer and winter trends obtained for Arctic sites (dashed lines; derived from ln (1+ δ) in Morin et al., 2008).

Mis en forme : Justifié, Pas de paragraphes solidaires, Pas de lignes solidaires

Page 1 : [1] Supprimé	Cole,Amanda [Ontario]	08/05/2018 3:29:00 PM

r

Page 1 : [1] Supprimé	Cole,Amanda [Ontario]	08/05/2018 3:29:00 PM

r

Page 1 : [1] Supprimé	Cole,Amanda [Ontario]	08/05/2018 3:29:00 PM

r

Page 1 : [1] Supprimé	Cole,Amanda [Ontario]	08/05/2018 3:29:00 PM

r

Page 1 : [1] Supprimé	Cole,Amanda [Ontario]	08/05/2018 3:29:00 PM

r

Page 1 : [1] Supprimé	Cole,Amanda [Ontario]	08/05/2018 3:29:00 PM

r

Page 1 : [1] Supprimé	Cole,Amanda [Ontario]	08/05/2018 3:29:00 PM

r

Page 1 : [1] Supprimé	Cole,Amanda [Ontario]	08/05/2018 3:29:00 PM

r

Page 1 : [1] Supprimé	Cole,Amanda [Ontario]	08/05/2018 3:29:00 PM

r

Page 1 : [2] Supprimé	Savard, Martine	23/03/2018 2:23:00 PM

polluted

Page 1 : [2] Supprimé	Savard, Martine	23/03/2018 2:23:00 PM

polluted

Page 1 : [2] Supprimé	Savard, Martine	23/03/2018 2:23:00 PM

polluted

Page 1 : [3] Supprimé	Cole,Amanda [Ontario]	07/05/2018 4:08:00 PM

pathways

Page 1 : [3] Supprimé	Cole,Amanda [Ontario]	07/05/2018 4:08:00 PM

pathways

Page 1 : [3] Supprimé	Cole,Amanda [Ontario]	07/05/2018 4:08:00 PM

pathways

Page 1 : [3] Supprimé	Cole,Amanda [Ontario]	07/05/2018 4:08:00 PM

pathways

Page 1 : [4] Supprimé Savard, Martine 24/01/2018 1:11:00 PM

five different

Page 1 : [4] Supprimé Savard, Martine 24/01/2018 1:11:00 PM

five different

Page 1 : [5] Supprimé Cole,Amanda [Ontario] 07/05/2018 4:08:00 PM

the

Page 1 : [5] Supprimé Cole,Amanda [Ontario] 07/05/2018 4:08:00 PM

the

Page 1 : [5] Supprimé Cole,Amanda [Ontario] 07/05/2018 4:08:00 PM

the

Page 1 : [5] Supprimé Cole,Amanda [Ontario] 07/05/2018 4:08:00 PM

the

Page 1 : [6] Supprimé Savard, Martine 25/04/2018 4:31:00 PM

The summer pattern

Page 1 : [6] Supprimé Savard, Martine 25/04/2018 4:31:00 PM

The summer pattern

Page 1 : [6] Supprimé Savard, Martine 25/04/2018 4:31:00 PM

The summer pattern

Page 1 : [6] Supprimé Savard, Martine 25/04/2018 4:31:00 PM

The summer pattern

Page 1 : [6] Supprimé Savard, Martine 25/04/2018 4:31:00 PM

The summer pattern

Page 1 : [6] Supprimé Savard, Martine 25/04/2018 4:31:00 PM

The summer pattern

Page 1 : [6] Supprimé Savard, Martine 25/04/2018 4:31:00 PM

The summer pattern

Page 1 : [6] Supprimé Savard, Martine 25/04/2018 4:31:00 PM

The summer pattern

Page 1 : [7] Supprimé Cole,Amanda [Ontario] 07/05/2018 4:09:00 PM

valid

Page 1 : [7] Supprimé Cole,Amanda [Ontario] 07/05/2018 4:09:00 PM

valid

Page 1 : [8] Supprimé **Savard, Martine** **25/04/2018 10:02:00 AM**

while the l

Page 1 : [8] Supprimé **Savard, Martine** **25/04/2018 10:02:00 AM**

while the l

Page 1 : [8] Supprimé **Savard, Martine** **25/04/2018 10:02:00 AM**

while the l

Page 1 : [8] Supprimé **Savard, Martine** **25/04/2018 10:02:00 AM**

while the l

Page 1 : [8] Supprimé **Savard, Martine** **25/04/2018 10:02:00 AM**

while the l

Page 6 : [9] Supprimé **Savard, Martine** **24/05/2018 9:49:00 AM**

Concentration of nitrates on Teflon and Nylon filter extracts, [AC1]and in precipitation samples were determined at Institut national de la recherche scientifique–Eau, Terre, Environnement (INRS-ETE). The determinations used an automated QuikChem 8000 FIA+ analyzer (Lachat Instruments), equipped with an ASX-260 series autosampler. The detection limit for the method (# 31-107-04-1-A with sulfanilamide) was 2 ppb N-NO_3/L (0.03 N-NO_3 umol/L). The concentration for NO and NO_2 collected with samplers of Maxxam Analytics were determined by Maxxam Analytics using an ion chromatograph.

Page 8 : [10] Supprimé **Savard, Martine** **22/03/2018 2:55:00 PM**

3.3 Covariations of $\Delta^{17}O$ and $\delta^{18}O$ values in nitrates from individual sources

The p-NO_3^-, w-NO_3^- and HNO_3 values co-vary when identified by source type in the $\delta^{18}O$ and $\Delta^{17}O$ space (Fig. 1). The isotopic range for a single source can be as large as 6 ‰ for $\Delta^{17}O$ values and 19 ‰ for $\delta^{18}O$ values in HNO_3, 12 and 17 ‰ in w-NO_3^-, and 7 and 21 ‰ in p-NO_3. Each source type clearly exhibits nitrate $\Delta^{17}O$ and $\delta^{18}O$ with a specific grouping. The CFPP w-NO_3^- results show a range similar to the HNO_3 results, but lower $\delta^{18}O$ values than the HNO_3 and p-NO_3^- groups. The few other precipitation samples show $\delta^{18}O$ and $\Delta^{17}O$ values generally higher than the p-NO_3^- and HNO_3 samples, again with exception of the chemical and metal industries.

The HNO_3 samples from a given source type tend to have a higher $\delta^{18}O$ value for a given $\Delta^{17}O$ value than p-NO_3^- (or *vice versa*; Fig. 1). These observations suggest that the contribution of oxidation pathways leading to HNO_3 and p-NO_3^- are not identical, or that there is an isotope fractionation in the conversion of HNO_3 to p-NO_3^-.

Regarding the potential for identifying nitrate sources, it appears that using $\delta^{18}O$ and $\Delta^{17}O$ values for such a task is not feasible, as previously suggested in the literature (Michalski et al., 2003). This interpretation stems from the fact that nitrate species show either continuous trends regardless of their sources (p- and w- NO_3) or overlapping source results (HNO_3; Fig. 1).

The individual range of points identified by source may partly reflect different initial ambient conditions and rates of changes in ambient conditions during NO_x oxidation (Fig. 1; see Section 3.5). Specifically, each isotopic range may depict the progressively changing influence of ozone due to ambient conditions through time. Indeed, the atmospheric samples were collected repeatedly over several weeks or months at a given site (near a given source), and consecutively from one site to the other over more than three years; samples undeniably incorporate N-species produced under significantly changing ambient conditions.

Page 11 : [11] Supprimé Cole,Amanda [Ontario] 22/05/2018 12:29:00 AM

Sub-sections 3.3 to 3.6 determined the main atmospheric chemical pathways responsible for the production of the Alberta nitrates. In the next section, we will further peruse the isotopic specificities of the produced data set and outline other key mechanisms affecting the distribution of nitrates.

Page 11 : [12] Supprimé Savard, Martine 22/03/2018 10:37:00 AM

The Alberta nitrate values do not fall on a single line but, rather, show a vertical extent in the $\delta^{18}O$ and $\Delta^{17}O$ space (Fig. 2) that exceeds the precision of the data (Section 2.3 and Table 2). This observation differs from several studies that measured bulk nitrate or a single nitrate species and reported $\delta^{18}O$ and $\Delta^{17}O$ sets as linear.

Page 11 : [13] Supprimé Cole,Amanda [Ontario] 24/05/2018 12:28:00 AM

Considering the relevant oxidation reactions shown in Table 5, anthropogenic atmospheric nitrates incorporate O atoms from three main molecules, O_2 (via RO_2 - R3, and possibly source NO_x- R1), O_3 (via NO_2, NO_3^- and N_2O_5 – R2, R4, R7-R8) and H_2O (via OH, R5-R6). These molecules carry distinct isotopic signals that will partly determine the final $\delta^{18}O$ and $\Delta^{17}O$ values of the nitrate products. The $\delta^{18}O$ and $\Delta^{17}O$ values of O_2 are 23.5 and 0 ‰, respectively. Anthropogenic emitters involving combustion (O_2) may generate primary NO_x at or near sources that tend to carry low $\delta^{18}O$ and $\Delta^{17}O$ values(Zel'dovich, 1946; Lavoie et al., 1969). This primary NO_x (>90 % emitted as NO) cycles through NO-NO_2-O_3-NO numerous times before it is removed in R6. OH typically has negative $\delta^{18}O$ values and a $\Delta^{17}O$ value equal to 0 ‰ as it rapidly exchanges O isotopes with water vapour (Dubey et al., 1997; Röckmann et al., 1998). We obtained the average of precipitation $\delta^{18}O$ values for each sampling period at the studied sites (OPIC, 2017), and calculated the vapour signal using water-vapour fractionation factors (Clark and Fritz, 1997). Next, using fractionation factors between OH in equilibrium with H_2O vapour (Walters and Michalski, 2016), we calculated that the $\delta^{18}O$ values would range between -83 and -62 ‰. Peroxy radicals mostly derive from O_2 at mid latitudes (Michalski et al., 2003; Morin et al., 2007; Alexander et al., 2009), but they have a non-zero $\Delta^{17}O$ signal (1-2 ‰) due to the role of ozone in the HO_x cycle (Morin et al., 2011). However, their $\delta^{18}O$ values are difficult to measure, so they can only be inferred based on assumptions (+23.9 ‰; Fang et al., 2011; Guha et al., 2017). The $\delta^{18}O$ and $\Delta^{17}O$ values of bulk

O_3 are generally between 90 and 120 ‰, and 30 and 34 ‰, respectively, but the transferable signals are suggested to be around 130 and 39 ‰ at mid-latitudes (Vicars and Savarino, 2014). Moreover, NO_x modelled at isotopic steady state with tropospheric O_3 yields 117 and 45 ‰ in $\delta^{18}O$ and $\Delta^{17}O$, respectively (Michalski et al., 2014). This neglects the contribution of NO oxidation by RO_2 (R3), which will reduce the steady-state $\Delta^{17}O$ and $\delta^{18}O$ of NO_x below the O_3-only oxidation value. The foregoing review of isotopic signals provides context to the interpretation of our data, keeping in mind that mass-dependent fractionation has likely played a role in determining nitrate $\delta^{18}O$ values[AC2].[AC3]Amanda to revisit… (see section SM.1)

Page 13 : [14] Supprimé **Cole,Amanda [Ontario]** **22/05/2018 12:58:00 PM**

Another argument supporting this interpretation is the strong correlation between $\Delta^{17}O$ values and the maturity of a plume as expressed by the NO_2 content divided by sum of dry nitrates (Fig. 6). The results reflect the higher content of O_3-derived O in dry nitrates from mature plumes, i.e., with relatively low NO_2 contents. Seasonal changes in the planetary boundary layer height may also affect the impingement of emission plumes on the measurement sites, and thereby the relative amounts of fresh vs background nitrates.

Supplementary Material – ACP 1103

The $\Delta^{17}O$ and $\delta^{18}O$ values of atmospheric nitrates simultaneously collected downwind of anthropogenic sources – Implications for polluted air masses

Martine M. Savard[1*], Amanda Cole[2], Robert Vet[2], Anna Smirnoff[1]

[1] Geological Survey of Canada (Natural Resources Canada), 490 de la Couronne, Québec (QC), G1K 9A9, Canada
[2] Air Quality Research Division, Environment and Climate Change Canada, 4905 Dufferin St., Toronto (ON), M3H 5T4, Canada

Correspondence to: Martine M. Savard (martinem.savard@canada.ca)

Supprimé: simultaneously collected

Supprimé: from

Table SM-1. Sampling sites, duration of sampling, average results obtained for the parallel sampling with the CAPMoN systems.

							$p\text{-}NO_3^-$					HNO_3						
#	Site	Deployment	Collection	Days	Sampling hours	Mean (total for pooled) air volume (m^3)	Mean (total for pooled) loading (ug N)	Air conc (ug N/m^3)	$\delta^{18}O$ (‰)	$\delta^{17}O$ (‰)	$\Delta^{17}O$ (‰)	Mean (total for pooled) loading (ug N)	Air conc (ug N/m3)	$\delta^{18}O$ (‰)	$\delta^{17}O$ (‰)	$\Delta^{17}O$ (‰)	Daylight fraction (sunrise to sunset)	NO_2 in sample train* (ug N/m^3)
1	Genesee	2010-09-30	2010-10-05	5	23	59	8.0	0.14	70.3	63.8	26.9	8.4	0.15	66.9	59.4	24.3	0.49	
2	Genesee	2010-10-08	2010-10-18	10	42	99						6.6	0.07	63.3	56.1	22.9	0.65	
3	Genesee	2010-10-18	2010-11-08	21	39	87	13.4	0.15	62.1	55.9	23.3	10.2	0.12	69.2	61.1	24.8	0.33	
4	Genesee	2010-11-08	2011-01-31	84	360	517	181.6	0.35	83.2	74.2	30.5	40.2	0.08	81.7	71.9	29.0	0.31	
5	Genesee	2011-02-22	2011-04-28	65														
6	Genesee	2011-04-28	2011-06-20	53	144	189	19.4	0.10	67.3	60.9	25.6	24.9	0.13	67.6	60.2	24.7	0.71	*0.82*
7	Vauxhall	2011-10-25	2011-11-17	23	152	255	22.1	0.09	64.8	61.3	27.3	6.9	0.03	68.3	61.4	25.5	0.35	*0.05*
8	Vauxhall	2011-11-17	2011-12-01	14	89	176	15.9	0.09	60.7	57.0	25.1	4.8	0.03	61.7	55.9	23.5	0.28	*0.12*
9	Vauxhall	2011-12-01	2011-12-13	12	128	235	31.1	0.13	63.9	60.2	26.7						0.34	
10	Terrace Heights	2012-07-24	2012-08-12	19	213	112	3.2	0.03	56.6	50.6	20.9	3.7	0.03	62.4	52.9	20.2	0.73	
11	Terrace Heights	2012-08-23	2012-09-10	18	288	103	2.5	0.02	62.9	56.6	23.6	1.4	0.01	68.7	57.5	21.4	0.64	1.1
12	Terrace Heights	2012-10-01	2012-10-10	9	128	39	1.4	0.04	59.3	54.1	23.0	0.8	0.02	65.9	56.5	21.9	0.51	1.2
13	Terrace Heights	2012-10-19	2012-10-25	6														1.8
14	Fort Saskatchewan	2013-04-14	2013-04-28	15	115	37	4.3	0.11	51.8	46.0	18.8	3.0	0.09	67.7	60.1	24.6	0.75	5.2
15	Fort Saskatchewan	2013-05-02	2013-06-03	32	108	39	9.6	0.26	58.0	53.2	22.8	4.8	0.13	64.9	56.8	22.8	0.84	14.9
16	Fort Saskatchewan	2013-06-14	2013-07-11	27	151	44	1.9	0.06	48.4	39.2	13.8	2.4	0.07	64.4	53.2	19.4	0.74	9.1
17	Fort Saskatchewan	2013-07-19	2013-09-06	49	223	76	4.4	0.06	60.2	50.6	19.0	4.5	0.06	65.8	55.0	20.5	0.74	4.4
18	Fort Saskatchewan	2013-09-29	2014-01-19	113	107	31	7.3	0.24	69.5	60.3	23.8	3.3	0.05	63.2	52.5	19.3	0.33	1.1

*Sum of upstream and downstream NO_2 filters where breakthrough <15%. Sum of NO_2 and NO filters where there was no downstream filter to check for breakthrough (samples in italics).

Table SM-2. Sampling sites, duration of sampling, and results obtained for precipitation.

		Sampling duration			**w-NO_3**			
#	Site	Deployment	End	Days	Concentration (mg N/L)	$\delta^{18}O$ (‰)	$\delta^{17}O$ (‰)	$\Delta^{17}O$ (‰)
4	Genesee	2010-11-14	2011-01-06	49	0.18	69.2	64.3	28.0
4	Genesee	2011-01-06	2011-01-24	19	0.27	74.4	69.2	30.1
5	Genesee	2011-02-04	2011-04-28	79	0.48	57.4	49.3	19.2
6	Genesee	2011-04-28	2011-06-21	58	0.17	63.3	57.4	24.2
10	Terr. Heights	2012-07-24	2012-08-12	19	0.28	66.8	59.4	24.3
11	Terr. Heights	2012-08-23	2012-09-10	18	0.15	67.6	59.9	24.4
15	F. Saskachewan	2013-05-02	2013-06-05	33	0.46	60.0	55.1	23.6
16	F. Saskachewan	2013-06-14	2013-07-11	27	0.30	63.8	52.7	19.2
18	F. Saskachewan	2013-09-20	2014-01-20	122		71.4	63.1	25.6

Code de champ modifié

Table SM-3. Sampling sites and other measured parameters.

sample	Site	Nearest air quality data site(s)	Distance from sampler (km)	Bearing from sampler	Mean T (°C)	Wind speed (km/h)	Wind direction (°)	RH (%)	O_3 (ppb)	SO_2 (ppb)	$PM_{2.5}$ ($\mu g/m^3$)	Nearest source (km)
1	Genesee	Genesee	5	W	11.7	15.8	316	62.9	15.5	4.3	4.9	7
2	Genesee				12.2	16.2	304	43.5	26.1	1.8	3.3	7
3	Genesee				5.5	9.4	308	64.3	18.7	1.5	2.9	7
4	Genesee				-9.8	13.9	313	76.1	16.3	1.0	4.7	7
5	Genesee				-0.9	7.7	298	62.6	36.6			7
6	Genesee				12.2	16.3	312	64.8	27.4	2.2	5.0	7
7	Vauxhall	Lethbridge	65	SW	2.6							n/a
8	Vauxhall				-0.7	-	-	-	-	-	-	n/a
9	Vauxhall				-3.5							n/a
10	Terrace Heights	Edmonton East	4.5	E	20.3	11.0	276	60.3	25.5	1.1	7.5	4
11	Terrace Heights				15.6	13.9	277	60.6	19.7	1.1	7.2	4
12	Terrace Heights				7.9	11.3	313	63.3	21.1	0.4	1.6	4
13	Terrace Heights				-1.8	10.2	309	66.3	15.2	0.8	0.9	4
14	Fort Saskatchewan	Ross Creek; Fort Saskatchewan (O3)	4.3; 6.1	W	4.3	10.8	298		42.5	0.2	2.3	3
15	Fort Saskatchewan				15.7	8.8	300		37.8	0.3	4.0	3
16	Fort Saskatchewan				16.3	8.6	293		25.5	0.4	5.7	3
17	Fort Saskatchewan				17.7	6.3	302		22.1	0.5	5.2	3
18	Fort Saskatchewan	Range Rd 220	4.0	N	-8.1	10.3	351		18.6	0.8	5.8	9

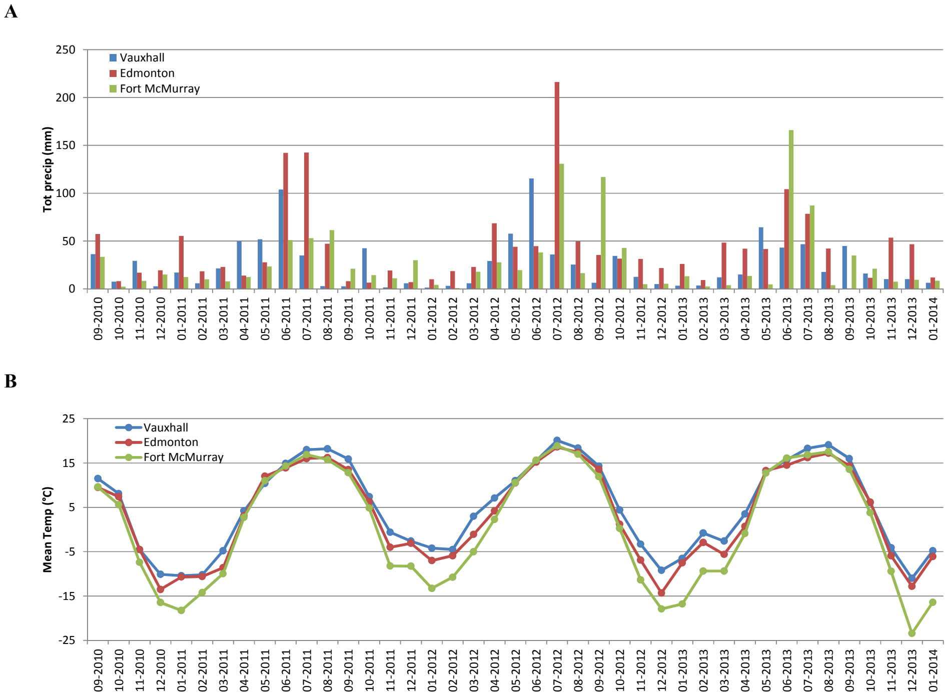


Figure SM-1. Monthly total precipitation (A) and mean temperature (B) for the Vauxhall region (feedlots and gas compressors), great Edmonton area (CFPP, chemical and metal industries, city traffic, fertilizers and oil refinery), and oil sands mining lower Athabasca region, recorded over the period of sampling. The Edmonton area and Vauxhall meteorological conditions only differ from the oil sands ones by having higher winter temperature.

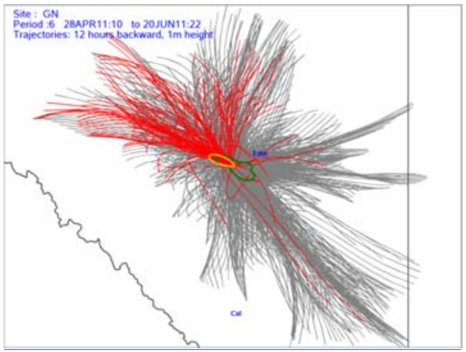


Figure SM-2. Twelve-hour HYSPLIT back trajectories during sample 6 (at Genesee), with red trajectories showing the times when winds were from the sampled sector.

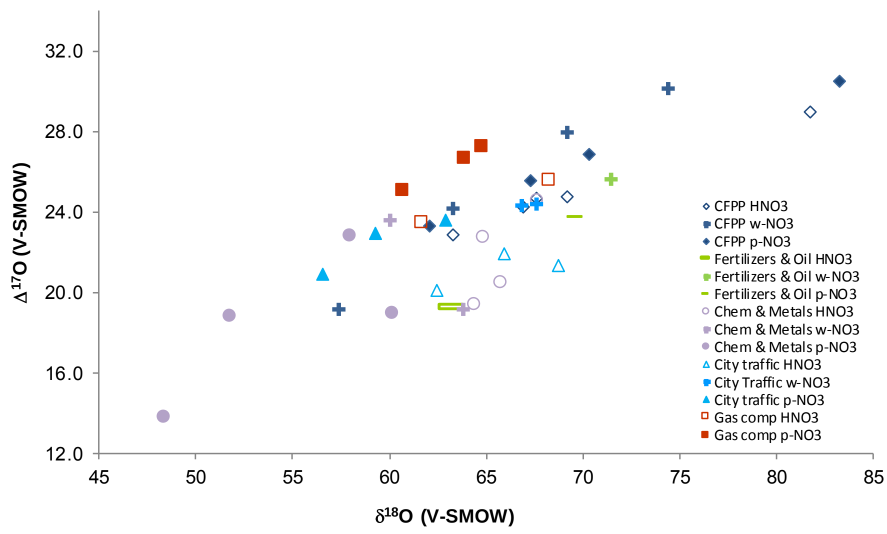


Figure SM-3. Triple oxygen isotopic results (‰) obtained for simultaneously sampled atmospheric HNO_3 (empty symbols), w-NO_3^- (crosses) and p-NO_3^- (full symbols) downwind of the various sources.

Supprimé: ¶

Supprimé: 2

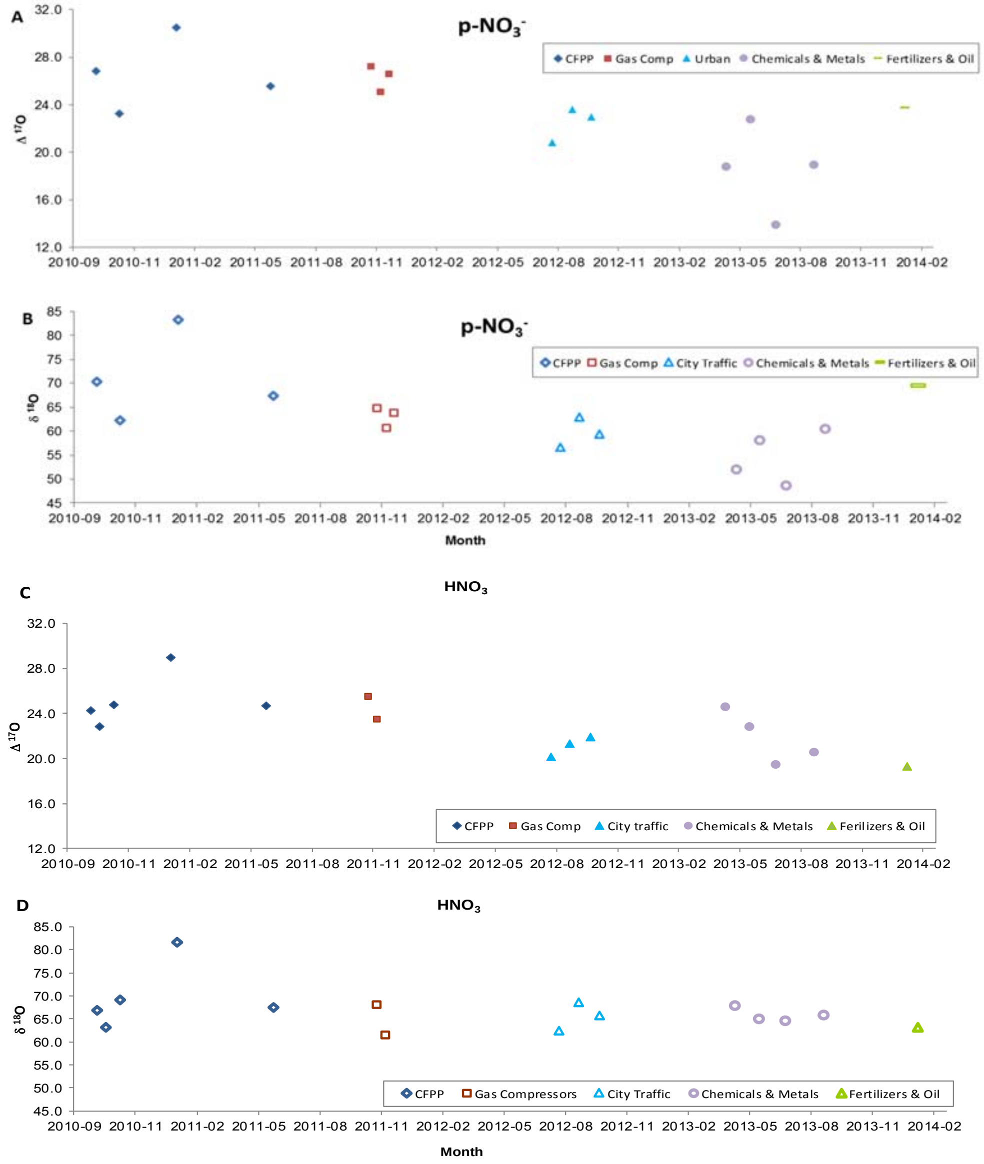


Figure SM-4. Oxygen isotopic variations as a function of sampling period labelled by emitter types: p-NO_3^- (A) $\Delta^{17}O$ and (B) $\delta^{18}O$ values; and HNO_3 (C) $\Delta^{17}O$ and (D) $\delta^{18}O$ values.

Supprimé: 3

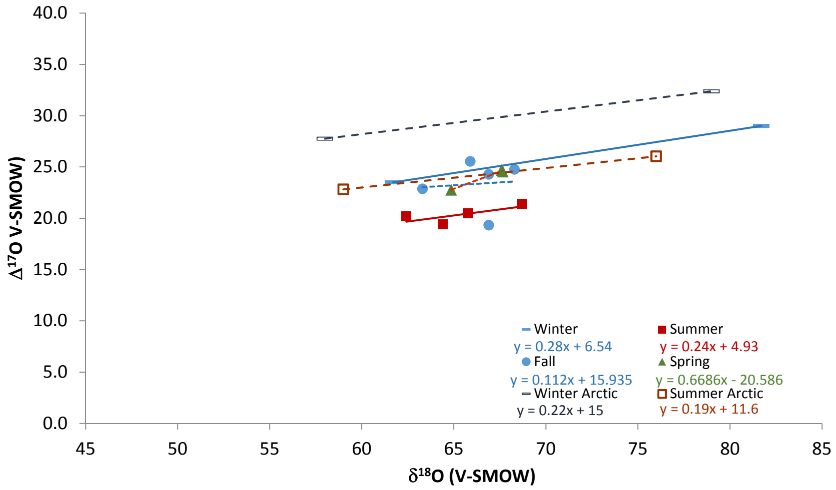


Figure SM-5. Triple oxygen isotopic (‰) results for HNO_3 from Southern and central Alberta (solid symbols) and p-NO_3^- (empty symbols) for High Arctic (Morin et al., 2008).

Supprimé: 4