

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

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10 **Abstract.** There are clear motivations for better understanding the atmospheric processes that transform nitrogen (N) oxides ( $\text{NO}_x$ ) emitted from anthropogenic sources into nitrates ( $\text{NO}_3^-$ ), two of them being that  $\text{NO}_3^-$  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 delta values ( $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ ) are frequently applied to infer the chemical pathways leading to the observed mass independent isotopic anomalies from interaction with  $^{17}\text{O}$ -rich ozone ( $\text{O}_3$ ). Recent laboratory experiments suggest that the isotopic equilibrium between  $\text{NO}_2$  (the main precursor of  $\text{NO}_3^-$ ) and  $\text{O}_3$  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  $\text{NO}_3^-$  in precipitation (w- $\text{NO}_3^-$ ) and in particulate (p- $\text{NO}_3^-$ ) 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  $\text{HNO}_3$  with  $\Delta^{17}\text{O}$  values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample  $\text{HNO}_3$  and p- $\text{NO}_3^-$ , and co-collect w- $\text{NO}_3^-$ . The nitrates are from various distances (<1 to >125 km) downwind of different anthropogenic emitters, and consequently from varying time lapses after emission.

25 The separate collection of nitrates shows that the  $\text{HNO}_3$   $\delta^{18}\text{O}$  ranges are distinct from those of w- and p- $\text{NO}_3^-$ . Interestingly, the  $\Delta^{17}\text{O}$  differences between p- $\text{NO}_3^-$  and  $\text{HNO}_3$  shift from positive during cold sampling periods to negative during warm periods. The low p- $\text{NO}_3^-$   $\Delta^{17}\text{O}$  values observed during warm periods may partly derive from the involvement of  $^{17}\text{O}$ -depleted peroxy radicals ( $\text{RO}_2$ ) oxidizing  $\text{NO}$  during that season. Another possibility is that nitrates derive from  $\text{NO}_x$  that has not yet reached isotopic equilibrium with  $\text{O}_3$ . However, these mechanisms, individually or together, cannot explain the observed p- $\text{NO}_3^-$  minus  $\text{HNO}_3$  isotopic changes. We propose differences in dry depositional rates, faster for  $\text{HNO}_3$ , as a mechanism for the observed shifts. Larger proportions of p- $\text{NO}_3^-$  formed *via* the  $\text{N}_2\text{O}_5$  pathway would explain the opposite fall-winter patterns. Our results show that the separate  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  isotopic signals can be used to further our understanding of  $\text{NO}_x$  oxidation and deposition. Future research should investigate all tropospheric nitrate species as well as  $\text{NO}_x$  to refine our understanding of nitrate distribution worldwide and to develop effective emission reduction strategies.

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## 1 Introduction

Anthropogenic NO<sub>x</sub> (NO and NO<sub>2</sub>) emissions are oxidized to nitrate in the atmosphere in the form of gaseous, wet or particulate forms, HNO<sub>3</sub> being one of the main precursors of p-NO<sub>3</sub><sup>-</sup>. 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<sub>3</sub>, HNO<sub>3</sub> and w-NO<sub>3</sub>).

Triple oxygen isotopes (δ<sup>18</sup>O and δ<sup>17</sup>O) have been used to decipher atmospheric oxidation pathways of NO<sub>x</sub> leading to ambient nitrate. Michalski et al. (2003) performed the first measurement of δ<sup>17</sup>O values in atmospheric nitrate. The authors found nitrate highly enriched in <sup>18</sup>O and <sup>17</sup>O, likely due to the transfer of anomalous oxygen atoms from ozone (O<sub>3</sub>) via the NO<sub>x</sub>-ozone photochemical cycle and oxidation to nitrate. During its formation, O<sub>3</sub> inherits abnormally high δ<sup>18</sup>O and δ<sup>17</sup>O values through mass independent fractionation. The specific δ<sup>17</sup>O departure from the terrestrial mass dependent fractionation line, named the <sup>17</sup>O anomaly, is often expressed as Δ<sup>17</sup>O = δ<sup>17</sup>O - 0.517 × δ<sup>18</sup>O (Thiemens, 1999). Further investigations suggested that the δ<sup>18</sup>O and δ<sup>17</sup>O values of w-NO<sub>3</sub><sup>-</sup> and p-NO<sub>3</sub><sup>-</sup> reflect several reactions taking place after the atmospheric emission of NO<sub>x</sub>, *i.e.*, atmospheric oxidation pathways transforming NO<sub>x</sub> 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 δ<sup>18</sup>O differences in w-NO<sub>3</sub><sup>-</sup> 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; Smirnov et al., 2012), transfer of the ozone <sup>17</sup>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<sub>3</sub><sup>-</sup> samples are not yet widespread. Also rare are the nitrate δ<sup>18</sup>O and Δ<sup>17</sup>O values of field samples downwind from NO<sub>x</sub>-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). The few existing studies have chiefly characterized w-NO<sub>3</sub><sup>-</sup> or the sum of p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (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<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> were generally collected together (without differentiation). Therefore, no studies have separately and simultaneously collected and analyzed the HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> δ<sup>18</sup>O and Δ<sup>17</sup>O values, and discussed these isotopic characteristics of nitrate collected downwind of anthropogenic emitters. While HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> can be in equilibrium (e.g. if p-NO<sub>3</sub><sup>-</sup> is in the form of solid NH<sub>4</sub>NO<sub>3</sub>), 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 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  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  as well as  $\text{w-NO}_3^-$  downwind of the source types. The objective of this work was to assess the atmospheric  $\text{NO}_x$  reaction pathways and determine processes responsible for the distribution of  $\text{HNO}_3$ , and  $\text{w-}$  and  $\text{p-NO}_3^-$  in a mid-latitudinal region.

## 2 Methodology

### 2.1 Regional context

While national reported  $\text{NO}_x$  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  $\text{PM}_{2.5}$  (particulate matter less than  $2.5 \mu\text{m}$ ) 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  $\text{NO}_x$  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 ( $\text{p-NO}_3^-$ ,  $\text{HNO}_3$  and  $\text{w-NO}_3^-$ ) 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 ( $5.6^\circ\text{C}$ ) and total annual precipitation lower (320 mm) than in central Alberta ( $3.9^\circ\text{C}$ ; 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

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<sub>x</sub> 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<sub>3</sub>) 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<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub> on the Teflon filter, <3% breakthrough of HNO<sub>3</sub> from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> of approximately 0.2 µg N<sub>per</sub> 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<sub>3</sub><sup>-</sup> and positive bias in HNO<sub>3</sub> 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<sub>3</sub> between filter packs and denuder and/or TDLAS systems (Anlauf et al., 1986; Sickles Li 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<sub>2</sub> (nitrous acid) on the nylon filter in two samples (Sickles Li et al., 1999). Based on the conditions in Alberta, we estimate that there is little or no volatilization of NH<sub>4</sub>NO<sub>3</sub> 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.

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After the first five sample periods, an experimental active sampling system for NO<sub>2</sub> and NO<sub>x</sub> 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<sub>2</sub>, and one- or two-stage filter pack containing two identical Maxxam Analytics' impregnated filters designed to collect NO<sub>x</sub> (mostly NO due to upstream collection of NO<sub>2</sub>). Oxygen isotopes in NO<sub>2</sub> and NO<sub>x</sub> 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](#).

Here we report on oxygen isotopes in the simultaneously sampled HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup>, along with co-sampled w-NO<sub>3</sub><sup>-</sup> 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.

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.

### 2.3 Analytical procedures

Nitric acid from nylon filters were extracted using 10 mL of 0.01M solution of NaCl. Particulate-NO<sub>3</sub> 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 (0.03  $\mu\text{mol/L}$  of  $\text{NO}_3^-$ -N). Nitrite concentrations were also measured in the extracts. Nitrite concentrations above the detection limit (1.14  $\mu\text{mol/L}$  of  $\text{NO}_2^-$ -N) were found in a handful of samples at Terrace Heights. These samples were excluded from the reported data.

We characterized the  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  ratios of  $\text{HNO}_3$ , w- $\text{NO}_3^-$ , and p- $\text{NO}_3^-$ , along with the  $\delta^{15}\text{N}$  values of  $\text{NH}_3$ , w- $\text{NH}_4$ , p- $\text{NH}_4$  and  $\text{NO}_x$  (all N isotopic results are in Savard et al., 2017). The present article deals solely with the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values obtained for the three nitrate species. We treated the samples using the chemical conversion and thermal decomposition of  $\text{N}_2\text{O}$  protocols, providing the ability to simultaneously analyze low-concentration N- and O-containing species (Smirnov 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  $\mu\text{mol/L}$  of  $\text{NO}_3^-$ -N). Therefore, not all samples could be diluted to produce volumes sufficient for reduction of  $\text{NO}_3^-$  to  $\text{NO}_2$  and subsequent conversion to  $\text{N}_2\text{O}$ , the final product before isotope analysis. Samples with an initial concentration below 2.3  $\mu\text{mol/L}$  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 ( $\text{NO}_2^-$ ) using a custom-made cadmium column. The final preparation step involved using sodium azide to ultimately produce  $\text{N}_2\text{O}$  (McIlvin and Altabet, 2005; Smirnov et al., 2012). All extracted  $\text{N}_2\text{O}$  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; Smirnov et al., 2012). The utilized approach allows the spectrum of  $\delta^{15}\text{N}$ ,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values 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  $\text{N}_2\text{O}$ . The laboratory analytical precision (average of replicates) determined during the present study was 0.6 ‰ for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values in gaseous (n=12) and solid nitrates (n=20). For w- $\text{NO}_3$ , analytical replicates gave 0.6 and 0.5 ‰, for  $\delta^{18}\text{O}$  (n=3) and  $\delta^{17}\text{O}$  (n=4) values, respectively. The  $\Delta^{17}\text{O}$  values are defined as  $1000 \times \ln \left( \frac{1+\delta^{17}\text{O}/1000}{1+\delta^{18}\text{O}/1000} \right) - 0.516 \times 1000 \times \ln \left( \frac{1+\delta^{18}\text{O}/1000}{1+\delta^{18}\text{O}/1000} \right)$ , relative to Vienna Standard Mean Ocean Water (VSMOW).

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### 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  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\text{NH}_4\text{NO}_3$  on the particle filter into  $\text{HNO}_3$  and  $\text{NH}_3$ , 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  $\text{p-NO}_3^-$  isotopic values ( $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) to be generally higher during winter than during summer (see Section 3.4). Moreover, the  $\text{p-NO}_3^-$   $\delta^{18}\text{O}$  minus  $\text{HNO}_3$   $\delta^{18}\text{O}$  differences are negative during summer (see Section 3.6), 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  $\delta^{15}\text{N}$  values in  $\text{NH}_3$  and  $\text{NH}_4$ ; 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  $^{17}\text{O}$  anomaly; therefore,  $\Delta^{17}\text{O}$  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  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  (Elliott et al., 2009).

#### 3.2 Concentrations and isotopic ratios of nitrates in Alberta samples

The range of  $\text{HNO}_3\text{-N}$  concentrations measured by the filters (from 0.01 to 0.15  $\mu\text{g}/\text{m}^3$ ; average of 0.06) are slightly lower than those of  $\text{p-NO}_3^-\text{-N}$  (from 0.02 to 0.35  $\mu\text{g}/\text{m}^3$ ; 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  $\mu\text{g}/\text{m}^3$  for  $\text{HNO}_3\text{-N}$  and from 0.007 to 0.45  $\mu\text{g}/\text{m}^3$  for  $\text{p-NO}_3^-\text{-N}$  (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

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northern Alberta border revealed similar average concentrations of 0.02  $\mu\text{g}/\text{m}^3$  of  $\text{NO}_3^-$ -N for both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  (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  $\text{NO}_3^-$ -N concentrations of the  $\text{w-NO}_3^-$  samples was 0.15 – 0.48  $\text{mg}/\text{L}$ . 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  $\text{mg}/\text{L}$  of  $\text{NO}_3^-$ -N, while at the most polluted site in southern Ontario (Longwoods) the volume-weighted mean concentration was approximately 0.3  $\text{mg}/\text{L}$  (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.

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The average  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of  $\text{HNO}_3$  (gas),  $\text{w-}$  and  $\text{p-NO}_3^-$  show no apparent systematic ordering (Table 3; Tables SM-1 and 2), in contrast to what was found for  $\delta^{15}\text{N}$  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  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  have the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages, but not the highest delta values for  $\text{w-NO}_3^-$  values; chemical industries show the lowest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages for  $\text{w-}$  and  $\text{p-NO}_3^-$ , but not for  $\text{HNO}_3$ . Though the number of samples were limited,  $\text{w-NO}_3^-$   $\Delta^{17}\text{O}$  values were roughly correlated with the weighted average  $\Delta^{17}\text{O}$  values of  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  in samples covering the same time periods, consistent with scavenging of both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  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).

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Considering all nitrate species, the Alberta  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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  $\text{NO}_x$  cycling and oxidation (nitrate derived through combustion in  $\text{O}_2$  would show  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of 23.5 and 0 ‰, respectively). When examining the existing  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data for  $\text{w-}$  and  $\text{p-NO}_3^-$  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  $\delta^{18}\text{O}$  range of atmospheric  $\text{NO}_3^-$  previously suggested to be between 60 and 95 ‰ (Hastings et al., 2003; Kendall et al., 2007).

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Previous studies that report triple isotope oxygen results in atmospheric  $\text{NO}_3^-$  samples are scarce (Table 4). The  $\text{HNO}_3$  range documented here is within the broad spectrum of  $\text{p-NO}_3^-$  values compiled for remote to contaminated sites. Elliott et al. (2009) reported  $\text{HNO}_3$  oxygen results for  $\delta^{18}\text{O}$  values only, with a range of +51.6 to +94.0 ‰ (mean of 77.4), with simultaneously-sampled  $\text{p-NO}_3^-$   $\delta^{18}\text{O}$  values between +45.2 and +92.7 ‰ (mean of 75.2). Those ranges are broader than the  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  values obtained in the present study.

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

The  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  ranges for  $\text{HNO}_3$  identified by sampling period are narrower than those of the simultaneously collected  $\text{p-NO}_3^-$  (Fig. 2; Table SM-1), suggesting that there are additional mechanisms affecting  $\text{HNO}_3$ , or that  $\text{p-NO}_3^-$  is derived from



different pathways with more variation in isotopic signatures. Overall, the  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  results for  $\text{HNO}_3$ ,  $\text{w-NO}_3^-$  and  $\text{p-NO}_3^-$  clearly show higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during cold periods relative to warm periods (Fig. 2), with the exception of  $\text{HNO}_3$   $\delta^{18}\text{O}$  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  $0^\circ\text{C}$  (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- $\text{NO}_3^-$ .

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,  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) is produced through reactions of air  $\text{N}_2$  with atmospheric  $\text{O}_2$  at high temperatures (reactions R1; Table 5). Then,  $\text{NO}_x$  cycles between  $\text{NO}$  and  $\text{NO}_2$  through a series of reactions involving sunlight (R5),  $\text{O}_3$  (R2, R4), and peroxy ( $\text{HO}_2$ ) or alkyl peroxy ( $\text{RO}_2$ ) radicals (R3; Morin et al., 2007; Fang et al., 2011; Michalski et al., 2014; here we use  $\text{RO}_2$  to refer collectively to  $\text{HO}_2$  and  $\text{RO}_2$ ).

The oxidation of  $\text{NO}_x$  (specifically  $\text{NO}_2$ ) to  $\text{HNO}_3$  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,  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  (R8),  $\text{HNO}_3$  is likely to be retained on the reaction particle as p- $\text{NO}_3^-$  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  $\text{NO}_x$  with hydrocarbons (R12) since they are predicted to have a minimal contribution to nitrate formation in this region (Alexander et al., 2009). Finally,  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of w- and p- $\text{NO}_3^-$  formed during summer are lower than those during winter due to higher contribution from the  $\text{N}_2\text{O}_5$  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- $\text{NO}_3^-$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data presented here follow the same patterns for warm and cold months (Fig. 2). In contrast, the less commonly studied  $\text{HNO}_3$  shows similar  $\delta^{18}\text{O}$  values during warm and cold seasons, but summer  $\Delta^{17}\text{O}$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  samples (n of w- $\text{NO}_3^-$  too low) with meteorological and air quality parameters measured routinely at nearby monitoring stations where available (Table SM-3). We found that the p- $\text{NO}_3^-$  and  $\text{HNO}_3$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values correlate with RH, with p- $\text{NO}_3^-$  values showing stronger statistical links than  $\text{HNO}_3$  (Table 6). The  $\text{N}_2\text{O}_5$  hydrolysis reaction (R8) rate increases with humidity (Kane et al., 2001), which may explain this positive correlation. Significant inverse

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relationships exist between temperature and  $p\text{-NO}_3^- \delta^{18}\text{O}$ ,  $p\text{-NO}_3^- \Delta^{17}\text{O}$ , and  $\text{HNO}_3 \Delta^{17}\text{O}$ . These negative links likely arise since  $\text{N}_2\text{O}_5$  is more stable under cold conditions, leading to a higher contribution of R8. The stronger links with  $p\text{-NO}_3^-$  may be due to R8 taking place on surfaces (such as particles) with liquid water, which is likely to retain the  $\text{HNO}_3$  as  $p\text{-NO}_3^-$  rather than release it to the gas phase. Therefore, in winter, R8 may contribute more to  $p\text{-NO}_3^-$  than to  $\text{HNO}_3(\text{g})$ . Moreover, the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values for both  $p\text{-NO}_3^-$  and  $\text{HNO}_3$  were found for fall-winter samples collected at high RH (76 %) and low temperature ( $-10^\circ\text{C}$ ). In contrast, the lowest  $p\text{-NO}_3^-$  isotopic values were found for samples with similar proportions of  $\text{HNO}_3$  and  $p\text{-NO}_3^-$ , and sampled during moderately humid (60-63 %) and warm ( $8\text{-}20^\circ\text{C}$ ) periods. The accompanying shift in  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  differences between  $p\text{-NO}_3^-$  and  $\text{HNO}_3$ , will help infer the mechanisms dominating during the cold and warm periods (Section 4.2).

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Concentrations of oxidants, co-contaminants (e.g.,  $\text{SO}_4^-$  aerosols) and  $\text{NO}_x$  influence the dominance and rates of the discussed reactions (Brown et al., 2006; Michalski et al., 2014). However, while temperature, RH and  $\text{O}_3$  are well captured within a 5 km radius, other pollutant measurements like continuous  $\text{SO}_2$ ,  $\text{PM}_{2.5}$  and  $\text{NO}_x$  can have large gradients near sources, therefore it is not surprising that no correlations were found with  $\text{SO}_2$  or  $\text{PM}_{2.5}$  measured at sites 4-5 km away (Table 6). Surprisingly, only the  $p\text{-NO}_3^- \Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values.

### 3.5 Comparison with high-latitude $p\text{-NO}_3^-$

An interesting aspect of the Alberta  $p\text{-NO}_3^-$  cold-period  $\Delta^{17}\text{O}$  ranges is that they compare relatively well with the range obtained for the Canadian Arctic (Fig. 4), during winter, when nighttime conditions and the  $\text{N}_2\text{O}_5$  pathway prevail without interruption (Morin et al., 2008; for comparison with  $\text{HNO}_3$  values see Fig. SM-4). This observation supports the suggestion that the  $\text{N}_2\text{O}_5$  pathway produces around 90 % of nitrates during mid-latitude cold months (Michalski et al., 2003; Section 4.1). The  $\delta^{18}\text{O}$  ranges of cold months are similar in Alberta and in the Arctic. This similarity goes against previous suggestions that at higher latitudes, nitrate  $\delta^{18}\text{O}$  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  $\text{N}_2\text{O}_5$  pathway during the Arctic winter (Fang et al., 2011).

The  $\Delta^{17}\text{O}$  departure between the Alberta and Arctic winter parallel lines is about 3 ‰. Such difference is slightly larger than the one calculated for winter  $\text{NO}_3^-$  at 80 and  $40^\circ\text{N}$  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  $\Delta^{17}\text{O}$  values is similar at the mid- and high-latitude 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  $\Delta^{17}\text{O}$  values of  $\text{NO}_x$  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<sub>2</sub>O<sub>5</sub> pathways during summer and winter, respectively. Finally, the  $\Delta^{17}\text{O}$  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<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup>

5 As far as the isotopic characteristics are concerned, an important feature to keep in mind is that the HNO<sub>3</sub> of central and southern Alberta has distinct properties relative to simultaneously sampled p-NO<sub>3</sub><sup>-</sup>. In practical terms, the relationships between the simultaneously sampled HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> are of four types (Fig. 3): (i) HNO<sub>3</sub>  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  are both lower than p-NO<sub>3</sub><sup>-</sup>; (ii) HNO<sub>3</sub> has lower  $\Delta^{17}\text{O}$  but higher  $\delta^{18}\text{O}$  values than p-NO<sub>3</sub><sup>-</sup>; (iii) HNO<sub>3</sub> has higher  $\delta^{18}\text{O}$  values and similar  $\Delta^{17}\text{O}$  ones relative to p-NO<sub>3</sub><sup>-</sup>; and (iv) HNO<sub>3</sub> has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than p-NO<sub>3</sub><sup>-</sup> (Fig. 3).

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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<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> in northeastern USA with similar seasonal changes of  $\delta^{18}\text{O}$  differences (no  $\Delta^{17}\text{O}$  measurement). The HNO<sub>3</sub>  $\delta^{18}\text{O}$  were generally similar or lower than the p-NO<sub>3</sub><sup>-</sup> values during winter and fall, and slightly to much higher during spring and summer, with the spring and autumn p-NO<sub>3</sub><sup>-</sup>-HNO<sub>3</sub> relationships being roughly intermediate between the winter and summer ones. The average  $\delta^{18}\text{O}$  difference of p-NO<sub>3</sub><sup>-</sup> minus HNO<sub>3</sub> reported between winter and summer (15 ‰) by Elliott et al. (2009) agrees with the difference for fall-winter and summer obtained here (12 ‰).

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The marked shifts in isotopic differences between the separately analyzed HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> 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<sub>x</sub> source.

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## 25 4 Discussion

### 4.1 Estimation of $\Delta^{17}\text{O}$ values of NO<sub>x</sub> precursor to the studied nitrates- Highlighting oxidation mechanisms

In the present sub-section, we estimate the  $\Delta^{17}\text{O}$  values of NO<sub>2</sub> 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<sub>2</sub>O<sub>5</sub> due to interaction with O<sub>3</sub> (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<sub>2</sub>O (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<sub>2</sub>, 1/6 from O<sub>3</sub> and 1/6 from H<sub>2</sub>O, while the second produces nitrates via R6 with 2 out of 3 O atoms coming from NO<sub>2</sub> and 1/3 from OH (e.g., Michalski et al., 2003). Using these proportions with the Alberta  $\Delta^{17}\text{O}$  values of p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> in weighted averages allows us to make a rough estimation of the maximum and minimum  $\Delta^{17}\text{O}$  values of NO<sub>2</sub> oxidized to nitrates in the air masses sampled. The calculations assume the O from O<sub>3</sub> contributes a signal of ~39 ‰ as

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was recently measured (Vicars et al., 2014) and that  $\Delta^{17}\text{O}$  of OH and  $\text{H}_2\text{O}$  are zero. The estimated  $\text{NO}_2$   $\Delta^{17}\text{O}$  values for fall-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  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  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  $\text{NO}_2$   $\Delta^{17}\text{O}$  ranges indicate that the potential parent  $\text{NO}_2$  had a smaller  $^{17}\text{O}$  anomaly than  $\text{O}_3$  (39 ‰; Vicars and Savarino, 2014) or  $\text{NO}_2$  in isotopic equilibrium with  $\text{O}_3$  alone (45 ‰; Michalski et al., 2014) in all possible scenarios.

Two mechanisms could be responsible for the  $\Delta^{17}\text{O}$  differences between these estimates and  $\text{NO}_2$  in isotopic equilibrium with  $\text{O}_3$ . One is the competition of R3 with R2 in oxidizing NO to  $\text{NO}_2$ , since  $\text{RO}_2$  will decrease the  $\Delta^{17}\text{O}$  values relative to an ozone-only equilibrium. The relative reaction rates of R2 and R3 have previously been presumed to control the  $\text{NO}_2$  isotopic composition (e.g., Alexander et al., 2009) based on the assumption of isotopic steady state. A larger contribution of  $\text{RO}_2$  is expected in the  $\text{NO}_2$  precursors for summer relative to winter, since biogenic VOCs that are major sources of  $\text{RO}_2$  radicals are much higher in the summer (e.g., Fuentes and Wang, 1999). This suggestion is consistent with the lower  $\Delta^{17}\text{O}$  ranges in summer reported here. A second possibility is that the nitrates were formed from some  $\text{NO}_x$  that did not reach isotopic steady state with  $\text{O}_3$ , retaining some of its original signature (assumed to be  $\Delta^{17}\text{O}=0$  ‰). Most studies have assumed that isotopic steady state is established between  $\text{O}_3$  and  $\text{NO}_2$  within a few minutes after emission of  $\text{NO}_x$  from a combustion source – or at least, that nitrate formation is negligible before  $\text{NO}_x$  isotopic equilibrium is reached. However, recent modeling by Michalski et al. (2014) suggests that isotopic equilibration of  $\text{NO}_x$  with  $\text{O}_3$  could take several minutes up to a few hours at the relatively low  $\text{O}_3$  concentrations in rural Alberta. At the measured average wind speeds on site of 8-19  $\text{km h}^{-1}$ , transit times from the nearest sources to observation sites are estimated to be 9-55 minutes. While the fraction of  $\text{NO}_x$  converted to nitrate in this transit time may be small, these are large sources of  $\text{NO}_x$  in an area with very low background nitrates. For example, a plume containing 10  $\mu\text{mol mol}^{-1}$  of  $\text{NO}_2$  mixing with background air with 0.1  $\mu\text{mol mol}^{-1}$  of OH (Howell et al., 2014) would produce  $\text{HNO}_3$  via R6 at a rate of 0.011  $\mu\text{g m}^{-3} \text{min}^{-1}$  of  $\text{NO}_3\text{-N}$  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  $\text{O}_3$  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  $\text{NO}_x$  that had not yet reached isotopic steady state with  $\text{O}_3$ . These two mechanisms are not exclusive and could both contribute to lower  $\text{NO}_x$  and therefore nitrate,  $\Delta^{17}\text{O}$  values.

An additional piece of evidence suggests that the  $\text{NO}_x$  plumes themselves, rather than ambient conditions, are the source of low- $\Delta^{17}\text{O}$  nitrates in these samples. There is a strong correlation between the total nitrate  $\Delta^{17}\text{O}$  values and the maturity of the plume as expressed by the  $\text{NO}_2$  concentration divided by sum of  $\text{HNO}_3$  and p- $\text{NO}_3^-$  concentrations (Fig. 5). This observation is consistent with the unequilibrated  $\text{NO}_2$  hypothesis. However, it does not rule out the possible contribution of  $\text{RO}_2$ , since VOC releases from the  $\text{NO}_x$  sources could lead to elevated  $\text{RO}_2$  concentrations in the plume.

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#### 4.2 Causes of shifts in HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences

A challenging question is why do the HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences shift seasonally (Fig. 3)? One factor that may influence the relationship between HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> is mass-dependent isotopic equilibrium between NH<sub>4</sub>NO<sub>3</sub> and HNO<sub>3</sub> (R10); however, this mechanism would result in higher δ<sup>18</sup>O in p-NO<sub>3</sub><sup>-</sup> and unchanged Δ<sup>17</sup>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<sub>2</sub>O<sub>5</sub> pathway is likely to produce more p-NO<sub>3</sub><sup>-</sup> than HNO<sub>3</sub>(g), which would result in a higher contribution from ozone and explain why δ<sup>18</sup>O and Δ<sup>17</sup>O values are both higher in p-NO<sub>3</sub><sup>-</sup>. A previous study addressing why p-NO<sub>3</sub><sup>-</sup> 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 δ<sup>18</sup>O and Δ<sup>17</sup>O values were lower in p-NO<sub>3</sub><sup>-</sup> than in HNO<sub>3</sub> (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<sub>3</sub> dry deposits to surfaces more rapidly than p-NO<sub>3</sub><sup>-</sup> (Zhang et al., 2009; Benedict et al., 2013), which would create the discussed isotopic shifts in the situation where NO<sub>2</sub> has low Δ<sup>17</sup>O values in a fresh plume.

The first nitrates formed in the plume shortly after emission from the NO<sub>x</sub> source have low δ<sup>18</sup>O and Δ<sup>17</sup>O values, either because NO<sub>x</sub> has not yet reached isotopic steady state with O<sub>3</sub> or because it reacted with <sup>17</sup>O-poor RO<sub>2</sub> present in the plume due to VOC emissions. Those nitrates that form as p-NO<sub>3</sub><sup>-</sup> or that partition to p-NO<sub>3</sub><sup>-</sup> remain in the plume for longer than HNO<sub>3</sub>, which is removed from the plume rapidly upon contact with vegetation or other surfaces. As the plume travels, the NO<sub>x</sub> becomes more enriched, and the newly formed nitrates take on higher δ<sup>18</sup>O and Δ<sup>17</sup>O values. However, p-NO<sub>3</sub><sup>-</sup> collected further downwind will derive from a mixture of low-δ<sup>18</sup>O and -Δ<sup>17</sup>O p-NO<sub>3</sub><sup>-</sup> formed earlier, plus high-δ<sup>18</sup>O and -Δ<sup>17</sup>O p-NO<sub>3</sub><sup>-</sup> formed more recently, while HNO<sub>3</sub> will have a larger proportion formed more recently and will therefore have higher δ<sup>18</sup>O and Δ<sup>17</sup>O values. The fact that we find the lowest isotopic values in summer p-NO<sub>3</sub><sup>-</sup> 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<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences between cold and warm sampling periods – differential N<sub>2</sub>O<sub>5</sub> contribution resulting in higher Δ<sup>17</sup>O values in p-NO<sub>3</sub><sup>-</sup> than in HNO<sub>3</sub>, and differential deposition resulting in lower Δ<sup>17</sup>O values in p-NO<sub>3</sub><sup>-</sup> – would essentially compete against each other, with local conditions and chemistry influencing the results. In winter, when the N<sub>2</sub>O<sub>5</sub> pathway is most important, the first mechanism dominates, as supported by the observation that p-NO<sub>3</sub><sup>-</sup> concentrations are higher during that season (trend *i*). Conversely, in summer, when the N<sub>2</sub>O<sub>5</sub> 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 δ<sup>18</sup>O differences.

For instance, kinetic fractionation may be involved in the production of trend *iii*.

In summary, examining the isotopic relationship of HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> (Fig. 3), reveals the complexity of anthropogenic NO<sub>x</sub> oxidation mechanisms. The lower p-NO<sub>3</sub><sup>-</sup> isotopic values relative to the HNO<sub>3</sub> values during warm months may reflect differential removal rates from plumes containing NO<sub>2</sub> temporarily low in <sup>17</sup>O.

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Supprimé: between p-NO<sub>3</sub><sup>-</sup> an

Supprimé: d HNO<sub>3</sub>

#### 5 4.3 - Low δ<sup>18</sup>O and Δ<sup>17</sup>O trends in global w- and p-NO<sub>3</sub><sup>-</sup> - 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<sub>x</sub> 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<sub>3</sub> and oxidation through the well-known OH and N<sub>2</sub>O<sub>5</sub> oxidation paths. However, NO<sub>2</sub> not in isotopic equilibrium with O<sub>3</sub>, and/or NO reacted with RO<sub>2</sub> 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<sub>2</sub> and/or HO<sub>2</sub> 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?

15 The full Δ<sup>17</sup>O and δ<sup>18</sup>O ranges for p-NO<sub>3</sub><sup>-</sup>, w-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (between 13.8 and 20.5 ‰, 48.4 and 83.2 ‰; Table 4) compare well with the isotopic ranges obtained for bulk deposition NO<sub>3</sub><sup>-</sup> 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  
20 (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 δ<sup>18</sup>O and Δ<sup>17</sup>O values.

Previous work in the Athabasca region reported very low δ<sup>18</sup>O and near-zero Δ<sup>17</sup>O values for p-NO<sub>3</sub><sup>-</sup> 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<sub>2</sub>. Similar isotopic signatures are very likely produced in source emissions of NO<sub>x</sub> in the studied Edmonton and Vauxhall areas (e.g., CFPP, gas compressors, industries). This source signature may persist into p-NO<sub>3</sub><sup>-</sup> collected close to the sources. Within the first few hours in the atmosphere (less, in polluted areas), the NO<sub>x</sub> δ<sup>18</sup>O and Δ<sup>17</sup>O values rapidly increase due to isotope exchange with O<sub>3</sub> (R2, R3, R5 and O<sub>3</sub> formation, Table 5; Michalski et al., 2014) and reach isotopic equilibrium. Though the e-folding lifetime for NO<sub>x</sub> oxidation to nitrates may be longer than these few hours,  
30 depending on the NO<sub>x</sub>/VOC ratio, only a fraction of the oxidized source NO<sub>x</sub> 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 Δ<sup>17</sup>O values within 12 km of the emission sites, and where direct stack emissions of p-NO<sub>3</sub><sup>-</sup> were ~5000 times lower than NO<sub>x</sub> emissions (Wang et al., 2012).

35 In a methodological test study, we obtained low values for w-NO<sub>3</sub><sup>-</sup> sampled near a high traffic volume highway in Ontario, Canada (Smirnov et al., 2012). Low δ<sup>18</sup>O and Δ<sup>17</sup>O values in atmospheric nitrates during warm months (65 and 20 ‰ or less,

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  $\delta^{18}\text{O}$  values in w- $\text{NO}_3^-$  from a polluted city (Fang et al., 2011), in p- $\text{NO}_3^-$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values in summer nitrates may reflect the involvement of air masses that include nitrates from oxidation of  $\text{NO}_2$  with light isotopes in plumes. In such cases, while not ruling out a higher contribution from  $\text{RO}_2$  oxidation of  $\text{NO}$ , it is also possible that significant portions of the collected nitrate were formed before the  $\text{NO}_x\text{-O}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  may reflect relative proximity to anthropogenic N emitters in general. Further research work on plume  $\text{NO}_x$  to nitrates chemical mechanisms may help to validate this suggestion. In the future, the assumption of  $\text{NO}_x$  isotopic steady state with  $\text{O}_3$  should be explored, given recent findings (Michalski et al., 2014), the critical importance of  $\text{NO}_x$  isotope characteristics on resulting nitrate isotopic values (Alexander et al., 2009), and the suggestion regarding the evolution of  $\text{NO}_x\text{-NO}_3^-$  signals in fresh anthropogenic plumes (present study).

## 5 Conclusion

The  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  from anthropogenic sources in central and southern Alberta, simultaneously collected with wind sector-based conditional sampling systems produced  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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 ( $\text{HNO}_3$ ) 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- $\text{NO}_3^-$  in these samples generally shows higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than  $\text{HNO}_3$  in the fall-winter period as the heterogeneous  $\text{N}_2\text{O}_5$  pathway favours the production of p- $\text{NO}_3^-$ . In contrast,  $\text{HNO}_3$  has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during warm periods, which we propose is due to faster dry deposition rates relative to p- $\text{NO}_3^-$  in the event that low- $\Delta^{17}\text{O}$   $\text{NO}_2$  is oxidized in the plume. The mechanisms conferring nitrate with relatively low isotopic values, whether oxidation before  $\text{NO}_x\text{-O}_3$  equilibrium is reached or higher contributions from  $\text{RO}_2$ , 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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values may reflect nitrates produced from undifferentiated anthropogenic  $\text{NO}_x$  emissions.

Future research should explore the assumption of NO<sub>x</sub> isotopic equilibration with O<sub>3</sub>, given the critical importance of NO<sub>x</sub> 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<sub>x</sub> 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.

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**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 <sub>x</sub> sources; fertilizer plant largest NH <sub>3</sub> 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 <sub>3</sub> and NO <sub>x</sub> source, oil refinery major NO <sub>x</sub> source

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

5 **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)	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$
<i>Teflon filters</i> p-NO <sub>3</sub> <sup>-</sup> (19)	2	1
<i>Nylon filters</i> HNO <sub>3</sub> (18)	1	0.7

10

**Table 3. Average oxygen isotopic ratios (‰) for NO<sub>3</sub><sup>-</sup> sampled as gas (HNO<sub>3</sub>), w (precipitation) and p (particulate matter) relative to VSMOW.**

Matrix Source	Gas			w			p		
	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$
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)	- (3)	63.1 (3)	24.5 (2)	- (3)	26.4 (3)			
City traffic	65.7 (3)	67.2 (2)	59.6 (3)	21.2 (3)	24.4 (2)	22.5 (3)			
<b>Mean</b>	<b>66.8</b>	<b>66.0</b>	<b>62.6</b>	<b>23.0</b>	<b>24.3</b>	<b>23.4</b>			

(n): number of sampling periods characterized

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

$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	Regional context	Location	Authors
<b>HNO<sub>3</sub></b>				
62.4-81.7	19.3-29.0	Various contaminated sites	Alberta, Canada	<i>This study</i>
<b>p-NO<sub>3</sub><sup>-</sup></b>				
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	<i>This study</i>
<b>w-NO<sub>3</sub><sup>-</sup></b>				
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	Smirnov 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	<i>This study</i>
<b>Undifferentiated and Bulk NO<sub>3</sub><sup>-</sup></b>				
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	<i>This study</i>

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<sub>3</sub> and p-NO<sub>3</sub> isotopic results.

5

**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) $\text{O}_2 + \text{Q} \rightarrow \text{O} + \text{O} + \text{Q}$ ; $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$ ; $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	
(R2) $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3$ ; $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	
(R3) $\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO}$	
	(R4) $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$
(R5) $\text{NO}_2 + h\nu$ (sunlight) $\rightarrow \text{NO} + \text{O}$	
(R6) $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	(R7) $\text{NO}_2 + \text{NO}_3^- \rightleftharpoons \text{N}_2\text{O}_5$
	(R8) $\text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{surface}) \rightarrow 2\text{HNO}_3(\text{aq})^*$
(R9) $\text{HNO}_3(\text{g}) \rightleftharpoons \text{HNO}_3(\text{aq})^* \rightarrow \text{NO}_3^-(\text{aq})^* + \text{H}^+(\text{aq})$	
(R10) $\text{HNO}_3(\text{g}) + \text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_4\text{NO}_3(\text{s})$	
(R11) $\text{HNO}_3(\text{g}) + \text{CaCO}_3(\text{s}) \rightarrow \text{Ca}(\text{NO}_3)_2(\text{s}) + \text{HCO}_3^-$	
(R12) $\text{NO}_2 + \text{HC}(\text{CH}_3)_2\text{S} \rightarrow \text{HNO}_3 + \text{products}$	

*Q* is a stable molecule of high energy; *M* is either O<sub>2</sub> or N<sub>2</sub>; RO<sub>2</sub> stands for both HO<sub>2</sub> and alkyl peroxy. HC stand for hydrocarbons. \*This aqueous nitrate may be on a particle.

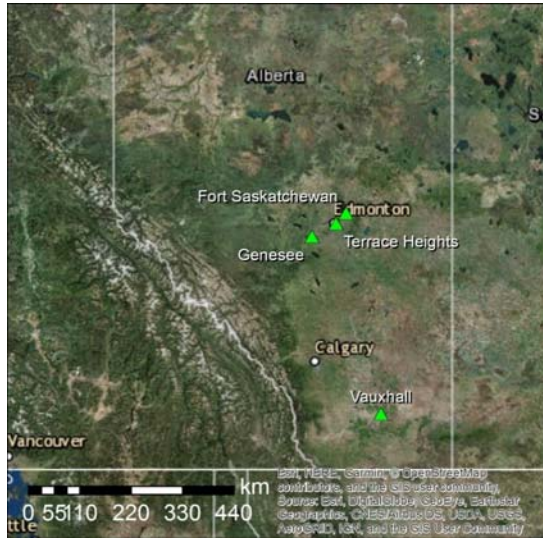
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**Table 6. Correlations of NO<sub>3</sub><sup>-</sup> isotopic results (‰) with meteorological parameters and concentration (or ratio) of co-contaminants.**

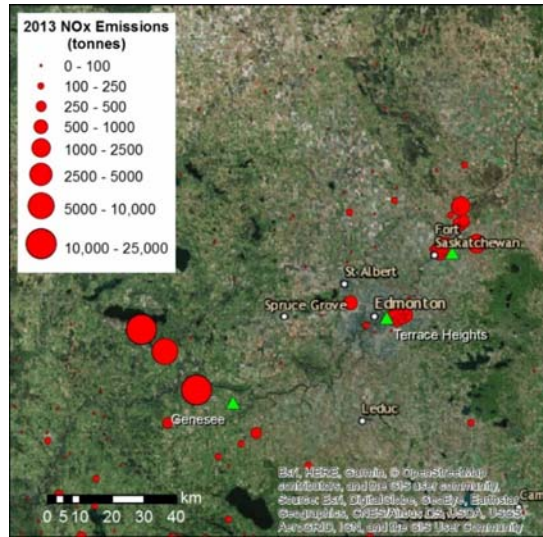
	Relative Humidity		Temperature		Daylight (fraction)		PM	SO <sub>2</sub>	O <sub>3</sub>	
	r	R <sup>2</sup>	r	R <sup>2</sup>	r	R <sup>2</sup>	r	r	r	R <sup>2</sup>
<b>HNO<sub>3</sub></b>										
δ <sup>18</sup> O	<b>0.8</b>	0.59	-0.4		-0.3		0.1	0.0	-0.29	
n	8		15		15		13	13		13
Δ <sup>17</sup> O	0.6		<b>-0.5</b>	0.24	-0.4		0.4	0.3	-0.03	
n	8		15		15		13	13		13
<b>p-NO<sub>3</sub><sup>-</sup></b>										
δ <sup>18</sup> O	<b>0.9</b>	0.79	<b>-0.6</b>	0.34	<b>-0.6</b>	0.35	0.1	0.5	<b>-0.61</b>	0.38
n	7		15		15		12	12		12
Δ <sup>17</sup> O	<b>0.9</b>	0.73	<b>-0.6</b>	0.34	<b>-0.7</b>	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

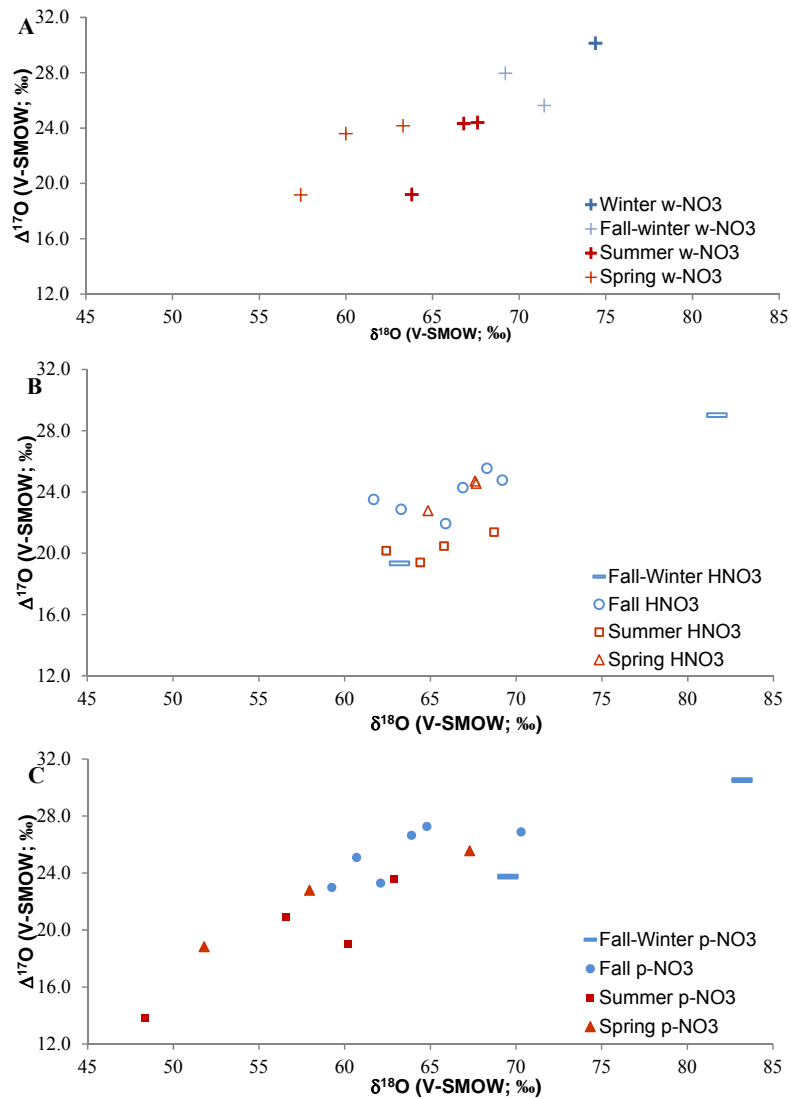
A



B



5 **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<sub>x</sub> as tonnes of NO<sub>2</sub> reported to the National Pollutant Release Inventory for 2013 (Environment and Climate Change Canada, 2018b).



5 Figure 2: Triple O isotopic results obtained for simultaneously collected atmospheric HNO<sub>3</sub> (A), w-NO<sub>3</sub><sup>-</sup> (B) and p-NO<sub>3</sub><sup>-</sup> (C), in Alberta, identified by sampling periods (cold months - blue; warm months - red).

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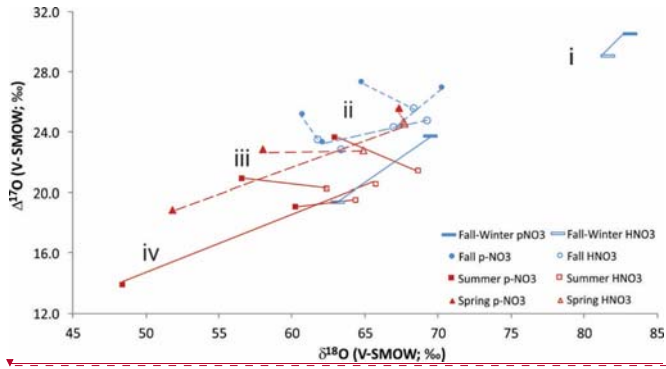
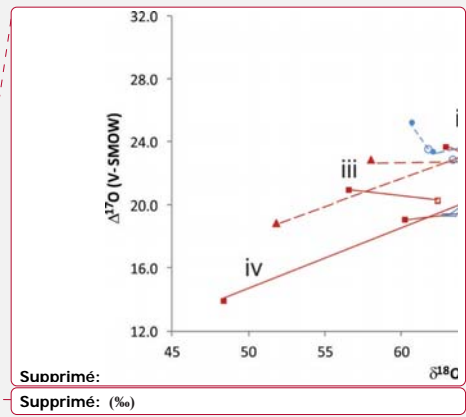


Figure 3: Line-connected  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values for simultaneously collected  $\text{HNO}_3$  (empty symbols) and  $\text{p-NO}_3^-$  (solid symbols) from cold (blue) and warm (red) sampling periods.



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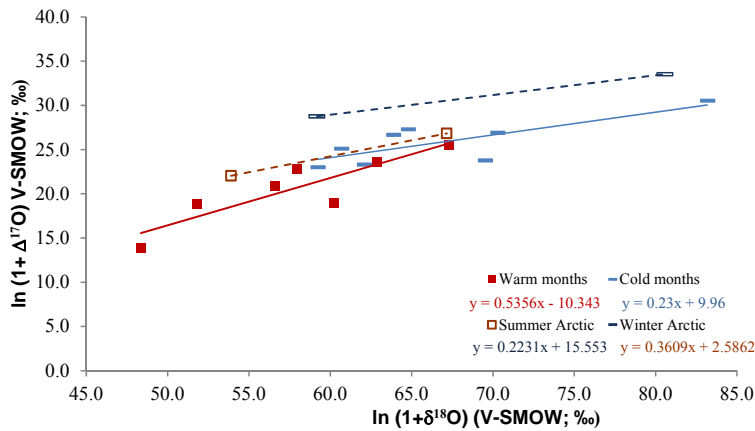


Figure 4: Isotopic results for  $\text{p-NO}_3^-$  identified by sampling periods (solid lines), compared with summer and winter trends obtained for Arctic sites (dashed lines; derived from  $\ln(1 + \delta)$  in Morin et al., 2008).

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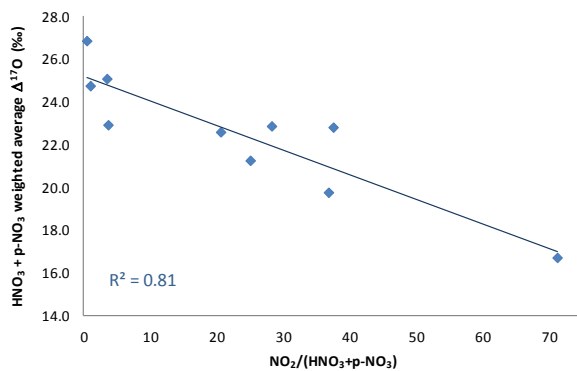
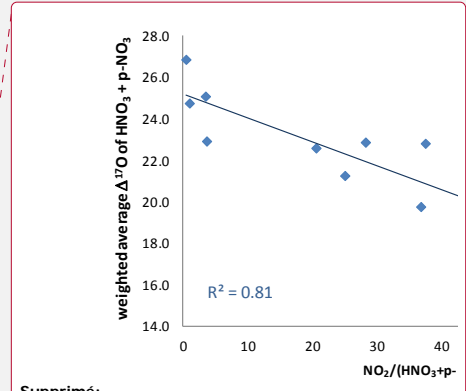


Figure 5: Weighted  $\Delta^{17}\text{O}$  average for the sum of dry nitrates as a function of  $\text{NO}_2$  concentration divided by  $\text{p-NO}_3$  plus  $\text{HNO}_3$  concentrations, a ratio indicative of the maturity of a plume.



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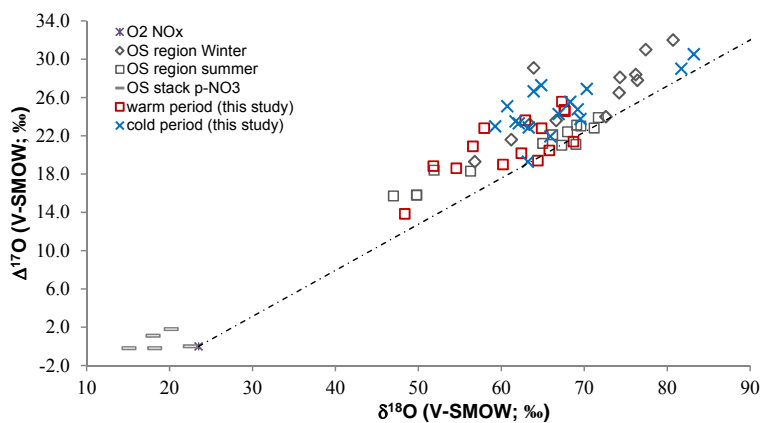


Figure 6: Isotopic ratios for atmospheric  $\text{p-NO}_3^-$ ,  $\text{w-NO}_3^-$  and  $\text{HNO}_3$  samples in cold and warm periods from central and southern Alberta (this study), compared with previously published winter and summer bulk and throughfall deposition samples from the oil sands (OS) region from northern Alberta (Proemse et al., 2013), and  $\text{p-NO}_3^-$  in-stack emissions data for an OS upgrader located in the same region (Proemse et al., 2012). The grey dotted line connects  $\text{NO}_x$  from theoretical combustion with  $\text{O}_2$  isotopic composition and at isotopic equilibrium with tropospheric  $\text{O}_3$  (Michalski et al., 2014).

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**Acp-2017-1103**

**Minor corrections suggested by Dr. Jan Kaiser (Editor)**

1) Please adhere to the International System of Units (SI), which has not always been applied in the present version of the manuscript. Please consult the SI brochure published by BIPM (http://www.bipm.org/en/publications/si-brochure/) and chapter 1 of the IUPAC Green Book (http://media.iupac.org/publications/books/gbook/IUPAC-GB3-2ndPrinting-Online-22apr2011.pdf)

Specifically, chemical symbols and units should not be mixed, i.e. it is not permissible to write "10 mg N m<sup>-3</sup>". To correct this, the chemical species must be identified by the quantity symbol (not the unit), e.g. "c(NO<sub>3</sub><sup>-</sup>-N) = 10 mg m<sup>-3</sup>", or, in the text, "10 mg m<sup>-3</sup> of NO<sub>3</sub><sup>-</sup>-N", or "10 mg m<sup>-3</sup> as N equivalents", or "a nitrate-N concentration of 10 mg m<sup>-3</sup>"

REPLY: All corrected.

This also applies to the tables in the supplementary material.

REPLY: All corrected.

2) Table 3, Figs. 2, 3, 4, 6 & Figs. SM-3 & 5: Axis labels should be  $\delta/\text{‰}$  or  $10^3 \delta (\ln(1+\delta))/\text{‰}$  in case of Fig. 4). See BIPM brochure and IUPAC Green Book for correct examples.

REPLY: The ‰ was previously indicated in the captions of all figures. We now have removed it from the captions and placed it on each axis. All corrected, including Figure 5.

1/13: Replace "ratios" with "delta values".

REPLY: DONE

3/10: Replace "/filter" with "per filter".

REPLY: CORRECTED on 4/25

6/4: The unit "ppb N-NO<sub>3</sub>/L" does not make sense. Also, please see comment 1 above and remove "N-NO<sub>3</sub>" here and from "0.03 N-NO<sub>3</sub> umol/L".

REPLY: DONE on 4/6

6/5: Please convert 0.016 µg to µmol and remove "N".

REPLY: DONE

6/25: Replace "ratios" with "values."

REPLY: DONE

6/32: Delete extraneous "/1000" divisors.

REPLY: We have corrected the equation as in Miller (2002), by adding 1000x to the two parts:  $1000 \times \ln(1+\delta^{17}\text{O}/1000) - 0.516 \times 1000 \times \ln(1+\delta^{18}\text{O}/1000)$ .

7/20: Replace "ratios" with "delta values" or "deltas".

5 REPLY: DONE

7/21 & 7/23 & 10/6 "Isotopic difference" is meaningless as a quantitative term on its own. Please rephrase so as that it is clear which delta values are meant. Also, it would be clearer to say explicitly whether particulate nitrate or HNO<sub>3</sub> have higher or lower delta values.

REPLY: DONE

10 8/13: Change to "not the highest delta values for w-NO<sub>3</sub>-".

REPLY: DONE

8/22: Subscript "x" in "NO<sub>x</sub>". "x" should be in italics.

REPLY: DONE

8/28: "NO<sub>3</sub>-".

15 REPLY: DONE

9/4: Add space between 0 and °C. .

REPLY: DONE

9/19 & R12 Table 5: "NO<sub>3</sub>" (neutral radical) .

REPLY: DONE

20 12/22: The correct unit symbol for "hour" is "h"..

REPLY: DONE

12/25: Please replace "ppb" and "ppt" with the SI units "nmol mol<sup>-1</sup>" and "pmol mol<sup>-1</sup>".

REPLY: DONE

14/2: "The negative isotopic differences between p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> ..." is unclear. Please rephrase so that it is clear which species has lower delta values.

25 REPLY: rephrased to « The lower p-NO<sub>3</sub><sup>-</sup> isotopic values relative to the HNO<sub>3</sub> values... »

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

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10 **Abstract.** There are clear motivations for better understanding the atmospheric processes that transform nitrogen (N) oxides ( $\text{NO}_x$ ) emitted from anthropogenic sources into nitrates ( $\text{NO}_3^-$ ), two of them being that  $\text{NO}_3^-$  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 delta values ( $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ ) are frequently applied to infer the chemical pathways leading to the observed mass independent isotopic anomalies from interaction with  $^{17}\text{O}$ -rich ozone ( $\text{O}_3$ ). Recent laboratory experiments suggest that the isotopic equilibrium between  $\text{NO}_2$  (the main precursor of  $\text{NO}_3^-$ ) and  $\text{O}_3$  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  $\text{NO}_3^-$  in precipitation (w- $\text{NO}_3^-$ ) and in particulate (p- $\text{NO}_3^-$ ) 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  $\text{HNO}_3$  with  $\Delta^{17}\text{O}$  values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample  $\text{HNO}_3$  and p- $\text{NO}_3^-$ , and co-collect w- $\text{NO}_3^-$ . The nitrates are from various distances (<1 to >125 km) downwind of different anthropogenic emitters, and consequently from varying time lapses after emission.

25 The separate collection of nitrates shows that the  $\text{HNO}_3$   $\delta^{18}\text{O}$  ranges are distinct from those of w- and p- $\text{NO}_3^-$ . Interestingly, the  $\Delta^{17}\text{O}$  differences between p- $\text{NO}_3^-$  and  $\text{HNO}_3$  shift from positive during cold sampling periods to negative during warm periods. The low p- $\text{NO}_3^-$   $\Delta^{17}\text{O}$  values observed during warm periods may partly derive from the involvement of  $^{17}\text{O}$ -depleted peroxy radicals ( $\text{RO}_2$ ) oxidizing  $\text{NO}$  during that season. Another possibility is that nitrates derive from  $\text{NO}_x$  that has not yet reached isotopic equilibrium with  $\text{O}_3$ . However, these mechanisms, individually or together, cannot explain the observed p- $\text{NO}_3^-$  minus  $\text{HNO}_3$  isotopic changes. We propose differences in dry depositional rates, faster for  $\text{HNO}_3$ , as a mechanism for the observed shifts. Larger proportions of p- $\text{NO}_3^-$  formed *via* the  $\text{N}_2\text{O}_5$  pathway would explain the opposite fall-winter patterns. Our results show that the separate  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  isotopic signals can be used to further our understanding of  $\text{NO}_x$  oxidation and deposition. Future research should investigate all tropospheric nitrate species as well as  $\text{NO}_x$  to refine our understanding of nitrate distribution worldwide and to develop effective emission reduction strategies.

35

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## 1 Introduction

Anthropogenic NO<sub>x</sub> (NO and NO<sub>2</sub>) emissions are oxidized to nitrate in the atmosphere in the form of gaseous, wet or particulate forms, HNO<sub>3</sub> being one of the main precursors of p-NO<sub>3</sub><sup>-</sup>. 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<sub>3</sub>, HNO<sub>3</sub> and w-NO<sub>3</sub>).

Triple oxygen isotopes ( $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ ) have been used to decipher atmospheric oxidation pathways of NO<sub>x</sub> leading to ambient nitrate. Michalski et al. (2003) performed the first measurement of  $\delta^{17}\text{O}$  values in atmospheric nitrate. The authors found nitrate highly enriched in <sup>18</sup>O and <sup>17</sup>O, likely due to the transfer of anomalous oxygen atoms from ozone (O<sub>3</sub>) via the NO<sub>x</sub>-ozone photochemical cycle and oxidation to nitrate. During its formation, O<sub>3</sub> inherits abnormally high  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values through mass independent fractionation. The specific  $\delta^{17}\text{O}$  departure from the terrestrial mass dependent fractionation line, named the <sup>17</sup>O anomaly, is often expressed as  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.517 \times \delta^{18}\text{O}$  (Thiemens, 1999). Further investigations suggested that the  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values of w-NO<sub>3</sub><sup>-</sup> and p-NO<sub>3</sub><sup>-</sup> reflect several reactions taking place after the atmospheric emission of NO<sub>x</sub>, *i.e.*, atmospheric oxidation pathways transforming NO<sub>x</sub> 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  $\delta^{18}\text{O}$  differences in w-NO<sub>3</sub><sup>-</sup> 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; Smirnov et al., 2012), transfer of the ozone <sup>17</sup>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<sub>3</sub><sup>-</sup> samples are not yet widespread. Also rare are the nitrate  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of field samples downwind from NO<sub>x</sub>-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). The few existing studies have chiefly characterized w-NO<sub>3</sub><sup>-</sup> or the sum of p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (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<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> were generally collected together (without differentiation). Therefore, no studies have separately and simultaneously collected and analyzed the HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup>  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values, and discussed these isotopic characteristics of nitrate collected downwind of anthropogenic emitters. While HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> can be in equilibrium (e.g. if p-NO<sub>3</sub><sup>-</sup> is in the form of solid NH<sub>4</sub>NO<sub>3</sub>), 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 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  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  as well as  $\text{w-NO}_3^-$  downwind of the source types. The objective of this work was to assess the atmospheric  $\text{NO}_x$  reaction pathways and determine processes responsible for the distribution of  $\text{HNO}_3$ , and  $\text{w-}$  and  $\text{p-NO}_3^-$  in a mid-latitude region.

## 2 Methodology

### 2.1 Regional context

While national reported  $\text{NO}_x$  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  $\text{PM}_{2.5}$  (particulate matter less than  $2.5 \mu\text{m}$ ) 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  $\text{NO}_x$  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 ( $\text{p-NO}_3^-$ ,  $\text{HNO}_3$  and  $\text{w-NO}_3^-$ ) 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 ( $5.6^\circ\text{C}$ ) and total annual precipitation lower (320 mm) than in central Alberta ( $3.9^\circ\text{C}$ ; 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

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<sub>x</sub> 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<sub>3</sub>) 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<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub> on the Teflon filter, <3% breakthrough of HNO<sub>3</sub> from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> of approximately 0.2 µg N<sub>per</sub> 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<sub>3</sub><sup>-</sup> and positive bias in HNO<sub>3</sub> 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<sub>3</sub> between filter packs and denuder and/or TDLAS systems (Anlauf et al., 1986; Sickles Li 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<sub>2</sub> (nitrous acid) on the nylon filter in two samples (Sickles Li et al., 1999). Based on the conditions in Alberta, we estimate that there is little or no volatilization of NH<sub>4</sub>NO<sub>3</sub> 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.

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After the first five sample periods, an experimental active sampling system for NO<sub>2</sub> and NO<sub>x</sub> 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<sub>2</sub>, and one- or two-stage filter pack containing two identical Maxxam Analytics' impregnated filters designed to collect NO<sub>x</sub> (mostly NO due to upstream collection of NO<sub>2</sub>). Oxygen isotopes in NO<sub>2</sub> and NO<sub>x</sub> 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](#).

Here we report on oxygen isotopes in the simultaneously sampled HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup>, along with co-sampled w-NO<sub>3</sub><sup>-</sup> 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.

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.

### 2.3 Analytical procedures

Nitric acid from nylon filters were extracted using 10 mL of 0.01M solution of NaCl. Particulate-NO<sub>3</sub> 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 (0.03  $\mu\text{mol/L}$  of  $\text{NO}_3^-$ -N). Nitrite concentrations were also measured in the extracts. Nitrite concentrations above the detection limit (1.14  $\mu\text{mol/L}$  of  $\text{NO}_2^-$ -N) were found in a handful of samples at Terrace Heights. These samples were excluded from the reported data.

We characterized the  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  ratios of  $\text{HNO}_3$ , w- $\text{NO}_3^-$ , and p- $\text{NO}_3^-$ , along with the  $\delta^{15}\text{N}$  values of  $\text{NH}_3$ , w- $\text{NH}_4$ , p- $\text{NH}_4$  and  $\text{NO}_x$  (all N isotopic results are in Savard et al., 2017). The present article deals solely with the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values obtained for the three nitrate species. We treated the samples using the chemical conversion and thermal decomposition of  $\text{N}_2\text{O}$  protocols, providing the ability to simultaneously analyze low-concentration N- and O-containing species (Smirnov 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  $\mu\text{mol/L}$  of  $\text{NO}_3^-$ -N). Therefore, not all samples could be diluted to produce volumes sufficient for reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  and subsequent conversion to  $\text{N}_2\text{O}$ , the final product before isotope analysis. Samples with an initial concentration below 2.3  $\mu\text{mol/L}$  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 ( $\text{NO}_2^-$ ) using a custom-made cadmium column. The final preparation step involved using sodium azide to ultimately produce  $\text{N}_2\text{O}$  (McIlvin and Altabet, 2005; Smirnov et al., 2012). All extracted  $\text{N}_2\text{O}$  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; Smirnov et al., 2012). The utilized approach allows the spectrum of  $\delta^{15}\text{N}$ ,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values 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  $\text{N}_2\text{O}$ . The laboratory analytical precision (average of replicates) determined during the present study was 0.6 ‰ for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values in gaseous (n=12) and solid nitrates (n=20). For w- $\text{NO}_3^-$ , analytical replicates gave 0.6 and 0.5 ‰, for  $\delta^{18}\text{O}$  (n=3) and  $\delta^{17}\text{O}$  (n=4) values, respectively. The  $\Delta^{17}\text{O}$  values are defined as  $1000 \times \ln \left( \frac{1+\delta^{17}\text{O}/1000}{1+\delta^{18}\text{O}/1000} \right) - 0.516 \times 1000 \times \ln \left( \frac{1+\delta^{18}\text{O}/1000}{1+\delta^{18}\text{O}/1000} \right)$ , relative to Vienna Standard Mean Ocean Water (VSMOW).

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### 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  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\text{NH}_4\text{NO}_3$  on the particle filter into  $\text{HNO}_3$  and  $\text{NH}_3$ , 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  $\text{p-NO}_3^-$  isotopic values ( $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) to be generally higher during winter than during summer (see Section 3.4). Moreover, the  $\text{p-NO}_3^-$   $\delta^{18}\text{O}$  minus  $\text{HNO}_3$   $\delta^{18}\text{O}$  differences are negative during summer (see Section 3.6), 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  $\delta^{15}\text{N}$  values in  $\text{NH}_3$  and  $\text{NH}_4$ ; 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  $^{17}\text{O}$  anomaly; therefore,  $\Delta^{17}\text{O}$  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  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  (Elliott et al., 2009).

#### 3.2 Concentrations and isotopic ratios of nitrates in Alberta samples

The range of  $\text{HNO}_3\text{-N}$  concentrations measured by the filters (from 0.01 to 0.15  $\mu\text{g}/\text{m}^3$ ; average of 0.06) are slightly lower than those of  $\text{p-NO}_3^-\text{-N}$  (from 0.02 to 0.35  $\mu\text{g}/\text{m}^3$ ; 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  $\mu\text{g}/\text{m}^3$  for  $\text{HNO}_3\text{-N}$  and from 0.007 to 0.45  $\mu\text{g}/\text{m}^3$  for  $\text{p-NO}_3^-\text{-N}$  (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

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northern Alberta border revealed similar average concentrations of 0.02  $\mu\text{g}/\text{m}^3$  of  $\text{NO}_3^-$ -N for both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  (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  $\text{NO}_3^-$ -N concentrations of the  $\text{w-NO}_3^-$  samples was 0.15 – 0.48  $\text{mg}/\text{L}$ . 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  $\text{mg}/\text{L}$  of  $\text{NO}_3^-$ -N, while at the most polluted site in southern Ontario (Longwoods) the volume-weighted mean concentration was approximately 0.3  $\text{mg}/\text{L}$  (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.

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The average  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of  $\text{HNO}_3$  (gas),  $\text{w-}$  and  $\text{p-NO}_3^-$  show no apparent systematic ordering (Table 3; Tables SM-1 and 2), in contrast to what was found for  $\delta^{15}\text{N}$  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  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  have the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages, but not the highest delta values for  $\text{w-NO}_3^-$  values; chemical industries show the lowest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages for  $\text{w-}$  and  $\text{p-NO}_3^-$ , but not for  $\text{HNO}_3$ . Though the number of samples were limited,  $\text{w-NO}_3^-$   $\Delta^{17}\text{O}$  values were roughly correlated with the weighted average  $\Delta^{17}\text{O}$  values of  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  in samples covering the same time periods, consistent with scavenging of both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  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).

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Considering all nitrate species, the Alberta  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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  $\text{NO}_x$  cycling and oxidation (nitrate derived through combustion in  $\text{O}_2$  would show  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of 23.5 and 0 ‰, respectively). When examining the existing  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data for  $\text{w-}$  and  $\text{p-NO}_3^-$  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  $\delta^{18}\text{O}$  range of atmospheric  $\text{NO}_3^-$  previously suggested to be between 60 and 95 ‰ (Hastings et al., 2003; Kendall et al., 2007).

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Previous studies that report triple isotope oxygen results in atmospheric  $\text{NO}_3^-$  samples are scarce (Table 4). The  $\text{HNO}_3$  range documented here is within the broad spectrum of  $\text{p-NO}_3^-$  values compiled for remote to contaminated sites. Elliott et al. (2009) reported  $\text{HNO}_3$  oxygen results for  $\delta^{18}\text{O}$  values only, with a range of +51.6 to +94.0 ‰ (mean of 77.4), with simultaneously-sampled  $\text{p-NO}_3^-$   $\delta^{18}\text{O}$  values between +45.2 and +92.7 ‰ (mean of 75.2). Those ranges are broader than the  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  values obtained in the present study.

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

The  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  ranges for  $\text{HNO}_3$  identified by sampling period are narrower than those of the simultaneously collected  $\text{p-NO}_3^-$  (Fig. 2; Table SM-1), suggesting that there are additional mechanisms affecting  $\text{HNO}_3$ , or that  $\text{p-NO}_3^-$  is derived from

different pathways with more variation in isotopic signatures. Overall, the  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  results for  $\text{HNO}_3$ ,  $\text{w-NO}_3^-$  and  $\text{p-NO}_3^-$  clearly show higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during cold periods relative to warm periods (Fig. 2), with the exception of  $\text{HNO}_3$   $\delta^{18}\text{O}$  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  $0^\circ\text{C}$  (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- $\text{NO}_3^-$ .

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,  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) is produced through reactions of air  $\text{N}_2$  with atmospheric  $\text{O}_2$  at high temperatures (reactions R1; Table 5). Then,  $\text{NO}_x$  cycles between  $\text{NO}$  and  $\text{NO}_2$  through a series of reactions involving sunlight (R5),  $\text{O}_3$  (R2, R4), and peroxy ( $\text{HO}_2$ ) or alkyl peroxy ( $\text{RO}_2$ ) radicals (R3; Morin et al., 2007; Fang et al., 2011; Michalski et al., 2014; here we use  $\text{RO}_2$  to refer collectively to  $\text{HO}_2$  and  $\text{RO}_2$ ).

The oxidation of  $\text{NO}_x$  (specifically  $\text{NO}_2$ ) to  $\text{HNO}_3$  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,  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  (R8),  $\text{HNO}_3$  is likely to be retained on the reaction particle as p- $\text{NO}_3^-$  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  $\text{NO}_x$  with hydrocarbons (R12) since they are predicted to have a minimal contribution to nitrate formation in this region (Alexander et al., 2009). Finally,  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of w- and p- $\text{NO}_3^-$  formed during summer are lower than those during winter due to higher contribution from the  $\text{N}_2\text{O}_5$  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- $\text{NO}_3^-$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data presented here follow the same patterns for warm and cold months (Fig. 2). In contrast, the less commonly studied  $\text{HNO}_3$  shows similar  $\delta^{18}\text{O}$  values during warm and cold seasons, but summer  $\Delta^{17}\text{O}$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  samples (n of w- $\text{NO}_3^-$  too low) with meteorological and air quality parameters measured routinely at nearby monitoring stations where available (Table SM-3). We found that the p- $\text{NO}_3^-$  and  $\text{HNO}_3$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values correlate with RH, with p- $\text{NO}_3^-$  values showing stronger statistical links than  $\text{HNO}_3$  (Table 6). The  $\text{N}_2\text{O}_5$  hydrolysis reaction (R8) rate increases with humidity (Kane et al., 2001), which may explain this positive correlation. Significant inverse

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relationships exist between temperature and  $p\text{-NO}_3^- \delta^{18}\text{O}$ ,  $p\text{-NO}_3^- \Delta^{17}\text{O}$ , and  $\text{HNO}_3 \Delta^{17}\text{O}$ . These negative links likely arise since  $\text{N}_2\text{O}_5$  is more stable under cold conditions, leading to a higher contribution of R8. The stronger links with  $p\text{-NO}_3^-$  may be due to R8 taking place on surfaces (such as particles) with liquid water, which is likely to retain the  $\text{HNO}_3$  as  $p\text{-NO}_3^-$  rather than release it to the gas phase. Therefore, in winter, R8 may contribute more to  $p\text{-NO}_3^-$  than to  $\text{HNO}_3(\text{g})$ . Moreover, the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values for both  $p\text{-NO}_3^-$  and  $\text{HNO}_3$  were found for fall-winter samples collected at high RH (76 %) and low temperature ( $-10^\circ\text{C}$ ). In contrast, the lowest  $p\text{-NO}_3^-$  isotopic values were found for samples with similar proportions of  $\text{HNO}_3$  and  $p\text{-NO}_3^-$ , and sampled during moderately humid (60-63 %) and warm ( $8\text{-}20^\circ\text{C}$ ) periods. The accompanying shift in  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  differences between  $p\text{-NO}_3^-$  and  $\text{HNO}_3$ , will help infer the mechanisms dominating during the cold and warm periods (Section 4.2).

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Concentrations of oxidants, co-contaminants (e.g.,  $\text{SO}_4^-$  aerosols) and  $\text{NO}_x$  influence the dominance and rates of the discussed reactions (Brown et al., 2006; Michalski et al., 2014). However, while temperature, RH and  $\text{O}_3$  are well captured within a 5 km radius, other pollutant measurements like continuous  $\text{SO}_2$ ,  $\text{PM}_{2.5}$  and  $\text{NO}_x$  can have large gradients near sources, therefore it is not surprising that no correlations were found with  $\text{SO}_2$  or  $\text{PM}_{2.5}$  measured at sites 4-5 km away (Table 6). Surprisingly, only the  $p\text{-NO}_3^- \Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values.

### 3.5 Comparison with high-latitude $p\text{-NO}_3^-$

An interesting aspect of the Alberta  $p\text{-NO}_3^-$  cold-period  $\Delta^{17}\text{O}$  ranges is that they compare relatively well with the range obtained for the Canadian Arctic (Fig. 4), during winter, when nighttime conditions and the  $\text{N}_2\text{O}_5$  pathway prevail without interruption (Morin et al., 2008; for comparison with  $\text{HNO}_3$  values see Fig. SM-4). This observation supports the suggestion that the  $\text{N}_2\text{O}_5$  pathway produces around 90 % of nitrates during mid-latitude cold months (Michalski et al., 2003; Section 4.1). The  $\delta^{18}\text{O}$  ranges of cold months are similar in Alberta and in the Arctic. This similarity goes against previous suggestions that at higher latitudes, nitrate  $\delta^{18}\text{O}$  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  $\text{N}_2\text{O}_5$  pathway during the Arctic winter (Fang et al., 2011).

The  $\Delta^{17}\text{O}$  departure between the Alberta and Arctic winter parallel lines is about 3 ‰. Such difference is slightly larger than the one calculated for winter  $\text{NO}_3^-$  at 80 and  $40^\circ\text{N}$  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  $\Delta^{17}\text{O}$  values is similar at the mid- and high-latitude 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  $\Delta^{17}\text{O}$  values of  $\text{NO}_x$  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<sub>2</sub>O<sub>5</sub> pathways during summer and winter, respectively. Finally, the  $\Delta^{17}\text{O}$  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<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup>

5 As far as the isotopic characteristics are concerned, an important feature to keep in mind is that the HNO<sub>3</sub> of central and southern Alberta has distinct properties relative to simultaneously sampled p-NO<sub>3</sub><sup>-</sup>. In practical terms, the relationships between the simultaneously sampled HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> are of four types (Fig. 3): (i) HNO<sub>3</sub>  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  are both lower than p-NO<sub>3</sub><sup>-</sup>; (ii) HNO<sub>3</sub> has lower  $\Delta^{17}\text{O}$  but higher  $\delta^{18}\text{O}$  values than p-NO<sub>3</sub><sup>-</sup>; (iii) HNO<sub>3</sub> has higher  $\delta^{18}\text{O}$  values and similar  $\Delta^{17}\text{O}$  ones relative to p-NO<sub>3</sub><sup>-</sup>; and (iv) HNO<sub>3</sub> has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than p-NO<sub>3</sub><sup>-</sup> (Fig. 3).

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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<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> in northeastern USA with similar seasonal changes of  $\delta^{18}\text{O}$  differences (no  $\Delta^{17}\text{O}$  measurement). The HNO<sub>3</sub>  $\delta^{18}\text{O}$  were generally similar or lower than the p-NO<sub>3</sub><sup>-</sup> values during winter and fall, and slightly to much higher during spring and summer, with the spring and autumn p-NO<sub>3</sub><sup>-</sup>-HNO<sub>3</sub> relationships being roughly intermediate between the winter and summer ones. The average  $\delta^{18}\text{O}$  difference of p-NO<sub>3</sub><sup>-</sup> minus HNO<sub>3</sub> reported between winter and summer (15 ‰) by Elliott et al. (2009) agrees with the difference for fall-winter and summer obtained here (12 ‰).

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The marked shifts in isotopic differences between the separately analyzed HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> 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<sub>x</sub> source.

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## 25 4 Discussion

### 4.1 Estimation of $\Delta^{17}\text{O}$ values of NO<sub>x</sub> precursor to the studied nitrates- Highlighting oxidation mechanisms

In the present sub-section, we estimate the  $\Delta^{17}\text{O}$  values of NO<sub>2</sub> 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<sub>2</sub>O<sub>5</sub> due to interaction with O<sub>3</sub> (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<sub>2</sub>O (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<sub>2</sub>, 1/6 from O<sub>3</sub> and 1/6 from H<sub>2</sub>O, while the second produces nitrates via R6 with 2 out of 3 O atoms coming from NO<sub>2</sub> and 1/3 from OH (e.g., Michalski et al., 2003). Using these proportions with the Alberta  $\Delta^{17}\text{O}$  values of p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> in weighted averages allows us to make a rough estimation of the maximum and minimum  $\Delta^{17}\text{O}$  values of NO<sub>2</sub> oxidized to nitrates in the air masses sampled. The calculations assume the O from O<sub>3</sub> contributes a signal of ~39 ‰ as

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was recently measured (Vicars et al., 2014) and that  $\Delta^{17}\text{O}$  of OH and  $\text{H}_2\text{O}$  are zero. The estimated  $\text{NO}_2$   $\Delta^{17}\text{O}$  values for fall-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  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  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  $\text{NO}_2$   $\Delta^{17}\text{O}$  ranges indicate that the potential parent  $\text{NO}_2$  had a smaller  $^{17}\text{O}$  anomaly than  $\text{O}_3$  (39 ‰; Vicars and Savarino, 2014) or  $\text{NO}_2$  in isotopic equilibrium with  $\text{O}_3$  alone (45 ‰; Michalski et al., 2014) in all possible scenarios.

Two mechanisms could be responsible for the  $\Delta^{17}\text{O}$  differences between these estimates and  $\text{NO}_2$  in isotopic equilibrium with  $\text{O}_3$ . One is the competition of R3 with R2 in oxidizing NO to  $\text{NO}_2$ , since  $\text{RO}_2$  will decrease the  $\Delta^{17}\text{O}$  values relative to an ozone-only equilibrium. The relative reaction rates of R2 and R3 have previously been presumed to control the  $\text{NO}_2$  isotopic composition (e.g., Alexander et al., 2009) based on the assumption of isotopic steady state. A larger contribution of  $\text{RO}_2$  is expected in the  $\text{NO}_2$  precursors for summer relative to winter, since biogenic VOCs that are major sources of  $\text{RO}_2$  radicals are much higher in the summer (e.g., Fuentes and Wang, 1999). This suggestion is consistent with the lower  $\Delta^{17}\text{O}$  ranges in summer reported here. A second possibility is that the nitrates were formed from some  $\text{NO}_x$  that did not reach isotopic steady state with  $\text{O}_3$ , retaining some of its original signature (assumed to be  $\Delta^{17}\text{O}=0$  ‰). Most studies have assumed that isotopic steady state is established between  $\text{O}_3$  and  $\text{NO}_2$  within a few minutes after emission of  $\text{NO}_x$  from a combustion source – or at least, that nitrate formation is negligible before  $\text{NO}_x$  isotopic equilibrium is reached. However, recent modeling by Michalski et al. (2014) suggests that isotopic equilibration of  $\text{NO}_x$  with  $\text{O}_3$  could take several minutes up to a few hours at the relatively low  $\text{O}_3$  concentrations in rural Alberta. At the measured average wind speeds on site of 8-19  $\text{km h}^{-1}$ , transit times from the nearest sources to observation sites are estimated to be 9-55 minutes. While the fraction of  $\text{NO}_x$  converted to nitrate in this transit time may be small, these are large sources of  $\text{NO}_x$  in an area with very low background nitrates. For example, a plume containing 10  $\mu\text{mol mol}^{-1}$  of  $\text{NO}_2$  mixing with background air with 0.1  $\mu\text{mol mol}^{-1}$  of OH (Howell et al., 2014) would produce  $\text{HNO}_3$  via R6 at a rate of 0.011  $\mu\text{g m}^{-3} \text{min}^{-1}$  of  $\text{NO}_3\text{-N}$  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  $\text{O}_3$  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  $\text{NO}_x$  that had not yet reached isotopic steady state with  $\text{O}_3$ . These two mechanisms are not exclusive and could both contribute to lower  $\text{NO}_x$  and therefore nitrate,  $\Delta^{17}\text{O}$  values.

An additional piece of evidence suggests that the  $\text{NO}_x$  plumes themselves, rather than ambient conditions, are the source of low- $\Delta^{17}\text{O}$  nitrates in these samples. There is a strong correlation between the total nitrate  $\Delta^{17}\text{O}$  values and the maturity of the plume as expressed by the  $\text{NO}_2$  concentration divided by sum of  $\text{HNO}_3$  and p- $\text{NO}_3^-$  concentrations (Fig. 5). This observation is consistent with the unequilibrated  $\text{NO}_2$  hypothesis. However, it does not rule out the possible contribution of  $\text{RO}_2$ , since VOC releases from the  $\text{NO}_x$  sources could lead to elevated  $\text{RO}_2$  concentrations in the plume.

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#### 4.2 Causes of shifts in HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences

A challenging question is why do the HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences shift seasonally (Fig. 3)? One factor that may influence the relationship between HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> is mass-dependent isotopic equilibrium between NH<sub>4</sub>NO<sub>3</sub> and HNO<sub>3</sub> (R10); however, this mechanism would result in higher δ<sup>18</sup>O in p-NO<sub>3</sub><sup>-</sup> and unchanged Δ<sup>17</sup>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<sub>2</sub>O<sub>5</sub> pathway is likely to produce more p-NO<sub>3</sub><sup>-</sup> than HNO<sub>3</sub>(g), which would result in a higher contribution from ozone and explain why δ<sup>18</sup>O and Δ<sup>17</sup>O values are both higher in p-NO<sub>3</sub><sup>-</sup>. A previous study addressing why p-NO<sub>3</sub><sup>-</sup> 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 δ<sup>18</sup>O and Δ<sup>17</sup>O values were lower in p-NO<sub>3</sub><sup>-</sup> than in HNO<sub>3</sub> (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<sub>3</sub> dry deposits to surfaces more rapidly than p-NO<sub>3</sub><sup>-</sup> (Zhang et al., 2009; Benedict et al., 2013), which would create the discussed isotopic shifts in the situation where NO<sub>2</sub> has low Δ<sup>17</sup>O values in a fresh plume.

The first nitrates formed in the plume shortly after emission from the NO<sub>x</sub> source have low δ<sup>18</sup>O and Δ<sup>17</sup>O values, either because NO<sub>x</sub> has not yet reached isotopic steady state with O<sub>3</sub> or because it reacted with <sup>17</sup>O-poor RO<sub>2</sub> present in the plume due to VOC emissions. Those nitrates that form as p-NO<sub>3</sub><sup>-</sup> or that partition to p-NO<sub>3</sub><sup>-</sup> remain in the plume for longer than HNO<sub>3</sub>, which is removed from the plume rapidly upon contact with vegetation or other surfaces. As the plume travels, the NO<sub>x</sub> becomes more enriched, and the newly formed nitrates take on higher δ<sup>18</sup>O and Δ<sup>17</sup>O values. However, p-NO<sub>3</sub><sup>-</sup> collected further downwind will derive from a mixture of low-δ<sup>18</sup>O and -Δ<sup>17</sup>O p-NO<sub>3</sub><sup>-</sup> formed earlier, plus high-δ<sup>18</sup>O and -Δ<sup>17</sup>O p-NO<sub>3</sub><sup>-</sup> formed more recently, while HNO<sub>3</sub> will have a larger proportion formed more recently and will therefore have higher δ<sup>18</sup>O and Δ<sup>17</sup>O values. The fact that we find the lowest isotopic values in summer p-NO<sub>3</sub><sup>-</sup> 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<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences between cold and warm sampling periods – differential N<sub>2</sub>O<sub>5</sub> contribution resulting in higher Δ<sup>17</sup>O values in p-NO<sub>3</sub><sup>-</sup> than in HNO<sub>3</sub>, and differential deposition resulting in lower Δ<sup>17</sup>O values in p-NO<sub>3</sub><sup>-</sup> – would essentially compete against each other, with local conditions and chemistry influencing the results. In winter, when the N<sub>2</sub>O<sub>5</sub> pathway is most important, the first mechanism dominates, as supported by the observation that p-NO<sub>3</sub><sup>-</sup> concentrations are higher during that season (trend *i*). Conversely, in summer, when the N<sub>2</sub>O<sub>5</sub> 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 δ<sup>18</sup>O differences.

For instance, kinetic fractionation may be involved in the production of trend *iii*.

In summary, examining the isotopic relationship of HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> (Fig. 3), reveals the complexity of anthropogenic NO<sub>x</sub> oxidation mechanisms. The lower p-NO<sub>3</sub><sup>-</sup> isotopic values relative to the HNO<sub>3</sub> values during warm months may reflect differential removal rates from plumes containing NO<sub>2</sub> temporarily low in <sup>17</sup>O.

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#### 5 4.3 - Low δ<sup>18</sup>O and Δ<sup>17</sup>O trends in global w- and p-NO<sub>3</sub><sup>-</sup> - 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<sub>x</sub> 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<sub>3</sub> and oxidation through the well-known OH and N<sub>2</sub>O<sub>5</sub> oxidation paths. However, NO<sub>2</sub> not in isotopic equilibrium with O<sub>3</sub>, and/or NO reacted with RO<sub>2</sub> 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<sub>2</sub> and/or HO<sub>2</sub> 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?

15 The full Δ<sup>17</sup>O and δ<sup>18</sup>O ranges for p-NO<sub>3</sub><sup>-</sup>, w-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (between 13.8 and 20.5 ‰, 48.4 and 83.2 ‰; Table 4) compare well with the isotopic ranges obtained for bulk deposition NO<sub>3</sub><sup>-</sup> 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 δ<sup>18</sup>O and Δ<sup>17</sup>O values.

25 Previous work in the Athabasca region reported very low δ<sup>18</sup>O and near-zero Δ<sup>17</sup>O values for p-NO<sub>3</sub><sup>-</sup> 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<sub>2</sub>. Similar isotopic signatures are very likely produced in source emissions of NO<sub>x</sub> in the studied Edmonton and Vauxhall areas (e.g., CFPP, gas compressors, industries). This source signature may persist into p-NO<sub>3</sub><sup>-</sup> collected close to the sources. Within the first few hours in the atmosphere (less, in polluted areas), the NO<sub>x</sub> δ<sup>18</sup>O and Δ<sup>17</sup>O values rapidly increase due to isotope exchange with O<sub>3</sub> (R2, R3, R5 and O<sub>3</sub> formation, Table 5; Michalski et al., 2014) and reach isotopic equilibrium. Though the e-folding lifetime for NO<sub>x</sub> oxidation to nitrates may be longer than these few hours, depending on the NO<sub>x</sub>/VOC ratio, only a fraction of the oxidized source NO<sub>x</sub> 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 Δ<sup>17</sup>O values within 12 km of the emission sites, and where direct stack emissions of p-NO<sub>3</sub><sup>-</sup> were ~5000 times lower than NO<sub>x</sub> emissions (Wang et al., 2012).

35 In a methodological test study, we obtained low values for w-NO<sub>3</sub><sup>-</sup> sampled near a high traffic volume highway in Ontario, Canada (Smirnov et al., 2012). Low δ<sup>18</sup>O and Δ<sup>17</sup>O values in atmospheric nitrates during warm months (65 and 20 ‰ or less,

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  $\delta^{18}\text{O}$  values in w- $\text{NO}_3^-$  from a polluted city (Fang et al., 2011), in p- $\text{NO}_3^-$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values in summer nitrates may reflect the involvement of air masses that include nitrates from oxidation of  $\text{NO}_2$  with light isotopes in plumes. In such cases, while not ruling out a higher contribution from  $\text{RO}_2$  oxidation of  $\text{NO}$ , it is also possible that significant portions of the collected nitrate were formed before the  $\text{NO}_x$ - $\text{O}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  may reflect relative proximity to anthropogenic N emitters in general. Further research work on plume  $\text{NO}_x$  to nitrates chemical mechanisms may help to validate this suggestion. In the future, the assumption of  $\text{NO}_x$  isotopic steady state with  $\text{O}_3$  should be explored, given recent findings (Michalski et al., 2014), the critical importance of  $\text{NO}_x$  isotope characteristics on resulting nitrate isotopic values (Alexander et al., 2009), and the suggestion regarding the evolution of  $\text{NO}_x$ - $\text{NO}_3^-$  signals in fresh anthropogenic plumes (present study).

## 5 Conclusion

The  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  from anthropogenic sources in central and southern Alberta, simultaneously collected with wind sector-based conditional sampling systems produced  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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 ( $\text{HNO}_3$ ) 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- $\text{NO}_3^-$  in these samples generally shows higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than  $\text{HNO}_3$  in the fall-winter period as the heterogeneous  $\text{N}_2\text{O}_5$  pathway favours the production of p- $\text{NO}_3^-$ . In contrast,  $\text{HNO}_3$  has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during warm periods, which we propose is due to faster dry deposition rates relative to p- $\text{NO}_3^-$  in the event that low- $\Delta^{17}\text{O}$   $\text{NO}_2$  is oxidized in the plume. The mechanisms conferring nitrate with relatively low isotopic values, whether oxidation before  $\text{NO}_x$ - $\text{O}_3$  equilibrium is reached or higher contributions from  $\text{RO}_2$ , 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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values may reflect nitrates produced from undifferentiated anthropogenic  $\text{NO}_x$  emissions.

Future research should explore the assumption of NO<sub>x</sub> isotopic equilibration with O<sub>3</sub>, given the critical importance of NO<sub>x</sub> 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<sub>x</sub> 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.

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**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 <sub>x</sub> sources; fertilizer plant largest NH <sub>3</sub> 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 <sub>3</sub> and NO <sub>x</sub> source, oil refinery major NO <sub>x</sub> source

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

5 **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)	δ <sup>18</sup> O	δ <sup>17</sup> O
<i>Teflon filters</i> p-NO <sub>3</sub> <sup>-</sup> (19)	2	1
<i>Nylon filters</i> HNO <sub>3</sub> (18)	1	0.7

10

**Table 3. Average oxygen isotopic ratios (‰) for NO<sub>3</sub><sup>-</sup> sampled as gas (HNO<sub>3</sub>), w (precipitation) and p (particulate matter) relative to VSMOW.**

Matrix Source	Gas			..w		
	w	p	..p	Gas	..w	..p
	δ <sup>18</sup> O			Δ <sup>17</sup> 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)	- (3)	63.1 (3)	24.5 (2)	- (3)	26.4 (3)
City traffic	65.7 (3)	67.2 (2)	59.6 (3)	21.2 (3)	24.4 (2)	22.5 (3)
<b>Mean</b>	<b>66.8</b>	<b>66.0</b>	<b>62.6</b>	<b>23.0</b>	<b>24.3</b>	<b>23.4</b>

(n): number of sampling periods characterized



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

$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	Regional context	Location	Authors
<b>HNO<sub>3</sub></b>				
62.4-81.7	19.3-29.0	Various contaminated sites	Alberta, Canada	<i>This study</i>
<b>p-NO<sub>3</sub><sup>-</sup></b>				
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	<i>This study</i>
<b>w-NO<sub>3</sub><sup>-</sup></b>				
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	Smirnov 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	<i>This study</i>
<b>Undifferentiated and Bulk NO<sub>3</sub><sup>-</sup></b>				
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	<i>This study</i>

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<sub>3</sub> and p-NO<sub>3</sub> isotopic results.

5

**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) $\text{O}_2 + \text{Q} \rightarrow \text{O} + \text{O} + \text{Q}$ ; $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$ ; $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	
(R2) $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3$ ; $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	
(R3) $\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO}$	(R4) $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$
(R5) $\text{NO}_2 + h\nu$ (sunlight) $\rightarrow \text{NO} + \text{O}$	
(R6) $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	(R7) $\text{NO}_2 + \text{NO}_3^- \rightleftharpoons \text{N}_2\text{O}_5$
	(R8) $\text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{surface}) \rightarrow 2\text{HNO}_3(\text{aq})^*$
(R9) $\text{HNO}_3(\text{g}) \rightleftharpoons \text{HNO}_3(\text{aq})^* \rightarrow \text{NO}_3^-(\text{aq})^* + \text{H}^+(\text{aq})$	
(R10) $\text{HNO}_3(\text{g}) + \text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_4\text{NO}_3(\text{s})$	
(R11) $\text{HNO}_3(\text{g}) + \text{CaCO}_3(\text{s}) \rightarrow \text{Ca}(\text{NO}_3)_2(\text{s}) + \text{HCO}_3^-$	
(R12) $\text{NO}_2 + \text{HC}(\text{CH}_3)_2\text{S} \rightarrow \text{HNO}_3 + \text{products}$	

*Q* is a stable molecule of high energy; *M* is either O<sub>2</sub> or N<sub>2</sub>; RO<sub>2</sub> stands for both HO<sub>2</sub> and alkyl peroxy. HC stand for hydrocarbons. \*This aqueous nitrate may be on a particle.

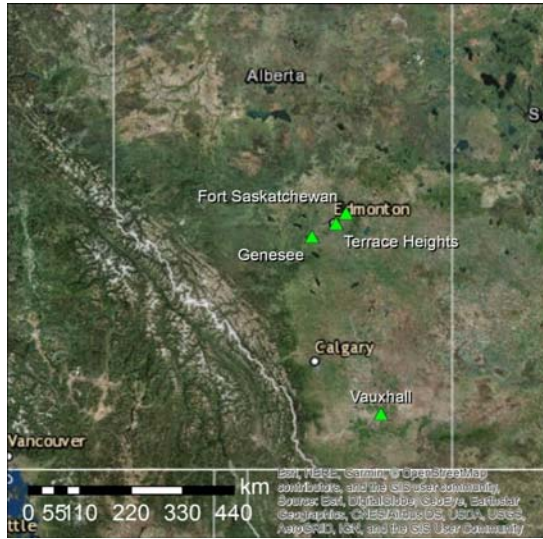
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**Table 6. Correlations of NO<sub>3</sub><sup>-</sup> isotopic results (‰) with meteorological parameters and concentration (or ratio) of co-contaminants.**

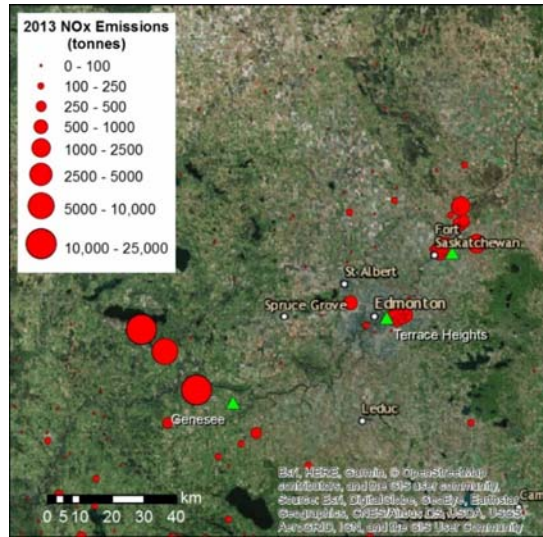
	Relative Humidity		Temperature		Daylight (fraction)		PM	SO <sub>2</sub>	O <sub>3</sub>	
	r	R <sup>2</sup>	r	R <sup>2</sup>	r	R <sup>2</sup>	r	r	r	R <sup>2</sup>
<b>HNO<sub>3</sub></b>										
δ <sup>18</sup> O	<b>0.8</b>	0.59	-0.4		-0.3		0.1	0.0	-0.29	
n	8		15		15		13	13		13
Δ <sup>17</sup> O	0.6		<b>-0.5</b>	0.24	-0.4		0.4	0.3	-0.03	
n	8		15		15		13	13		13
<b>p-NO<sub>3</sub><sup>-</sup></b>										
δ <sup>18</sup> O	<b>0.9</b>	0.79	<b>-0.6</b>	0.34	<b>-0.6</b>	0.35	0.1	0.5	<b>-0.61</b>	0.38
n	7		15		15		12	12		12
Δ <sup>17</sup> O	<b>0.9</b>	0.73	<b>-0.6</b>	0.34	<b>-0.7</b>	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

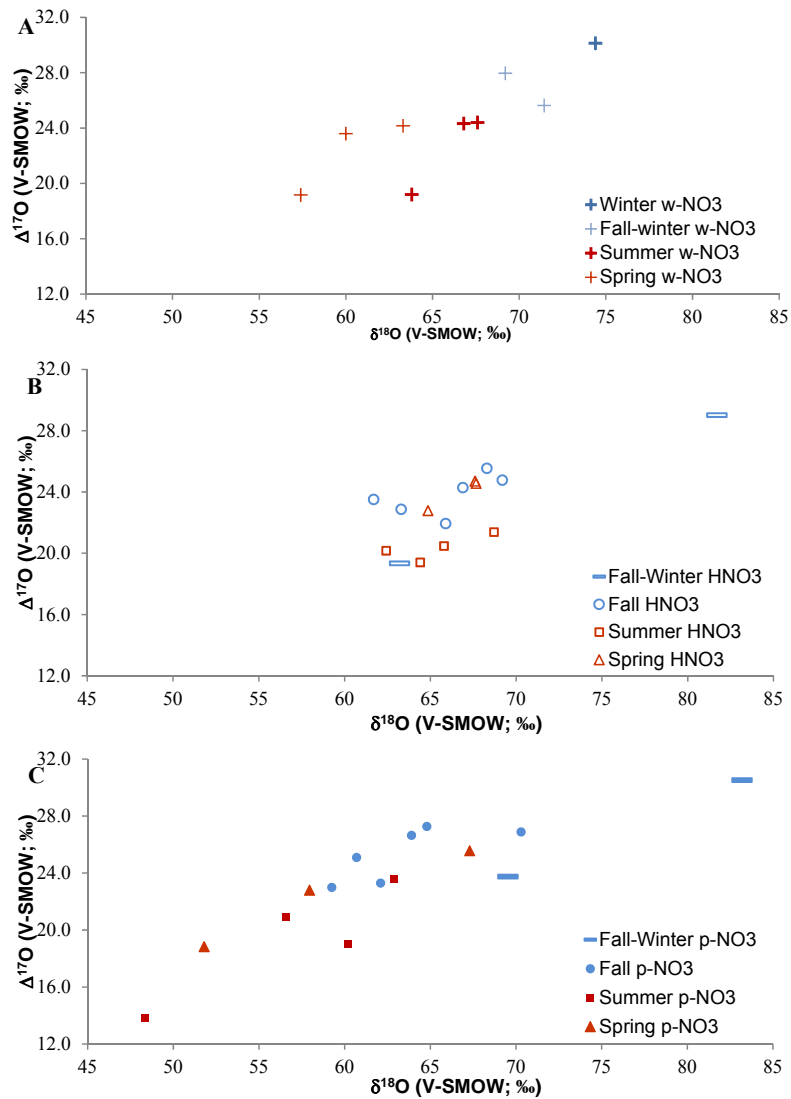
A



B



5 **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<sub>x</sub> as tonnes of NO<sub>2</sub> reported to the National Pollutant Release Inventory for 2013 (Environment and Climate Change Canada, 2018b).



5 Figure 2: Triple O isotopic results obtained for simultaneously collected atmospheric HNO<sub>3</sub> (A), w-NO<sub>3</sub><sup>-</sup> (B) and p-NO<sub>3</sub><sup>-</sup> (C), in Alberta, identified by sampling periods (cold months - blue; warm months - red).

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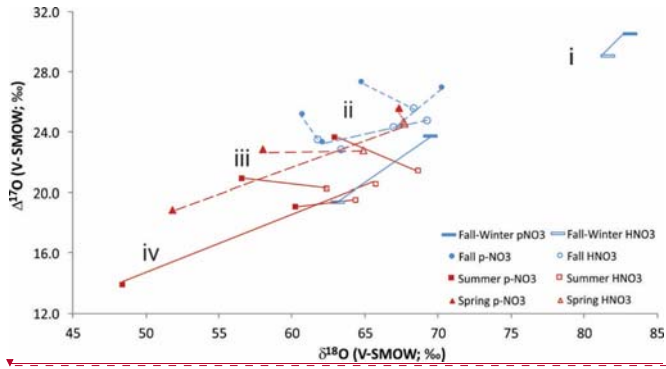
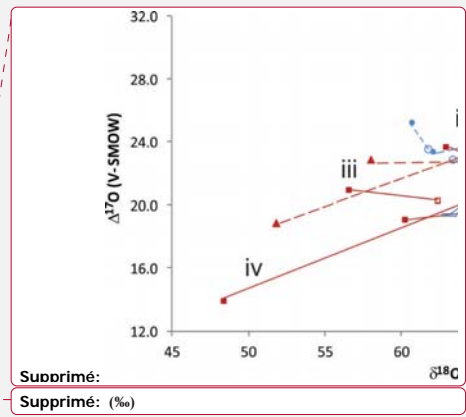


Figure 3: Line-connected  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values for simultaneously collected  $\text{HNO}_3$  (empty symbols) and  $\text{p-NO}_3^-$  (solid symbols) from cold (blue) and warm (red) sampling periods.



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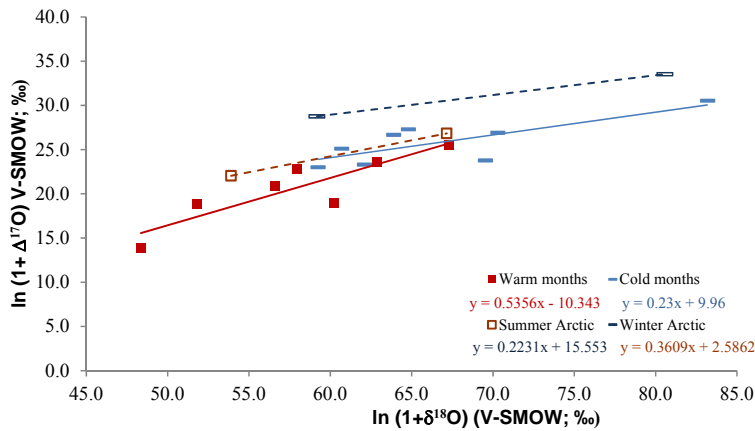


Figure 4: Isotopic results for  $\text{p-NO}_3^-$  identified by sampling periods (solid lines), compared with summer and winter trends obtained for Arctic sites (dashed lines; derived from  $\ln(1 + \delta)$  in Morin et al., 2008).

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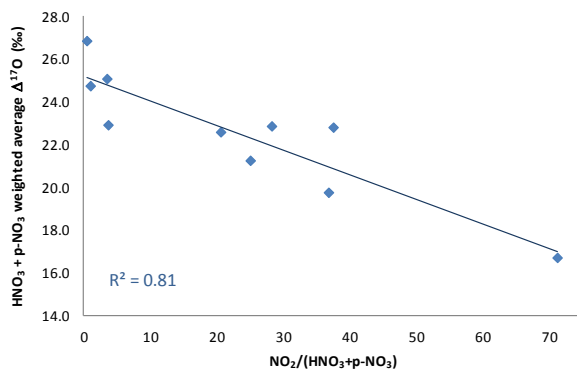
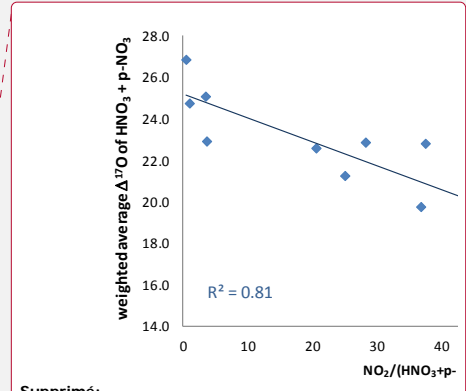


Figure 5: Weighted  $\Delta^{17}\text{O}$  average for the sum of dry nitrates as a function of  $\text{NO}_2$  concentration divided by  $\text{p-NO}_3$  plus  $\text{HNO}_3$  concentrations, a ratio indicative of the maturity of a plume.



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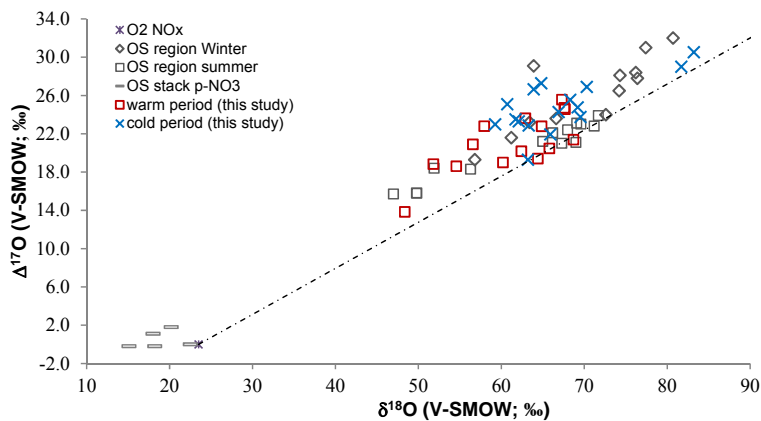


Figure 6: Isotopic ratios for atmospheric  $\text{p-NO}_3^-$ ,  $\text{w-NO}_3^-$  and  $\text{HNO}_3$  samples in cold and warm periods from central and southern Alberta (this study), compared with previously published winter and summer bulk and throughfall deposition samples from the oil sands (OS) region from northern Alberta (Proemse et al., 2013), and  $\text{p-NO}_3^-$  in-stack emissions data for an OS upgrader located in the same region (Proemse et al., 2012). The grey dotted line connects  $\text{NO}_x$  from theoretical combustion with  $\text{O}_2$  isotopic composition and at isotopic equilibrium with tropospheric  $\text{O}_3$  (Michalski et al., 2014).

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**Acp-2017-1103**

**Minor corrections suggested by Dr. Jan Kaiser (Editor)**

1) Please adhere to the International System of Units (SI), which has not always been applied in the present version of the manuscript. Please consult the SI brochure published by BIPM (http://www.bipm.org/en/publications/si-brochure/) and chapter 1 of the IUPAC Green Book (http://media.iupac.org/publications/books/gbook/IUPAC-GB3-2ndPrinting-Online-22apr2011.pdf)

Specifically, chemical symbols and units should not be mixed, i.e. it is not permissible to write "10 mg N m<sup>-3</sup>". To correct this, the chemical species must be identified by the quantity symbol (not the unit), e.g. "c(NO<sub>3</sub><sup>-</sup>-N) = 10 mg m<sup>-3</sup>", or, in the text, "10 mg m<sup>-3</sup> of NO<sub>3</sub><sup>-</sup>-N", or "10 mg m<sup>-3</sup> as N equivalents", or "a nitrate-N concentration of 10 mg m<sup>-3</sup>"

REPLY: All corrected.

This also applies to the tables in the supplementary material.

REPLY: All corrected.

2) Table 3, Figs. 2, 3, 4, 6 & Figs. SM-3 & 5: Axis labels should be  $\delta/\text{‰}$  or  $10^3 \delta (\ln(1+\delta))/\text{‰}$  in case of Fig. 4). See BIPM brochure and IUPAC Green Book for correct examples.

REPLY: The ‰ was previously indicated in the captions of all figures. We now have removed it from the captions and placed it on each axis. All corrected, including Figure 5.

1/13: Replace "ratios" with "delta values".

REPLY: DONE

3/10: Replace "/filter" with "per filter".

REPLY: CORRECTED on 4/25

6/4: The unit "ppb N-NO<sub>3</sub>/L" does not make sense. Also, please see comment 1 above and remove "N-NO<sub>3</sub>" here and from "0.03 N-NO<sub>3</sub> umol/L".

REPLY: DONE on 4/6

6/5: Please convert 0.016 µg to µmol and remove "N".

REPLY: DONE

6/25: Replace "ratios" with "values."

REPLY: DONE

6/32: Delete extraneous "/1000" divisors.

REPLY: We have corrected the equation as in Miller (2002), by adding 1000x to the two parts:  $1000 \times \ln(1+\delta^{17}\text{O}/1000) - 0.516 \times 1000 \times \ln(1+\delta^{18}\text{O}/1000)$ .

7/20: Replace "ratios" with "delta values" or "deltas".

5 REPLY: DONE

7/21 & 7/23 & 10/6 "Isotopic difference" is meaningless as a quantitative term on its own. Please rephrase so as that it is clear which delta values are meant. Also, it would be clearer to say explicitly whether particulate nitrate or HNO<sub>3</sub> have higher or lower delta values.

REPLY: DONE

10 8/13: Change to "not the highest delta values for w-NO<sub>3</sub>-".

REPLY: DONE

8/22: Subscript "x" in "NO<sub>x</sub>". "x" should be in italics.

REPLY: DONE

8/28: "NO<sub>3</sub>-".

15 REPLY: DONE

9/4: Add space between 0 and °C. .

REPLY: DONE

9/19 & R12 Table 5: "NO<sub>3</sub>" (neutral radical) .

REPLY: DONE

20 12/22: The correct unit symbol for "hour" is "h"..

REPLY: DONE

12/25: Please replace "ppb" and "ppt" with the SI units "nmol mol<sup>-1</sup>" and "pmol mol<sup>-1</sup>".

REPLY: DONE

14/2: "The negative isotopic differences between p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> ..." is unclear. Please rephrase so that it is clear which species has lower delta values.

25 REPLY: rephrased to « The lower p-NO<sub>3</sub><sup>-</sup> isotopic values relative to the HNO<sub>3</sub> values... »



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

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10 **Abstract.** There are clear motivations for better understanding the atmospheric processes that transform nitrogen (N) oxides ( $\text{NO}_x$ ) emitted from anthropogenic sources into nitrates ( $\text{NO}_3^-$ ), two of them being that  $\text{NO}_3^-$  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 delta values ( $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ ) are frequently applied to infer the chemical pathways leading to the observed mass independent isotopic anomalies from interaction with  $^{17}\text{O}$ -rich ozone ( $\text{O}_3$ ). Recent laboratory experiments suggest that the isotopic equilibrium between  $\text{NO}_2$  (the main precursor of  $\text{NO}_3^-$ ) and  $\text{O}_3$  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  $\text{NO}_3^-$  in precipitation (w- $\text{NO}_3^-$ ) and in particulate (p- $\text{NO}_3^-$ ) 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  $\text{HNO}_3$  with  $\Delta^{17}\text{O}$  values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample  $\text{HNO}_3$  and p- $\text{NO}_3^-$ , and co-collect w- $\text{NO}_3^-$ . The nitrates are from various distances (<1 to >125 km) downwind of different anthropogenic emitters, and consequently from varying time lapses after emission.

25 The separate collection of nitrates shows that the  $\text{HNO}_3$   $\delta^{18}\text{O}$  ranges are distinct from those of w- and p- $\text{NO}_3^-$ . Interestingly, the  $\Delta^{17}\text{O}$  differences between p- $\text{NO}_3^-$  and  $\text{HNO}_3$  shift from positive during cold sampling periods to negative during warm periods. The low p- $\text{NO}_3^-$   $\Delta^{17}\text{O}$  values observed during warm periods may partly derive from the involvement of  $^{17}\text{O}$ -depleted peroxy radicals ( $\text{RO}_2$ ) oxidizing  $\text{NO}$  during that season. Another possibility is that nitrates derive from  $\text{NO}_x$  that has not yet reached isotopic equilibrium with  $\text{O}_3$ . However, these mechanisms, individually or together, cannot explain the observed p- $\text{NO}_3^-$  minus  $\text{HNO}_3$  isotopic changes. We propose differences in dry depositional rates, faster for  $\text{HNO}_3$ , as a mechanism for the observed shifts. Larger proportions of p- $\text{NO}_3^-$  formed *via* the  $\text{N}_2\text{O}_5$  pathway would explain the opposite fall-winter patterns. Our results show that the separate  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  isotopic signals can be used to further our understanding of  $\text{NO}_x$  oxidation and deposition. Future research should investigate all tropospheric nitrate species as well as  $\text{NO}_x$  to refine our understanding of nitrate distribution worldwide and to develop effective emission reduction strategies.

35

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## 1 Introduction

Anthropogenic NO<sub>x</sub> (NO and NO<sub>2</sub>) emissions are oxidized to nitrate in the atmosphere in the form of gaseous, wet or particulate forms, HNO<sub>3</sub> being one of the main precursors of p-NO<sub>3</sub><sup>-</sup>. 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<sub>3</sub>, HNO<sub>3</sub> and w-NO<sub>3</sub>).

Triple oxygen isotopes ( $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ ) have been used to decipher atmospheric oxidation pathways of NO<sub>x</sub> leading to ambient nitrate. Michalski et al. (2003) performed the first measurement of  $\delta^{17}\text{O}$  values in atmospheric nitrate. The authors found nitrate highly enriched in <sup>18</sup>O and <sup>17</sup>O, likely due to the transfer of anomalous oxygen atoms from ozone (O<sub>3</sub>) via the NO<sub>x</sub>-ozone photochemical cycle and oxidation to nitrate. During its formation, O<sub>3</sub> inherits abnormally high  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values through mass independent fractionation. The specific  $\delta^{17}\text{O}$  departure from the terrestrial mass dependent fractionation line, named the <sup>17</sup>O anomaly, is often expressed as  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.517 \times \delta^{18}\text{O}$  (Thiemens, 1999). Further investigations suggested that the  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values of w-NO<sub>3</sub><sup>-</sup> and p-NO<sub>3</sub><sup>-</sup> reflect several reactions taking place after the atmospheric emission of NO<sub>x</sub>, *i.e.*, atmospheric oxidation pathways transforming NO<sub>x</sub> 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  $\delta^{18}\text{O}$  differences in w-NO<sub>3</sub><sup>-</sup> 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; Smirnov et al., 2012), transfer of the ozone <sup>17</sup>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<sub>3</sub><sup>-</sup> samples are not yet widespread. Also rare are the nitrate  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of field samples downwind from NO<sub>x</sub>-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). The few existing studies have chiefly characterized w-NO<sub>3</sub><sup>-</sup> or the sum of p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (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<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> were generally collected together (without differentiation). Therefore, no studies have separately and simultaneously collected and analyzed the HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup>  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values, and discussed these isotopic characteristics of nitrate collected downwind of anthropogenic emitters. While HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> can be in equilibrium (e.g. if p-NO<sub>3</sub><sup>-</sup> is in the form of solid NH<sub>4</sub>NO<sub>3</sub>), 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 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  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  as well as  $\text{w-NO}_3^-$  downwind of the source types. The objective of this work was to assess the atmospheric  $\text{NO}_x$  reaction pathways and determine processes responsible for the distribution of  $\text{HNO}_3$ , and  $\text{w-}$  and  $\text{p-NO}_3^-$  in a mid-latitudinal region.

## 2 Methodology

### 2.1 Regional context

While national reported  $\text{NO}_x$  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  $\text{PM}_{2.5}$  (particulate matter less than  $2.5 \mu\text{m}$ ) 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  $\text{NO}_x$  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 ( $\text{p-NO}_3^-$ ,  $\text{HNO}_3$  and  $\text{w-NO}_3^-$ ) 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 ( $5.6^\circ\text{C}$ ) and total annual precipitation lower (320 mm) than in central Alberta ( $3.9^\circ\text{C}$ ; 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

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<sub>x</sub> 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<sub>3</sub>) 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<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub> on the Teflon filter, <3% breakthrough of HNO<sub>3</sub> from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> of approximately 0.2 µg N<sub>per</sub> 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<sub>3</sub><sup>-</sup> and positive bias in HNO<sub>3</sub> 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<sub>3</sub> between filter packs and denuder and/or TDLAS systems (Anlauf et al., 1986; Sickles Li 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<sub>2</sub> (nitrous acid) on the nylon filter in two samples (Sickles Li et al., 1999). Based on the conditions in Alberta, we estimate that there is little or no volatilization of NH<sub>4</sub>NO<sub>3</sub> 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.

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After the first five sample periods, an experimental active sampling system for NO<sub>2</sub> and NO<sub>x</sub> 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<sub>2</sub>, and one- or two-stage filter pack containing two identical Maxxam Analytics' impregnated filters designed to collect NO<sub>x</sub> (mostly NO due to upstream collection of NO<sub>2</sub>). Oxygen isotopes in NO<sub>2</sub> and NO<sub>x</sub> 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](#).

Here we report on oxygen isotopes in the simultaneously sampled HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup>, along with co-sampled w-NO<sub>3</sub><sup>-</sup> 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.

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.

### 2.3 Analytical procedures

Nitric acid from nylon filters were extracted using 10 mL of 0.01M solution of NaCl. Particulate-NO<sub>3</sub> 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 (0.03  $\mu\text{mol/L}$  of  $\text{NO}_3^-$ -N). Nitrite concentrations were also measured in the extracts. Nitrite concentrations above the detection limit (1.14  $\mu\text{mol/L}$  of  $\text{NO}_2^-$ -N) were found in a handful of samples at Terrace Heights. These samples were excluded from the reported data.

We characterized the  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  ratios of  $\text{HNO}_3$ , w- $\text{NO}_3^-$ , and p- $\text{NO}_3^-$ , along with the  $\delta^{15}\text{N}$  values of  $\text{NH}_3$ , w- $\text{NH}_4$ , p- $\text{NH}_4$  and  $\text{NO}_x$  (all N isotopic results are in Savard et al., 2017). The present article deals solely with the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values obtained for the three nitrate species. We treated the samples using the chemical conversion and thermal decomposition of  $\text{N}_2\text{O}$  protocols, providing the ability to simultaneously analyze low-concentration N- and O-containing species (Smirnov 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  $\mu\text{mol/L}$  of  $\text{NO}_3^-$ -N). Therefore, not all samples could be diluted to produce volumes sufficient for reduction of  $\text{NO}_3^-$  to  $\text{NO}_2$  and subsequent conversion to  $\text{N}_2\text{O}$ , the final product before isotope analysis. Samples with an initial concentration below 2.3  $\mu\text{mol/L}$  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 ( $\text{NO}_2^-$ ) using a custom-made cadmium column. The final preparation step involved using sodium azide to ultimately produce  $\text{N}_2\text{O}$  (McIlvin and Altabet, 2005; Smirnov et al., 2012). All extracted  $\text{N}_2\text{O}$  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; Smirnov et al., 2012). The utilized approach allows the spectrum of  $\delta^{15}\text{N}$ ,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values 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  $\text{N}_2\text{O}$ . The laboratory analytical precision (average of replicates) determined during the present study was 0.6 ‰ for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values in gaseous (n=12) and solid nitrates (n=20). For w- $\text{NO}_3$ , analytical replicates gave 0.6 and 0.5 ‰, for  $\delta^{18}\text{O}$  (n=3) and  $\delta^{17}\text{O}$  (n=4) values, respectively. The  $\Delta^{17}\text{O}$  values are defined as  $1000 \times \ln \left( \frac{1+\delta^{17}\text{O}/1000}{1+\delta^{18}\text{O}/1000} \right) - 0.516 \times 1000 \times \ln \left( \frac{1+\delta^{18}\text{O}/1000}{1+\delta^{18}\text{O}/1000} \right)$ , relative to Vienna Standard Mean Ocean Water (VSMOW).

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### 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  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\text{NH}_4\text{NO}_3$  on the particle filter into  $\text{HNO}_3$  and  $\text{NH}_3$ , 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  $\text{p-NO}_3^-$  isotopic values ( $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) to be generally higher during winter than during summer (see Section 3.4). Moreover, the  $\text{p-NO}_3^-$   $\delta^{18}\text{O}$  minus  $\text{HNO}_3$   $\delta^{18}\text{O}$  differences are negative during summer (see Section 3.6), 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  $\delta^{15}\text{N}$  values in  $\text{NH}_3$  and  $\text{NH}_4$ ; 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  $^{17}\text{O}$  anomaly; therefore,  $\Delta^{17}\text{O}$  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  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  (Elliott et al., 2009).

#### 3.2 Concentrations and isotopic ratios of nitrates in Alberta samples

The range of  $\text{HNO}_3\text{-N}$  concentrations measured by the filters (from 0.01 to 0.15  $\mu\text{g}/\text{m}^3$ ; average of 0.06) are slightly lower than those of  $\text{p-NO}_3^-\text{-N}$  (from 0.02 to 0.35  $\mu\text{g}/\text{m}^3$ ; 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  $\mu\text{g}/\text{m}^3$  for  $\text{HNO}_3\text{-N}$  and from 0.007 to 0.45  $\mu\text{g}/\text{m}^3$  for  $\text{p-NO}_3^-\text{-N}$  (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

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northern Alberta border revealed similar average concentrations of 0.02  $\mu\text{g}/\text{m}^3$  of  $\text{NO}_3^-$ -N for both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  (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  $\text{NO}_3^-$ -N concentrations of the  $\text{w-NO}_3^-$  samples was 0.15 – 0.48  $\text{mg}/\text{L}$ . 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  $\text{mg}/\text{L}$  of  $\text{NO}_3^-$ -N, while at the most polluted site in southern Ontario (Longwoods) the volume-weighted mean concentration was approximately 0.3  $\text{mg}/\text{L}$  (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.

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The average  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of  $\text{HNO}_3$  (gas),  $\text{w-}$  and  $\text{p-NO}_3^-$  show no apparent systematic ordering (Table 3; Tables SM-1 and 2), in contrast to what was found for  $\delta^{15}\text{N}$  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  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  have the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages, but not the highest delta values for  $\text{w-NO}_3^-$  values; chemical industries show the lowest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages for  $\text{w-}$  and  $\text{p-NO}_3^-$ , but not for  $\text{HNO}_3$ . Though the number of samples were limited,  $\text{w-NO}_3^-$   $\Delta^{17}\text{O}$  values were roughly correlated with the weighted average  $\Delta^{17}\text{O}$  values of  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  in samples covering the same time periods, consistent with scavenging of both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  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).

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Considering all nitrate species, the Alberta  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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  $\text{NO}_x$  cycling and oxidation (nitrate derived through combustion in  $\text{O}_2$  would show  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of 23.5 and 0 ‰, respectively). When examining the existing  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data for  $\text{w-}$  and  $\text{p-NO}_3^-$  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  $\delta^{18}\text{O}$  range of atmospheric  $\text{NO}_3^-$  previously suggested to be between 60 and 95 ‰ (Hastings et al., 2003; Kendall et al., 2007).

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Previous studies that report triple isotope oxygen results in atmospheric  $\text{NO}_3^-$  samples are scarce (Table 4). The  $\text{HNO}_3$  range documented here is within the broad spectrum of  $\text{p-NO}_3^-$  values compiled for remote to contaminated sites. Elliott et al. (2009) reported  $\text{HNO}_3$  oxygen results for  $\delta^{18}\text{O}$  values only, with a range of +51.6 to +94.0 ‰ (mean of 77.4), with simultaneously-sampled  $\text{p-NO}_3^-$   $\delta^{18}\text{O}$  values between +45.2 and +92.7 ‰ (mean of 75.2). Those ranges are broader than the  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  values obtained in the present study.

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

The  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  ranges for  $\text{HNO}_3$  identified by sampling period are narrower than those of the simultaneously collected  $\text{p-NO}_3^-$  (Fig. 2; Table SM-1), suggesting that there are additional mechanisms affecting  $\text{HNO}_3$ , or that  $\text{p-NO}_3^-$  is derived from



different pathways with more variation in isotopic signatures. Overall, the  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  results for  $\text{HNO}_3$ ,  $\text{w-NO}_3^-$  and  $\text{p-NO}_3^-$  clearly show higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during cold periods relative to warm periods (Fig. 2), with the exception of  $\text{HNO}_3$   $\delta^{18}\text{O}$  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  $0^\circ\text{C}$  (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- $\text{NO}_3^-$ .

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,  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) is produced through reactions of air  $\text{N}_2$  with atmospheric  $\text{O}_2$  at high temperatures (reactions R1; Table 5). Then,  $\text{NO}_x$  cycles between  $\text{NO}$  and  $\text{NO}_2$  through a series of reactions involving sunlight (R5),  $\text{O}_3$  (R2, R4), and peroxy ( $\text{HO}_2$ ) or alkyl peroxy ( $\text{RO}_2$ ) radicals (R3; Morin et al., 2007; Fang et al., 2011; Michalski et al., 2014; here we use  $\text{RO}_2$  to refer collectively to  $\text{HO}_2$  and  $\text{RO}_2$ ).

The oxidation of  $\text{NO}_x$  (specifically  $\text{NO}_2$ ) to  $\text{HNO}_3$  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,  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  (R8),  $\text{HNO}_3$  is likely to be retained on the reaction particle as p- $\text{NO}_3^-$  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  $\text{NO}_x$  with hydrocarbons (R12) since they are predicted to have a minimal contribution to nitrate formation in this region (Alexander et al., 2009). Finally,  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of w- and p- $\text{NO}_3^-$  formed during summer are lower than those during winter due to higher contribution from the  $\text{N}_2\text{O}_5$  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- $\text{NO}_3^-$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data presented here follow the same patterns for warm and cold months (Fig. 2). In contrast, the less commonly studied  $\text{HNO}_3$  shows similar  $\delta^{18}\text{O}$  values during warm and cold seasons, but summer  $\Delta^{17}\text{O}$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  samples (n of w- $\text{NO}_3^-$  too low) with meteorological and air quality parameters measured routinely at nearby monitoring stations where available (Table SM-3). We found that the p- $\text{NO}_3^-$  and  $\text{HNO}_3$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values correlate with RH, with p- $\text{NO}_3^-$  values showing stronger statistical links than  $\text{HNO}_3$  (Table 6). The  $\text{N}_2\text{O}_5$  hydrolysis reaction (R8) rate increases with humidity (Kane et al., 2001), which may explain this positive correlation. Significant inverse

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relationships exist between temperature and  $p\text{-NO}_3^- \delta^{18}\text{O}$ ,  $p\text{-NO}_3^- \Delta^{17}\text{O}$ , and  $\text{HNO}_3 \Delta^{17}\text{O}$ . These negative links likely arise since  $\text{N}_2\text{O}_5$  is more stable under cold conditions, leading to a higher contribution of R8. The stronger links with  $p\text{-NO}_3^-$  may be due to R8 taking place on surfaces (such as particles) with liquid water, which is likely to retain the  $\text{HNO}_3$  as  $p\text{-NO}_3^-$  rather than release it to the gas phase. Therefore, in winter, R8 may contribute more to  $p\text{-NO}_3^-$  than to  $\text{HNO}_3(\text{g})$ . Moreover, the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values for both  $p\text{-NO}_3^-$  and  $\text{HNO}_3$  were found for fall-winter samples collected at high RH (76 %) and low temperature ( $-10^\circ\text{C}$ ). In contrast, the lowest  $p\text{-NO}_3^-$  isotopic values were found for samples with similar proportions of  $\text{HNO}_3$  and  $p\text{-NO}_3^-$ , and sampled during moderately humid (60-63 %) and warm ( $8\text{-}20^\circ\text{C}$ ) periods. The accompanying shift in  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  differences between  $p\text{-NO}_3^-$  and  $\text{HNO}_3$ , will help infer the mechanisms dominating during the cold and warm periods (Section 4.2).

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Concentrations of oxidants, co-contaminants (e.g.,  $\text{SO}_4^-$  aerosols) and  $\text{NO}_x$  influence the dominance and rates of the discussed reactions (Brown et al., 2006; Michalski et al., 2014). However, while temperature, RH and  $\text{O}_3$  are well captured within a 5 km radius, other pollutant measurements like continuous  $\text{SO}_2$ ,  $\text{PM}_{2.5}$  and  $\text{NO}_x$  can have large gradients near sources, therefore it is not surprising that no correlations were found with  $\text{SO}_2$  or  $\text{PM}_{2.5}$  measured at sites 4-5 km away (Table 6). Surprisingly, only the  $p\text{-NO}_3^- \Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values.

### 3.5 Comparison with high-latitude $p\text{-NO}_3^-$

An interesting aspect of the Alberta  $p\text{-NO}_3^-$  cold-period  $\Delta^{17}\text{O}$  ranges is that they compare relatively well with the range obtained for the Canadian Arctic (Fig. 4), during winter, when nighttime conditions and the  $\text{N}_2\text{O}_5$  pathway prevail without interruption (Morin et al., 2008; for comparison with  $\text{HNO}_3$  values see Fig. SM-4). This observation supports the suggestion that the  $\text{N}_2\text{O}_5$  pathway produces around 90 % of nitrates during mid-latitude cold months (Michalski et al., 2003; Section 4.1). The  $\delta^{18}\text{O}$  ranges of cold months are similar in Alberta and in the Arctic. This similarity goes against previous suggestions that at higher latitudes, nitrate  $\delta^{18}\text{O}$  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  $\text{N}_2\text{O}_5$  pathway during the Arctic winter (Fang et al., 2011).

The  $\Delta^{17}\text{O}$  departure between the Alberta and Arctic winter parallel lines is about 3 ‰. Such difference is slightly larger than the one calculated for winter  $\text{NO}_3^-$  at 80 and  $40^\circ\text{N}$  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  $\Delta^{17}\text{O}$  values is similar at the mid- and high-latitude 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  $\Delta^{17}\text{O}$  values of  $\text{NO}_x$  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<sub>2</sub>O<sub>5</sub> pathways during summer and winter, respectively. Finally, the  $\Delta^{17}\text{O}$  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<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup>

5 As far as the isotopic characteristics are concerned, an important feature to keep in mind is that the HNO<sub>3</sub> of central and southern Alberta has distinct properties relative to simultaneously sampled p-NO<sub>3</sub><sup>-</sup>. In practical terms, the relationships between the simultaneously sampled HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> are of four types (Fig. 3): (i) HNO<sub>3</sub>  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  are both lower than p-NO<sub>3</sub><sup>-</sup>; (ii) HNO<sub>3</sub> has lower  $\Delta^{17}\text{O}$  but higher  $\delta^{18}\text{O}$  values than p-NO<sub>3</sub><sup>-</sup>; (iii) HNO<sub>3</sub> has higher  $\delta^{18}\text{O}$  values and similar  $\Delta^{17}\text{O}$  ones relative to p-NO<sub>3</sub><sup>-</sup>; and (iv) HNO<sub>3</sub> has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than p-NO<sub>3</sub><sup>-</sup> (Fig. 3).

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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<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> in northeastern USA with similar seasonal changes of  $\delta^{18}\text{O}$  differences (no  $\Delta^{17}\text{O}$  measurement). The HNO<sub>3</sub>  $\delta^{18}\text{O}$  were generally similar or lower than the p-NO<sub>3</sub><sup>-</sup> values during winter and fall, and slightly to much higher during spring and summer, with the spring and autumn p-NO<sub>3</sub><sup>-</sup>-HNO<sub>3</sub> relationships being roughly intermediate between the winter and summer ones. The average  $\delta^{18}\text{O}$  difference of p-NO<sub>3</sub><sup>-</sup> minus HNO<sub>3</sub> reported between winter and summer (15 ‰) by Elliott et al. (2009) agrees with the difference for fall-winter and summer obtained here (12 ‰).

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The marked shifts in isotopic differences between the separately analyzed HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> 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<sub>x</sub> source.

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## 25 4 Discussion

### 4.1 Estimation of $\Delta^{17}\text{O}$ values of NO<sub>x</sub> precursor to the studied nitrates- Highlighting oxidation mechanisms

In the present sub-section, we estimate the  $\Delta^{17}\text{O}$  values of NO<sub>2</sub> 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<sub>2</sub>O<sub>5</sub> due to interaction with O<sub>3</sub> (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<sub>2</sub>O (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<sub>2</sub>, 1/6 from O<sub>3</sub> and 1/6 from H<sub>2</sub>O, while the second produces nitrates via R6 with 2 out of 3 O atoms coming from NO<sub>2</sub> and 1/3 from OH (e.g., Michalski et al., 2003). Using these proportions with the Alberta  $\Delta^{17}\text{O}$  values of p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> in weighted averages allows us to make a rough estimation of the maximum and minimum  $\Delta^{17}\text{O}$  values of NO<sub>2</sub> oxidized to nitrates in the air masses sampled. The calculations assume the O from O<sub>3</sub> contributes a signal of ~39 ‰ as

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was recently measured (Vicars et al., 2014) and that  $\Delta^{17}\text{O}$  of OH and  $\text{H}_2\text{O}$  are zero. The estimated  $\text{NO}_2$   $\Delta^{17}\text{O}$  values for fall-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  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  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  $\text{NO}_2$   $\Delta^{17}\text{O}$  ranges indicate that the potential parent  $\text{NO}_2$  had a smaller  $^{17}\text{O}$  anomaly than  $\text{O}_3$  (39 ‰; Vicars and Savarino, 2014) or  $\text{NO}_2$  in isotopic equilibrium with  $\text{O}_3$  alone (45 ‰; Michalski et al., 2014) in all possible scenarios.

Two mechanisms could be responsible for the  $\Delta^{17}\text{O}$  differences between these estimates and  $\text{NO}_2$  in isotopic equilibrium with  $\text{O}_3$ . One is the competition of R3 with R2 in oxidizing NO to  $\text{NO}_2$ , since  $\text{RO}_2$  will decrease the  $\Delta^{17}\text{O}$  values relative to an ozone-only equilibrium. The relative reaction rates of R2 and R3 have previously been presumed to control the  $\text{NO}_2$  isotopic composition (e.g., Alexander et al., 2009) based on the assumption of isotopic steady state. A larger contribution of  $\text{RO}_2$  is expected in the  $\text{NO}_2$  precursors for summer relative to winter, since biogenic VOCs that are major sources of  $\text{RO}_2$  radicals are much higher in the summer (e.g., Fuentes and Wang, 1999). This suggestion is consistent with the lower  $\Delta^{17}\text{O}$  ranges in summer reported here. A second possibility is that the nitrates were formed from some  $\text{NO}_x$  that did not reach isotopic steady state with  $\text{O}_3$ , retaining some of its original signature (assumed to be  $\Delta^{17}\text{O}=0$  ‰). Most studies have assumed that isotopic steady state is established between  $\text{O}_3$  and  $\text{NO}_2$  within a few minutes after emission of  $\text{NO}_x$  from a combustion source – or at least, that nitrate formation is negligible before  $\text{NO}_x$  isotopic equilibrium is reached. However, recent modeling by Michalski et al. (2014) suggests that isotopic equilibration of  $\text{NO}_x$  with  $\text{O}_3$  could take several minutes up to a few hours at the relatively low  $\text{O}_3$  concentrations in rural Alberta. At the measured average wind speeds on site of 8-19  $\text{km h}^{-1}$ , transit times from the nearest sources to observation sites are estimated to be 9-55 minutes. While the fraction of  $\text{NO}_x$  converted to nitrate in this transit time may be small, these are large sources of  $\text{NO}_x$  in an area with very low background nitrates. For example, a plume containing 10  $\mu\text{mol mol}^{-1}$  of  $\text{NO}_2$  mixing with background air with 0.1  $\mu\text{mol mol}^{-1}$  of OH (Howell et al., 2014) would produce  $\text{HNO}_3$  via R6 at a rate of 0.011  $\mu\text{g m}^{-3} \text{min}^{-1}$  of  $\text{NO}_3\text{-N}$  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  $\text{O}_3$  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  $\text{NO}_x$  that had not yet reached isotopic steady state with  $\text{O}_3$ . These two mechanisms are not exclusive and could both contribute to lower  $\text{NO}_x$  and therefore nitrate,  $\Delta^{17}\text{O}$  values.

An additional piece of evidence suggests that the  $\text{NO}_x$  plumes themselves, rather than ambient conditions, are the source of low- $\Delta^{17}\text{O}$  nitrates in these samples. There is a strong correlation between the total nitrate  $\Delta^{17}\text{O}$  values and the maturity of the plume as expressed by the  $\text{NO}_2$  concentration divided by sum of  $\text{HNO}_3$  and p- $\text{NO}_3^-$  concentrations (Fig. 5). This observation is consistent with the unequilibrated  $\text{NO}_2$  hypothesis. However, it does not rule out the possible contribution of  $\text{RO}_2$ , since VOC releases from the  $\text{NO}_x$  sources could lead to elevated  $\text{RO}_2$  concentrations in the plume.

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#### 4.2 Causes of shifts in HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences

A challenging question is why do the HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences shift seasonally (Fig. 3)? One factor that may influence the relationship between HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> is mass-dependent isotopic equilibrium between NH<sub>4</sub>NO<sub>3</sub> and HNO<sub>3</sub> (R10); however, this mechanism would result in higher δ<sup>18</sup>O in p-NO<sub>3</sub><sup>-</sup> and unchanged Δ<sup>17</sup>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<sub>2</sub>O<sub>5</sub> pathway is likely to produce more p-NO<sub>3</sub><sup>-</sup> than HNO<sub>3</sub>(g), which would result in a higher contribution from ozone and explain why δ<sup>18</sup>O and Δ<sup>17</sup>O values are both higher in p-NO<sub>3</sub><sup>-</sup>. A previous study addressing why p-NO<sub>3</sub><sup>-</sup> 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 δ<sup>18</sup>O and Δ<sup>17</sup>O values were lower in p-NO<sub>3</sub><sup>-</sup> than in HNO<sub>3</sub> (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<sub>3</sub> dry deposits to surfaces more rapidly than p-NO<sub>3</sub><sup>-</sup> (Zhang et al., 2009; Benedict et al., 2013), which would create the discussed isotopic shifts in the situation where NO<sub>2</sub> has low Δ<sup>17</sup>O values in a fresh plume.

The first nitrates formed in the plume shortly after emission from the NO<sub>x</sub> source have low δ<sup>18</sup>O and Δ<sup>17</sup>O values, either because NO<sub>x</sub> has not yet reached isotopic steady state with O<sub>3</sub> or because it reacted with <sup>17</sup>O-poor RO<sub>2</sub> present in the plume due to VOC emissions. Those nitrates that form as p-NO<sub>3</sub><sup>-</sup> or that partition to p-NO<sub>3</sub><sup>-</sup> remain in the plume for longer than HNO<sub>3</sub>, which is removed from the plume rapidly upon contact with vegetation or other surfaces. As the plume travels, the NO<sub>x</sub> becomes more enriched, and the newly formed nitrates take on higher δ<sup>18</sup>O and Δ<sup>17</sup>O values. However, p-NO<sub>3</sub><sup>-</sup> collected further downwind will derive from a mixture of low-δ<sup>18</sup>O and -Δ<sup>17</sup>O p-NO<sub>3</sub><sup>-</sup> formed earlier, plus high-δ<sup>18</sup>O and -Δ<sup>17</sup>O p-NO<sub>3</sub><sup>-</sup> formed more recently, while HNO<sub>3</sub> will have a larger proportion formed more recently and will therefore have higher δ<sup>18</sup>O and Δ<sup>17</sup>O values. The fact that we find the lowest isotopic values in summer p-NO<sub>3</sub><sup>-</sup> 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<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences between cold and warm sampling periods – differential N<sub>2</sub>O<sub>5</sub> contribution resulting in higher Δ<sup>17</sup>O values in p-NO<sub>3</sub><sup>-</sup> than in HNO<sub>3</sub>, and differential deposition resulting in lower Δ<sup>17</sup>O values in p-NO<sub>3</sub><sup>-</sup> – would essentially compete against each other, with local conditions and chemistry influencing the results. In winter, when the N<sub>2</sub>O<sub>5</sub> pathway is most important, the first mechanism dominates, as supported by the observation that p-NO<sub>3</sub><sup>-</sup> concentrations are higher during that season (trend *i*). Conversely, in summer, when the N<sub>2</sub>O<sub>5</sub> 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 δ<sup>18</sup>O differences.

For instance, kinetic fractionation may be involved in the production of trend *iii*.

In summary, examining the isotopic relationship of HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> (Fig. 3), reveals the complexity of anthropogenic NO<sub>x</sub> oxidation mechanisms. The lower p-NO<sub>3</sub><sup>-</sup> isotopic values relative to the HNO<sub>3</sub> values during warm months may reflect differential removal rates from plumes containing NO<sub>2</sub> temporarily low in <sup>17</sup>O.

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#### 5 4.3 - Low δ<sup>18</sup>O and Δ<sup>17</sup>O trends in global w- and p-NO<sub>3</sub><sup>-</sup> - 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<sub>x</sub> 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<sub>3</sub> and oxidation through the well-known OH and N<sub>2</sub>O<sub>5</sub> oxidation paths. However, NO<sub>2</sub> not in isotopic equilibrium with O<sub>3</sub>, and/or NO reacted with RO<sub>2</sub> 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<sub>2</sub> and/or HO<sub>2</sub> 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?

15 The full Δ<sup>17</sup>O and δ<sup>18</sup>O ranges for p-NO<sub>3</sub><sup>-</sup>, w-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (between 13.8 and 20.5 ‰, 48.4 and 83.2 ‰; Table 4) compare well with the isotopic ranges obtained for bulk deposition NO<sub>3</sub><sup>-</sup> 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  
20 (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 δ<sup>18</sup>O and Δ<sup>17</sup>O values.

Previous work in the Athabasca region reported very low δ<sup>18</sup>O and near-zero Δ<sup>17</sup>O values for p-NO<sub>3</sub><sup>-</sup> 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<sub>2</sub>. Similar isotopic signatures are very likely produced in source emissions of NO<sub>x</sub> in the studied Edmonton and Vauxhall areas (e.g., CFPP, gas compressors, industries). This source signature may persist into p-NO<sub>3</sub><sup>-</sup> collected close to the sources. Within the first few hours in the atmosphere (less, in polluted areas), the NO<sub>x</sub> δ<sup>18</sup>O and Δ<sup>17</sup>O values rapidly increase due to isotope exchange with O<sub>3</sub> (R2, R3, R5 and O<sub>3</sub> formation, Table 5; Michalski et al., 2014) and reach isotopic equilibrium. Though the e-folding lifetime for NO<sub>x</sub> oxidation to nitrates may be longer than these few hours,  
30 depending on the NO<sub>x</sub>/VOC ratio, only a fraction of the oxidized source NO<sub>x</sub> 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 Δ<sup>17</sup>O values within 12 km of the emission sites, and where direct stack emissions of p-NO<sub>3</sub><sup>-</sup> were ~5000 times lower than NO<sub>x</sub> emissions (Wang et al., 2012).

35 In a methodological test study, we obtained low values for w-NO<sub>3</sub><sup>-</sup> sampled near a high traffic volume highway in Ontario, Canada (Smirnov et al., 2012). Low δ<sup>18</sup>O and Δ<sup>17</sup>O values in atmospheric nitrates during warm months (65 and 20 ‰ or less,

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  $\delta^{18}\text{O}$  values in w- $\text{NO}_3^-$  from a polluted city (Fang et al., 2011), in p- $\text{NO}_3^-$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values in summer nitrates may reflect the involvement of air masses that include nitrates from oxidation of  $\text{NO}_2$  with light isotopes in plumes. In such cases, while not ruling out a higher contribution from  $\text{RO}_2$  oxidation of  $\text{NO}$ , it is also possible that significant portions of the collected nitrate were formed before the  $\text{NO}_x$ - $\text{O}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  may reflect relative proximity to anthropogenic N emitters in general. Further research work on plume  $\text{NO}_x$  to nitrates chemical mechanisms may help to validate this suggestion. In the future, the assumption of  $\text{NO}_x$  isotopic steady state with  $\text{O}_3$  should be explored, given recent findings (Michalski et al., 2014), the critical importance of  $\text{NO}_x$  isotope characteristics on resulting nitrate isotopic values (Alexander et al., 2009), and the suggestion regarding the evolution of  $\text{NO}_x$ - $\text{NO}_3^-$  signals in fresh anthropogenic plumes (present study).

## 5 Conclusion

The  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  from anthropogenic sources in central and southern Alberta, simultaneously collected with wind sector-based conditional sampling systems produced  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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 ( $\text{HNO}_3$ ) 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- $\text{NO}_3^-$  in these samples generally shows higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than  $\text{HNO}_3$  in the fall-winter period as the heterogeneous  $\text{N}_2\text{O}_5$  pathway favours the production of p- $\text{NO}_3^-$ . In contrast,  $\text{HNO}_3$  has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during warm periods, which we propose is due to faster dry deposition rates relative to p- $\text{NO}_3^-$  in the event that low- $\Delta^{17}\text{O}$   $\text{NO}_2$  is oxidized in the plume. The mechanisms conferring nitrate with relatively low isotopic values, whether oxidation before  $\text{NO}_x$ - $\text{O}_3$  equilibrium is reached or higher contributions from  $\text{RO}_2$ , 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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values may reflect nitrates produced from undifferentiated anthropogenic  $\text{NO}_x$  emissions.

Future research should explore the assumption of NO<sub>x</sub> isotopic equilibration with O<sub>3</sub>, given the critical importance of NO<sub>x</sub> 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<sub>x</sub> 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.

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**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 <sub>x</sub> sources; fertilizer plant largest NH <sub>3</sub> 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 <sub>3</sub> and NO <sub>x</sub> source, oil refinery major NO <sub>x</sub> source

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

5 **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)	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$
<i>Teflon filters</i> p-NO <sub>3</sub> <sup>-</sup> (19)	2	1
<i>Nylon filters</i> HNO <sub>3</sub> (18)	1	0.7

10

**Table 3. Average oxygen isotopic ratios (‰) for NO<sub>3</sub><sup>-</sup> sampled as gas (HNO<sub>3</sub>), w (precipitation) and p (particulate matter) relative to VSMOW.**

Matrix Source	Gas			w			p		
	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$
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)	- (3)	63.1 (3)	24.5 (2)	- (3)	26.4 (3)			
City traffic	65.7 (3)	67.2 (2)	59.6 (3)	21.2 (3)	24.4 (2)	22.5 (3)			
<b>Mean</b>	<b>66.8</b>	<b>66.0</b>	<b>62.6</b>	<b>23.0</b>	<b>24.3</b>	<b>23.4</b>			

(n): number of sampling periods characterized

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

$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	Regional context	Location	Authors
<b>HNO<sub>3</sub></b>				
62.4-81.7	19.3-29.0	Various contaminated sites	Alberta, Canada	<i>This study</i>
<b>p-NO<sub>3</sub><sup>-</sup></b>				
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	<i>This study</i>
<b>w-NO<sub>3</sub><sup>-</sup></b>				
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	Smirnov 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	<i>This study</i>
<b>Undifferentiated and Bulk NO<sub>3</sub><sup>-</sup></b>				
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	<i>This study</i>

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<sub>3</sub> and p-NO<sub>3</sub> isotopic results.

5

**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) $\text{O}_2 + \text{Q} \rightarrow \text{O} + \text{O} + \text{Q}$ ; $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$ ; $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	
(R2) $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3$ ; $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	
(R3) $\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO}$	
	(R4) $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$
(R5) $\text{NO}_2 + h\nu$ (sunlight) $\rightarrow \text{NO} + \text{O}$	
(R6) $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	(R7) $\text{NO}_2 + \text{NO}_3^- \rightleftharpoons \text{N}_2\text{O}_5$
	(R8) $\text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{surface}) \rightarrow 2\text{HNO}_3(\text{aq})^*$
(R9) $\text{HNO}_3(\text{g}) \rightleftharpoons \text{HNO}_3(\text{aq})^* \rightarrow \text{NO}_3^-(\text{aq})^* + \text{H}^+(\text{aq})$	
(R10) $\text{HNO}_3(\text{g}) + \text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_4\text{NO}_3(\text{s})$	
(R11) $\text{HNO}_3(\text{g}) + \text{CaCO}_3(\text{s}) \rightarrow \text{Ca}(\text{NO}_3)_2(\text{s}) + \text{HCO}_3^-$	
(R12) $\text{NO}_2 + \text{HC}(\text{CH}_3)_2\text{S} \rightarrow \text{HNO}_3 + \text{products}$	

*Q* is a stable molecule of high energy; *M* is either O<sub>2</sub> or N<sub>2</sub>; RO<sub>2</sub> stands for both HO<sub>2</sub> and alkyl peroxy. HC stand for hydrocarbons. \*This aqueous nitrate may be on a particle.

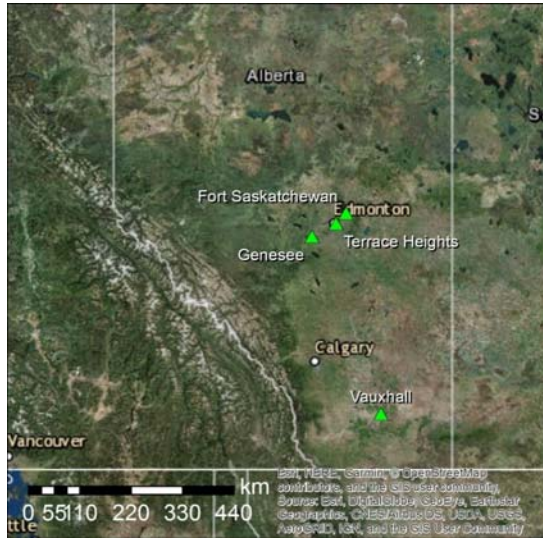
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**Table 6. Correlations of NO<sub>3</sub><sup>-</sup> isotopic results (‰) with meteorological parameters and concentration (or ratio) of co-contaminants.**

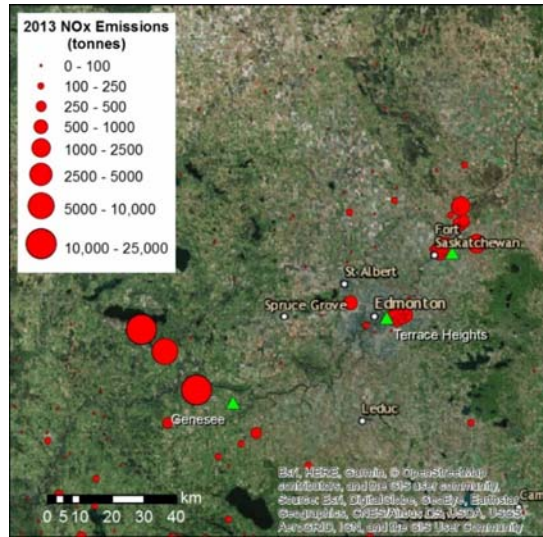
	Relative Humidity		Temperature		Daylight (fraction)		PM	SO <sub>2</sub>	O <sub>3</sub>	
	r	R <sup>2</sup>	r	R <sup>2</sup>	r	R <sup>2</sup>	r	r	r	R <sup>2</sup>
<b>HNO<sub>3</sub></b>										
δ <sup>18</sup> O	<b>0.8</b>	0.59	-0.4		-0.3		0.1	0.0	-0.29	
n	8		15		15		13	13		13
Δ <sup>17</sup> O	0.6		<b>-0.5</b>	0.24	-0.4		0.4	0.3	-0.03	
n	8		15		15		13	13		13
<b>p-NO<sub>3</sub><sup>-</sup></b>										
δ <sup>18</sup> O	<b>0.9</b>	0.79	<b>-0.6</b>	0.34	<b>-0.6</b>	0.35	0.1	0.5	<b>-0.61</b>	0.38
n	7		15		15		12	12		12
Δ <sup>17</sup> O	<b>0.9</b>	0.73	<b>-0.6</b>	0.34	<b>-0.7</b>	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

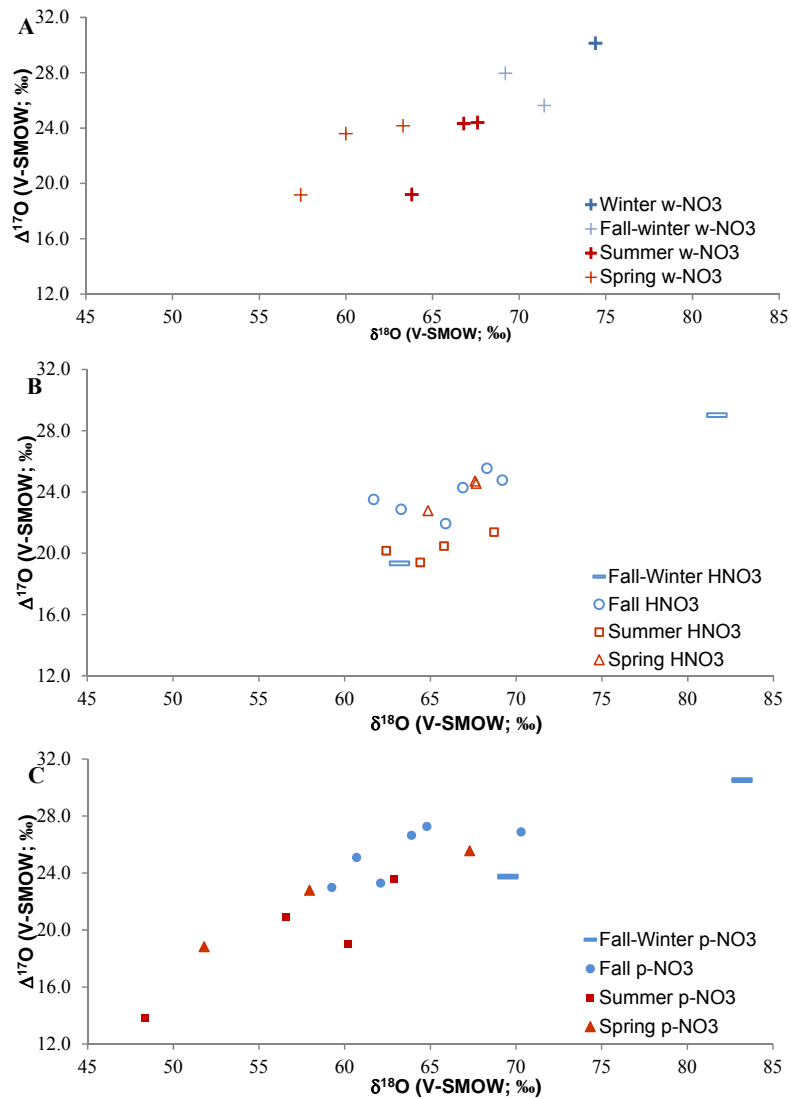
A



B



5 **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<sub>x</sub> as tonnes of NO<sub>2</sub> reported to the National Pollutant Release Inventory for 2013 (Environment and Climate Change Canada, 2018b).



5 Figure 2: Triple O isotopic results obtained for simultaneously collected atmospheric HNO<sub>3</sub> (A), w-NO<sub>3</sub><sup>-</sup> (B) and p-NO<sub>3</sub><sup>-</sup> (C), in Alberta, identified by sampling periods (cold months - blue; warm months - red).

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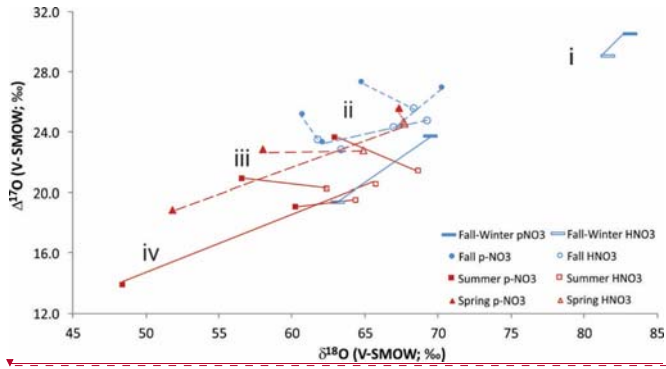
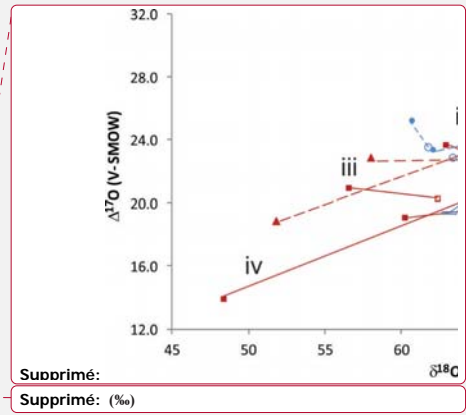


Figure 3: Line-connected  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values for simultaneously collected  $\text{HNO}_3$  (empty symbols) and  $\text{p-NO}_3^-$  (solid symbols) from cold (blue) and warm (red) sampling periods.



5

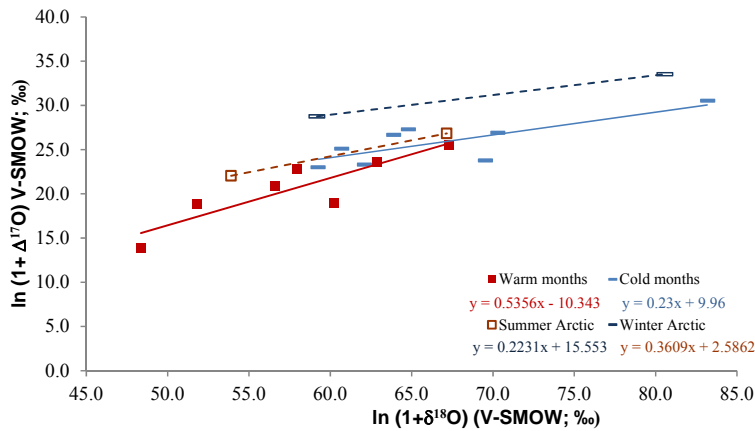


Figure 4: Isotopic results for  $\text{p-NO}_3^-$  identified by sampling periods (solid lines), compared with summer and winter trends obtained for Arctic sites (dashed lines; derived from  $\ln(1 + \delta)$  in Morin et al., 2008).

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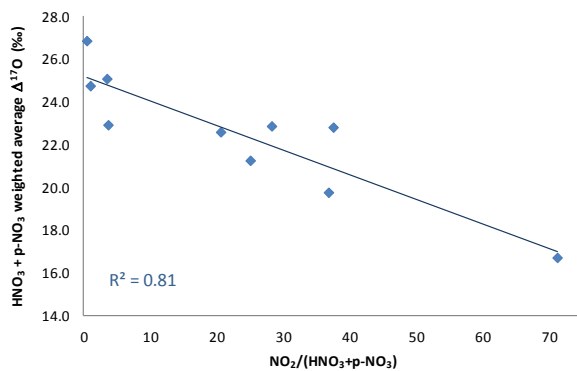
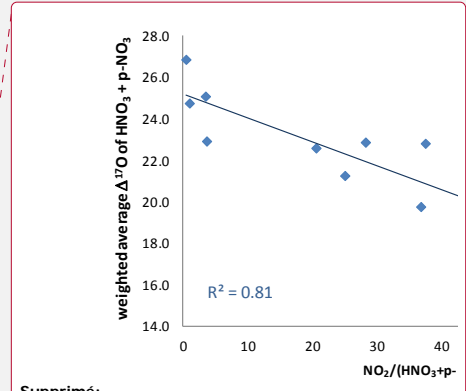


Figure 5: Weighted  $\Delta^{17}\text{O}$  average for the sum of dry nitrates as a function of  $\text{NO}_2$  concentration divided by  $\text{p-NO}_3$  plus  $\text{HNO}_3$  concentrations, a ratio indicative of the maturity of a plume.



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Supprimé:  $\Delta^{17}\text{O}$  (‰)

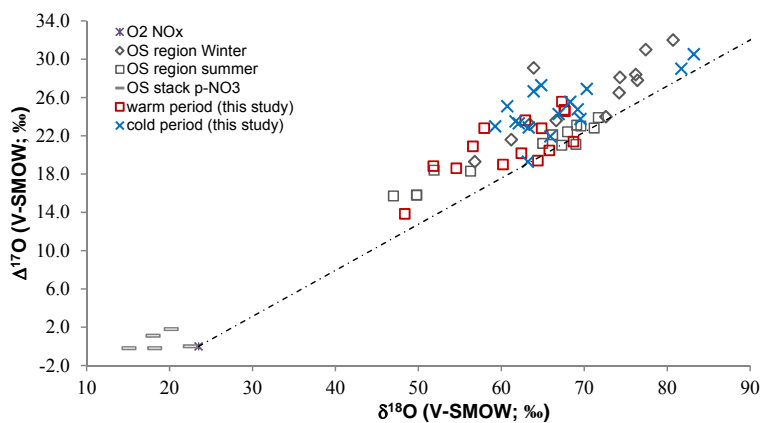


Figure 6: Isotopic ratios for atmospheric  $\text{p-NO}_3^-$ ,  $\text{w-NO}_3^-$  and  $\text{HNO}_3$  samples in cold and warm periods from central and southern Alberta (this study), compared with previously published winter and summer bulk and throughfall deposition samples from the oil sands (OS) region from northern Alberta (Proemse et al., 2013), and  $\text{p-NO}_3^-$  in-stack emissions data for an OS upgrader located in the same region (Proemse et al., 2012). The grey dotted line connects  $\text{NO}_x$  from theoretical combustion with  $\text{O}_2$  isotopic composition and at isotopic equilibrium with tropospheric  $\text{O}_3$  (Michalski et al., 2014).

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**Acp-2017-1103**

**Minor corrections suggested by Dr. Jan Kaiser (Editor)**

1) Please adhere to the International System of Units (SI), which has not always been applied in the present version of the manuscript. Please consult the SI brochure published by BIPM (http://www.bipm.org/en/publications/si-brochure/) and chapter 1 of the IUPAC Green Book (http://media.iupac.org/publications/books/gbook/IUPAC-GB3-2ndPrinting-Online-22apr2011.pdf)

Specifically, chemical symbols and units should not be mixed, i.e. it is not permissible to write "10 mg N m<sup>-3</sup>". To correct this, the chemical species must be identified by the quantity symbol (not the unit), e.g. "c(NO<sub>3</sub><sup>-</sup>-N) = 10 mg m<sup>-3</sup>", or, in the text, "10 mg m<sup>-3</sup> of NO<sub>3</sub><sup>-</sup>-N", or "10 mg m<sup>-3</sup> as N equivalents", or "a nitrate-N concentration of 10 mg m<sup>-3</sup>"

REPLY: All corrected.

This also applies to the tables in the supplementary material.

REPLY: All corrected.

2) Table 3, Figs. 2, 3, 4, 6 & Figs. SM-3 & 5: Axis labels should be  $\delta/\text{‰}$  or  $10^3 \delta (\ln(1+\delta))/\text{‰}$  in case of Fig. 4). See BIPM brochure and IUPAC Green Book for correct examples.

REPLY: The ‰ was previously indicated in the captions of all figures. We now have removed it from the captions and placed it on each axis. All corrected, including Figure 5.

1/13: Replace "ratios" with "delta values".

REPLY: DONE

3/10: Replace "/filter" with "per filter".

REPLY: CORRECTED on 4/25

6/4: The unit "ppb N-NO<sub>3</sub>/L" does not make sense. Also, please see comment 1 above and remove "N-NO<sub>3</sub>" here and from "0.03 N-NO<sub>3</sub> umol/L".

REPLY: DONE on 4/6

6/5: Please convert 0.016 µg to µmol and remove "N".

REPLY: DONE

6/25: Replace "ratios" with "values."

REPLY: DONE

6/32: Delete extraneous "/1000" divisors.

REPLY: We have corrected the equation as in Miller (2002), by adding 1000x to the two parts:  $1000 \times \ln(1+\delta^{17}\text{O}/1000) - 0.516 \times 1000 \times \ln(1+\delta^{18}\text{O}/1000)$ .

7/20: Replace "ratios" with "delta values" or "deltas".

5 REPLY: DONE

7/21 & 7/23 & 10/6 "Isotopic difference" is meaningless as a quantitative term on its own. Please rephrase so as that it is clear which delta values are meant. Also, it would be clearer to say explicitly whether particulate nitrate or HNO<sub>3</sub> have higher or lower delta values.

REPLY: DONE

10 8/13: Change to "not the highest delta values for w-NO<sub>3</sub>-".

REPLY: DONE

8/22: Subscript "x" in "NO<sub>x</sub>". "x" should be in italics.

REPLY: DONE

8/28: "NO<sub>3</sub>-".

15 REPLY: DONE

9/4: Add space between 0 and °C. .

REPLY: DONE

9/19 & R12 Table 5: "NO<sub>3</sub>" (neutral radical) .

REPLY: DONE

20 12/22: The correct unit symbol for "hour" is "h"..

REPLY: DONE

12/25: Please replace "ppb" and "ppt" with the SI units "nmol mol<sup>-1</sup>" and "pmol mol<sup>-1</sup>".

REPLY: DONE

14/2: "The negative isotopic differences between p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> ..." is unclear. Please rephrase so that it is clear which species has lower delta values.

25 REPLY: rephrased to « The lower p-NO<sub>3</sub><sup>-</sup> isotopic values relative to the HNO<sub>3</sub> values... »

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

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10 **Abstract.** There are clear motivations for better understanding the atmospheric processes that transform nitrogen (N) oxides ( $\text{NO}_x$ ) emitted from anthropogenic sources into nitrates ( $\text{NO}_3^-$ ), two of them being that  $\text{NO}_3^-$  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 ( $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ ) are frequently applied to infer the chemical pathways leading to the observed mass independent isotopic anomalies from interaction with  $^{17}\text{O}$ -rich ozone ( $\text{O}_3$ ). Recent laboratory experiments suggest that the isotopic equilibrium between  $\text{NO}_2$  (the main precursor of  $\text{NO}_3^-$ ) and  $\text{O}_3$  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  $\text{NO}_3^-$  in precipitation (w- $\text{NO}_3^-$ ) and in particulate (p- $\text{NO}_3^-$ ) 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  $\text{HNO}_3$  with  $\Delta^{17}\text{O}$  values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample  $\text{HNO}_3$  and p- $\text{NO}_3^-$ , and co-collect w- $\text{NO}_3^-$ . The nitrates are from various distances (<1 to >125 km) downwind of different anthropogenic emitters, and consequently from varying time lapses after emission.

25 The separate collection of nitrates shows that the  $\text{HNO}_3$   $\delta^{18}\text{O}$  ranges are distinct from those of w- and p- $\text{NO}_3^-$ . Interestingly, the  $\Delta^{17}\text{O}$  differences between p- $\text{NO}_3^-$  and  $\text{HNO}_3$  shift from positive during cold sampling periods to negative during warm periods. The low p- $\text{NO}_3^-$   $\Delta^{17}\text{O}$  values observed during warm periods may partly derive from the involvement of  $^{17}\text{O}$ -depleted peroxy radicals ( $\text{RO}_2$ ) oxidizing  $\text{NO}$  during that season. Another possibility is that nitrates derive from  $\text{NO}_x$  that has not yet reached isotopic equilibrium with  $\text{O}_3$ . However, these mechanisms, individually or together, cannot explain the observed p- $\text{NO}_3^-$  minus  $\text{HNO}_3$  isotopic changes. We propose differences in dry depositional rates, faster for  $\text{HNO}_3$ , as a mechanism for the observed shifts. Larger proportions of p- $\text{NO}_3^-$  formed via the  $\text{N}_2\text{O}_5$  pathway would explain the opposite fall-winter patterns. Our results show that the separate  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  isotopic signals can be used to further our understanding of  $\text{NO}_x$  oxidation and deposition. Future research should investigate all tropospheric nitrate species as well as  $\text{NO}_x$  to refine our understanding of nitrate distribution worldwide and to develop effective emission reduction strategies.

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Supprimé: simultaneously collected

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Supprimé: distribution of wet (w- $\text{NO}_3^-$ ), particulate (p- $\text{NO}_3^-$ ), and the sum of p- $\text{NO}_3^-$  and gaseous  $\text{HNO}_3$ ,

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Supprimé: while the gaseous form ( $\text{HNO}_3$ ) has never been separately characterized for  $^{17}\text{O}$ .

Supprimé: recent laboratory experiments suggest that the reveal time lapses between emission of  $\text{NO}_x$ ... isotopic equilibrium between  $\text{NO}_2$  (the main precursors... of  $\text{NO}_3^-$ ) and its isotopic equilibrium with  $\text{O}_3$  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... nitrates may be formed near emission sources with lower isotopic values than those at equilibrium... formed further downwind. Equally important, Previous research studies have investigated characterization of f... indeed, previously published field measurements of oxygen isotopes in  $\text{NO}_3^-$  in precipitation (w- $\text{NO}_3^-$ ... and in particulate (p- $\text{NO}_3^-$ ) ... [1]

Supprimé: or p- $\text{NO}_3^-$  +  $\text{HNO}_3$  from non-polluted or polluted air masses, and inferred seasonal changes in the dominance of oxidation pathways to account for higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values in winter relative to summer.

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Supprimé: polluted... if studies have deployed systems allowing collection of... samples specific to targeted emission ... [2]

Supprimé: pathways... isotopic signature due to moving... hanging wind directions, or separately characterized gaseous  $\text{HNO}_3$  with  $\Delta^{17}\text{O}$  values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample  $\text{HNO}_3$  and p- $\text{NO}_3^-$ , and co-collect w- $\text{NO}_3^-$ . The nitrates are from various distances (<1 to >125 km) downwind from... five ... [3]

Supprimé: five different... anthropogenic sources ... [4]

Supprimé: Overall, the w- and p- $\text{NO}_3^-$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values show expected differences between cold and warm seasons, but only the  $\Delta^{17}\text{O}$  values of  $\text{HNO}_3$  follow this pattern.

Supprimé: the... those of w- and p- $\text{NO}_3^-$  patterns... Interestingly, the  $\Delta^{17}\text{O}$  differences between p- $\text{NO}_3^-$  and  $\text{HNO}_3$  shifts... from positive during cold sampling periods to negative during warm periods. The very ... [5]

Supprimé: The summer pattern... may be... partly derive ue to... from the... involvement of  $^{17}\text{O}$ -depleted peroxy radicals ( $\text{RO}_2$ ) oxidizing  $\text{NO}$  during that season. Another possibility is that the presence of nitrates derived... from  $\text{NO}_x$  that has not yet reached isotopic equilibrium with  $\text{O}_3$ ... However, these mechanisms, individually or together, cannot explain the observed p- $\text{NO}_3^-$  minus  $\text{HNO}_3$  isotopic changes. We propose and subsequent ... [6]

Supprimé: valid... mechanism for the observed shifts. Subsequent increased renewal of  $\text{HNO}_3$  in the plume, with higher  $\Delta^{17}\text{O}$  values in newly formed  $\text{HNO}_3$  as  $\text{NO}_x$ - $\text{O}_3$  equilibrate with time. ... [7]

Supprimé: while the l... larger proportions of p- $\text{NO}_3^-$  formed via the  $\text{N}_2\text{O}_5$  pathway would can... explain the opposite fall-winter patterns. Very low p- $\text{NO}_3^-$   $\Delta^{17}\text{O}$  values observed during warm months may be due to this non-equilibrated  $\text{NO}_x$ , though contribution from  $\text{RO}_2$  oxidation remains a possibility. ... our results show that the separate  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  isotopic signals of  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  are not interchangeable and that their differences... can be used to further our understanding of  $\text{NO}_x$  oxidation and deposition. Future research should investigate all tropospheric nitrate species as well as  $\text{NO}_x$  to refine our understanding of nitrate distribution worldwide and to develop effective emission reduction strategies.¶ ... [8]

## 1 Introduction

Anthropogenic NO<sub>x</sub> (NO and NO<sub>2</sub>) emissions are oxidized to nitrate in the atmosphere in the form of gaseous, wet or particulate forms, HNO<sub>3</sub> being one of the main precursors of p-NO<sub>3</sub><sup>-</sup>. 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<sub>3</sub>, HNO<sub>3</sub> and w-NO<sub>3</sub>).

Triple oxygen isotopes ( $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ ), have been used to decipher atmospheric oxidation pathways of NO<sub>x</sub> leading to ambient nitrate. Michalski et al. (2003) performed the first measurement of  $\delta^{17}\text{O}$  values in atmospheric nitrate. The authors found nitrate highly enriched in  $^{18}\text{O}$  and  $^{17}\text{O}$ , likely due to the transfer of anomalous oxygen atoms from ozone (O<sub>3</sub>) via the NO<sub>x</sub>-ozone photochemical cycle and oxidation to nitrate. During its formation, O<sub>3</sub> inherits abnormally high  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values through mass independent fractionation. The specific  $\delta^{17}\text{O}$  departure from the terrestrial mass dependent fractionation line, named the  $^{17}\text{O}$  anomaly, is often expressed as  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.517 \times \delta^{18}\text{O}$  (Thiemens, 1999). Further investigations suggested that the  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values of w-NO<sub>3</sub><sup>-</sup> and p-NO<sub>3</sub><sup>-</sup> reflect several reactions taking place after the atmospheric emission of NO<sub>x</sub>, i.e., atmospheric oxidation pathways transforming NO<sub>x</sub> 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  $\delta^{18}\text{O}$  differences in w-NO<sub>3</sub><sup>-</sup> 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; Smirnov et al., 2012), transfer of the ozone  $^{17}\text{O}$  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<sub>3</sub><sup>-</sup> samples are not yet widespread. Also rare are the nitrate  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of field samples downwind from NO<sub>x</sub>-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). The few existing studies have chiefly characterized w-NO<sub>3</sub><sup>-</sup> or the sum of p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (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<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> were generally collected together (without differentiation). Therefore, no studies have separately and simultaneously collected and analyzed the HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup>  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values, and discussed these isotopic characteristics of nitrate collected downwind of anthropogenic emitters. While HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> can be in equilibrium (e.g. if p-NO<sub>3</sub><sup>-</sup> is in the form of solid NH<sub>4</sub>NO<sub>3</sub>), this is not always the case, for example, if nitrate is

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Supprimé: (Proemse et al., 2013) Even rarer are the nitrate  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of field samples downwind from NO<sub>x</sub>-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). In those studies,  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values were suggested to be useful to apportion the contribution of emission sources to regional atmospheric nitrate loads.

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Supprimé: However, the signals of precursor NO<sub>x</sub> emitted from the same sources may quickly get modified through isotopic equilibration with O<sub>3</sub>, so that the original source signals may be difficult to recognize.

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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<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> as well as w-NO<sub>3</sub><sup>-</sup> downwind of the source types. The objective of this work was to assess the atmospheric NO<sub>x</sub> reaction pathways and determine processes responsible for the distribution of HNO<sub>3</sub>, and w- and p-NO<sub>3</sub><sup>-</sup> in a mid-latitudinal region.

## 2 Methodology

### 2.1 Regional context

While national reported NO<sub>x</sub> 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 PM<sub>2.5</sub> (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<sub>x</sub> 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<sub>3</sub><sup>-</sup>, HNO<sub>3</sub> and w-NO<sub>3</sub><sup>-</sup>) 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

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Supprimé: Importantly, the rate of HNO<sub>3</sub> production depends on the atmospheric NO<sub>x</sub> amounts and production rates of oxidizing agents (e.g., O<sub>3</sub>, OH, RO<sub>2</sub>; see section 3.3), and further down the chain of reactions, atmospheric HNO<sub>3</sub> participates in forming p-NO<sub>3</sub><sup>-</sup> 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 NO<sub>x</sub>-O<sub>3</sub> isotopic disequilibrium. It is clear our working hypothesis is that

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While national reported NO<sub>x</sub> 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 PM<sub>2.5</sub> (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<sub>x</sub> emissions in Canada, and the area of southern Alberta, characterized by dense gas compressor station and agricultural emissions, have never been investigated. ¶

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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<sub>x</sub> 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<sub>3</sub>) [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<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub> on the Teflon filter](#), <3% breakthrough of HNO<sub>3</sub> from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub><sup>-</sup> and positive bias in HNO<sub>3</sub> 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<sub>3</sub> 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<sub>2</sub> \(nitrous acid\) 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<sub>4</sub>NO<sub>3</sub> 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.](#)

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After the first five sample periods, an experimental active sampling system for NO<sub>2</sub> and NO<sub>x</sub> 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<sub>2</sub>, and one- or two-stage filter pack containing two identical Maxxam Analytics' impregnated filters designed to collect NO<sub>x</sub> (mostly NO due to upstream collection of NO<sub>2</sub>). Oxygen isotopes in NO<sub>2</sub> and NO<sub>x</sub> 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.

Here we report on oxygen isotopes in the simultaneously sampled HNO<sub>3</sub> and p-NO<sub>3</sub>, along with co-sampled w-NO<sub>3</sub> 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.

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.

### 2.3 Analytical procedures

Nitric acid from nylon filters were extracted using 10 mL of 0.01M solution of NaCl. Particulate-NO<sub>3</sub> 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.

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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<sub>3</sub>/L (0.03 N-NO<sub>3</sub> 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  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  ratios of HNO<sub>3</sub>, w-NO<sub>3</sub><sup>-</sup>, and p-NO<sub>3</sub><sup>-</sup>, along with the  $\delta^{15}\text{N}$  values of NH<sub>3</sub>, w-NH<sub>4</sub><sup>+</sup>, p-NH<sub>4</sub><sup>+</sup> and NO<sub>x</sub> (all N isotopic results are in Savard et al., 2017). The present article deals solely with the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values obtained for the three nitrate species. We treated the samples using the chemical conversion and thermal decomposition of N<sub>2</sub>O protocols, providing the ability to simultaneously analyze low-concentration N- and O-containing species (Smirnov 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  $\mu\text{mol NO}_3/\text{L}$ ). Therefore, not all samples could be diluted to produce volumes sufficient for reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub> and subsequent conversion to N<sub>2</sub>O, the final product before isotope analysis. Samples with an initial concentration below 2.3  $\mu\text{mol/L}$  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<sub>2</sub><sup>-</sup>) using a custom-made cadmium column. The final preparation step involved using sodium azide to ultimately produce N<sub>2</sub>O (McIlvin and Altabet, 2005; Smirnov et al., 2012). All extracted N<sub>2</sub>O 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; Smirnov et al., 2012). The utilized approach allows the spectrum of  $\delta^{15}\text{N}$ ,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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<sub>2</sub>O. The laboratory analytical precision (average of replicates) determined during the present study was 0.6 ‰ for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values in gaseous (n=12) and solid nitrates (n=20). For w-NO<sub>3</sub><sup>-</sup>, analytical replicates gave 0.6 and 0.5 ‰, for  $\delta^{18}\text{O}$  (n=3) and  $\delta^{17}\text{O}$  (n=4) values, respectively. The  $\Delta^{17}\text{O}$  values are defined as  $\ln(1+\delta^{17}\text{O}/1000) - 0.516 \times \ln(1+\delta^{18}\text{O}/1000)$ , relative to Vienna Standard Mean Ocean Water (VSMOW).

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### 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  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\text{NH}_4\text{NO}_3$  on the particle filter into  $\text{HNO}_3$  and  $\text{NH}_3$ , 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- $\text{NO}_3^-$  isotopic ratios ( $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) to be generally higher during winter than during summer (see Section 3.4). Moreover, the p- $\text{NO}_3^-$  minus  $\text{HNO}_3$  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  $\delta^{15}\text{N}$  values in  $\text{NH}_3$  and  $\text{NH}_4$ ; 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  $^{17}\text{O}$  anomaly; therefore,  $\Delta^{17}\text{O}$  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- $\text{NO}_3^-$  and  $\text{HNO}_3$  (Elliott et al., 2009).

#### 3.2 Concentrations and isotopic ratios of nitrates in Alberta samples

The range of  $\text{HNO}_3$  concentrations measured by the filters (from 0.01 to 0.15  $\mu\text{g N/m}^3$ ; average of 0.06) are slightly lower than those of p- $\text{NO}_3^-$  (from 0.02 to 0.35  $\mu\text{g N/m}^3$ ; 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  $\mu\text{g N/m}^3$  for  $\text{HNO}_3$  and from 0.007 to 0.45  $\mu\text{g N/m}^3$  for p- $\text{NO}_3^-$  (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

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northern Alberta border revealed similar average concentrations of 0.02  $\mu\text{g N/m}^3$  for both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  (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  $\text{w-NO}_3^-$  samples was 0.15 – 0.48  $\text{mg N/L}$ . 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  $\text{mg N/L}$ , while at the most polluted site in southern Ontario (Longwoods) the volume-weighted mean concentration was approximately 0.3  $\text{mg N/L}$  (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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of  $\text{HNO}_3$  (gas),  $\text{w-}$  and  $\text{p-NO}_3^-$  show no apparent systematic ordering (Table 3; Tables SM-1 and 2), in contrast to what was found for  $\delta^{15}\text{N}$  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  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  have the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages, but not the highest  $\text{w-NO}_3^-$  values; chemical industries show the lowest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages for  $\text{w-}$  and  $\text{p-NO}_3^-$ , but not for  $\text{HNO}_3$ . Though the number of samples were limited,  $\text{w-NO}_3^-$   $\Delta^{17}\text{O}$  values were roughly correlated with the weighted average  $\Delta^{17}\text{O}$  values of  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  in samples covering the same time periods, consistent with scavenging of both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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  $\text{NO}_x$  cycling and oxidation (nitrate derived through combustion in  $\text{O}_2$  would show  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of 23.5 and 0 ‰, respectively). When examining the existing  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data for  $\text{w-}$  and  $\text{p-NO}_3^-$  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  $\delta^{18}\text{O}$  range of atmospheric  $\text{NO}_3^-$  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  $\text{NO}_3^-$  samples are scarce (Table 4). The  $\text{HNO}_3$  range documented here is within the broad spectrum of  $\text{p-NO}_3^-$  values compiled for remote to contaminated sites. Elliott et al. (2009) reported  $\text{HNO}_3$  oxygen results for  $\delta^{18}\text{O}$  values only, with a range of +51.6 to +94.0 ‰ (mean of 77.4), with simultaneously-sampled  $\text{p-NO}_3^-$   $\delta^{18}\text{O}$  values between +45.2 and +92.7 ‰ (mean of 75.2). Those ranges are broader than the  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  values obtained in the present study.

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

The  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  ranges for  $\text{HNO}_3$  identified by sampling period are narrower than those of the simultaneously collected  $\text{p-NO}_3^-$  (Fig. 2; Table SM-1), suggesting that there are additional mechanisms affecting  $\text{HNO}_3$ , or that  $\text{p-NO}_3^-$  is derived from different pathways with more variation in isotopic signatures. Overall, the  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  results for  $\text{HNO}_3$ ,  $\text{w-NO}_3^-$  and  $\text{p-NO}_3^-$

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The  $\text{p-NO}_3^-$ ,  $\text{w-NO}_3^-$  and  $\text{HNO}_3$  values co-vary when identified by source type in the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  space (Fig. 1). The isotopic range for a single source can be as large as 6 ‰ for  $\Delta^{17}\text{O}$  values and 19 ‰ for  $\delta^{18}\text{O}$  values in  $\text{HNO}_3$ , 12 and 17 ‰ in  $\text{w-NO}_3^-$ , and 7 and 21 ‰ in  $\text{p-NO}_3^-$ . Each source type clearly exhibits nitrate  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  with a specific grouping. The CFPP  $\text{w-NO}_3^-$  results show a range similar to the  $\text{HNO}_3$  results, but lower  $\delta^{18}\text{O}$  values than the  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  groups. The few other precipitation samples show  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values generally higher than the  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  samples, again with exception of the chemical and metal industries. ¶

¶ The  $\text{HNO}_3$  samples from a given source type tend to have a higher  $\delta^{18}\text{O}$  value for a given  $\Delta^{17}\text{O}$  value than  $\text{p-NO}_3^-$  (or vice versa; Fig. 1). These observations suggest that the contribution of oxidation pathways leading to  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  are not identical, or that there is an isotope fractionation in the conversion of  $\text{HNO}_3$  to  $\text{p-NO}_3^-$ . ¶

¶ Regarding the potential for identifying nitrate sources, it appears that using  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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 ( $\text{p-}$  and  $\text{w-NO}_3^-$ ) or overlapping source results ( $\text{HNO}_3$ ; 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  $\text{NO}_x$  oxidation (Fig. 1; see [10]). 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]

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clearly show higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during cold periods relative to warm periods (Fig. 2), with the exception of  $\text{HNO}_3$   $\delta^{18}\text{O}$  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  $0^\circ\text{C}$  (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- $\text{NO}_3^-$ .

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,  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) is produced through reactions of air  $\text{N}_2$  with atmospheric  $\text{O}_2$  at high temperatures (reactions R1; Table 5). Then,  $\text{NO}_x$  cycles between  $\text{NO}$  and  $\text{NO}_2$  through a series of reactions involving sunlight (R5),  $\text{O}_3$  (R2, R4), and peroxy ( $\text{HO}_2$ ) or alkyl peroxy ( $\text{RO}_2$ ) radicals (R3; Morin et al., 2007; Fang et al., 2011; Michalski et al., 2014; here we use  $\text{RO}_2$  to refer collectively to  $\text{HO}_2$  and  $\text{RO}_2$ ).

The oxidation of  $\text{NO}_x$  (specifically  $\text{NO}_2$ ) to  $\text{HNO}_3$  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,  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  (R8),  $\text{HNO}_3$  is likely to be retained on the reaction particle as p- $\text{NO}_3^-$  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  $\text{NO}_3^-$  with hydrocarbons (R12) since they are predicted to have a minimal contribution to nitrate formation in this region (Alexander et al., 2009). Finally,  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of w- and p- $\text{NO}_3^-$  formed during summer are lower than those during winter due to higher contribution from the  $\text{N}_2\text{O}_5$  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- $\text{NO}_3^-$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data presented here follow the same patterns for warm and cold months (Fig. 2). In contrast, the less commonly studied  $\text{HNO}_3$  shows similar  $\delta^{18}\text{O}$  values during warm and cold seasons, but summer  $\Delta^{17}\text{O}$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  samples (n of w- $\text{NO}_3^-$  too low) with meteorological and air quality parameters measured routinely at nearby monitoring stations where available (Table SM-3). We found that the p- $\text{NO}_3^-$  and  $\text{HNO}_3$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values correlate with RH, with p- $\text{NO}_3^-$  values showing stronger statistical links than  $\text{HNO}_3$  (Table 6). The  $\text{N}_2\text{O}_5$  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- $\text{NO}_3^-$   $\delta^{18}\text{O}$ , p- $\text{NO}_3^-$   $\Delta^{17}\text{O}$ , and  $\text{HNO}_3$   $\Delta^{17}\text{O}$ . These negative links likely arise since

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$N_2O_5$  is more stable under cold conditions, leading to a higher contribution of R8. The stronger links with  $p\text{-NO}_3^-$  may be due to R8 taking place on surfaces (such as particles) with liquid water, which is likely to retain the  $\text{HNO}_3$  as  $p\text{-NO}_3^-$  rather than release it to the gas phase. Therefore, in winter, R8 may contribute more to  $p\text{-NO}_3^-$  than to  $\text{HNO}_3(\text{g})$ . Moreover, the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values for both  $p\text{-NO}_3^-$  and  $\text{HNO}_3$  were found for fall-winter samples collected at high RH (76 %) and low temperature ( $-10^\circ\text{C}$ ). In contrast, the lowest  $p\text{-NO}_3^-$  isotopic values were found for samples with similar proportions of  $\text{HNO}_3$  and  $p\text{-NO}_3^-$ , and sampled during moderately humid (60-63 %) and warm ( $8\text{-}20^\circ\text{C}$ ) periods. The accompanying shift in isotopic differences between  $p\text{-NO}_3^-$  and  $\text{HNO}_3$ , will help infer the mechanisms dominating during the cold and warm periods (Section 4.2).

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Concentrations of oxidants, co-contaminants (e.g.,  $\text{SO}_4^-$  aerosols) and  $\text{NO}_x$  influence the dominance and rates of the discussed reactions (Brown et al., 2006; Michalski et al., 2014). However, while temperature, RH and  $\text{O}_3$  are well captured within a 5 km radius, other pollutant measurements like continuous  $\text{SO}_2$ ,  $\text{PM}_{2.5}$  and  $\text{NO}_x$  can have large gradients near sources, therefore it is not surprising that no correlations were found with  $\text{SO}_2$  or  $\text{PM}_{2.5}$  measured at sites 4-5 km away (Table 6). Surprisingly, only the  $p\text{-NO}_3^-$   $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values.

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### 3.5 Comparison with high-latitude $p\text{-NO}_3^-$

An interesting aspect of the Alberta  $p\text{-NO}_3^-$  cold-period  $\Delta^{17}\text{O}$  ranges is that they compare relatively well with the range obtained for the Canadian Arctic (Fig. 4), during winter, when nighttime conditions and the  $\text{N}_2\text{O}_5$  pathway prevail without interruption (Morin et al., 2008; for comparison with  $\text{HNO}_3$  values see Fig. SM-4). This observation supports the suggestion that the  $\text{N}_2\text{O}_5$  pathway produces around 90 % of nitrates during mid-latitude cold months (Michalski et al., 2003; Section 4.1). The  $\delta^{18}\text{O}$  ranges of cold months are similar in Alberta and in the Arctic. This similarity goes against previous suggestions that at higher latitudes, nitrate  $\delta^{18}\text{O}$  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  $\text{N}_2\text{O}_5$  pathway during the Arctic winter (Fang et al., 2011).

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The  $\Delta^{17}\text{O}$  departure between the Alberta and Arctic winter parallel lines is about 3 ‰. Such difference is slightly larger than the one calculated for winter  $\text{NO}_3^-$  at 80 and 40°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  $\Delta^{17}\text{O}$  values is similar at the mid- and high-latitude 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  $\Delta^{17}\text{O}$  values of  $\text{NO}_x$  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  $\text{N}_2\text{O}_5$  pathways during summer and winter, respectively. Finally, the

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$\Delta^{17}\text{O}$  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 $\text{HNO}_3$ and $\text{p-NO}_3^-$

As far as the isotopic characteristics are concerned, an important feature to keep in mind is that the  $\text{HNO}_3$  of central and southern Alberta has distinct properties relative to simultaneously sampled  $\text{p-NO}_3^-$ . In practical terms, the relationships between the simultaneously sampled  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  are of four types (Fig. 3): (i)  $\text{HNO}_3$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  are both lower than  $\text{p-NO}_3^-$ ; (ii)  $\text{HNO}_3$  has lower  $\Delta^{17}\text{O}$  but higher  $\delta^{18}\text{O}$  values than  $\text{p-NO}_3^-$ ; (iii)  $\text{HNO}_3$  has higher  $\delta^{18}\text{O}$  values and similar  $\Delta^{17}\text{O}$  ones relative to  $\text{p-NO}_3^-$ ; and (iv)  $\text{HNO}_3$  has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than  $\text{p-NO}_3^-$  (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  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  in northeastern USA with similar seasonal changes of  $\delta^{18}\text{O}$  differences (no  $\Delta^{17}\text{O}$  measurement). The  $\text{HNO}_3$   $\delta^{18}\text{O}$  were generally similar or lower than the  $\text{p-NO}_3^-$  values during winter and fall, and slightly to much higher during spring and summer, with the spring and autumn  $\text{p-NO}_3^-$ - $\text{HNO}_3$  relationships being roughly intermediate between the winter and summer ones. The average  $\delta^{18}\text{O}$  difference of  $\text{p-NO}_3^-$  minus  $\text{HNO}_3$  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  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  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  $\text{NO}_x$  source.

## 4 Discussion

### 4.1 Estimation of $\Delta^{17}\text{O}$ values of $\text{NO}_x$ precursor to the studied nitrates - Highlighting oxidation mechanisms

In the present sub-section, we estimate the  $\Delta^{17}\text{O}$  values of  $\text{NO}_2$  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  $\text{N}_2\text{O}_5$  due to interaction with  $\text{O}_3$  (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  $\text{H}_2\text{O}$  (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  $\text{NO}_2$ , 1/6 from  $\text{O}_3$  and 1/6 from  $\text{H}_2\text{O}$ , while the second produces nitrates via R6 with 2 out of 3 O atoms coming from  $\text{NO}_2$  and 1/3 from OH (e.g., Michalski et al., 2003). Using these proportions with the Alberta  $\Delta^{17}\text{O}$  values of  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  in weighted averages allows us to make a rough estimation of the maximum and minimum  $\Delta^{17}\text{O}$  values of  $\text{NO}_2$  oxidized to nitrates in the air masses sampled. The calculations assume the O from  $\text{O}_3$  contributes a signal of ~39 ‰ as was recently measured (Vicars et al., 2014) and that  $\Delta^{17}\text{O}$  of OH and  $\text{H}_2\text{O}$  are zero. The estimated  $\text{NO}_2$   $\Delta^{17}\text{O}$  values for fall-

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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<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> 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<sub>2</sub> Δ<sup>17</sup>O ranges indicate that the potential parent NO<sub>2</sub> had a smaller <sup>17</sup>O anomaly than O<sub>3</sub> (39 ‰; Vicars and Savarino, 2014) or NO<sub>2</sub> in isotopic equilibrium with O<sub>3</sub> alone (45 ‰; Michalski et al., 2014) in all possible scenarios.

Two mechanisms could be responsible for the Δ<sup>17</sup>O differences between these estimates and NO<sub>2</sub> in isotopic equilibrium with O<sub>3</sub>. One is the competition of R3 with R2 in oxidizing NO to NO<sub>2</sub>, since RO<sub>2</sub> will decrease the Δ<sup>17</sup>O values relative to an ozone-only equilibrium. The relative reaction rates of R2 and R3 have previously been presumed to control the NO<sub>2</sub> isotopic composition (e.g., Alexander et al., 2009) based on the assumption of isotopic steady state. A larger contribution of RO<sub>2</sub> is expected in the NO<sub>2</sub> precursors for summer relative to winter, since biogenic VOCs that are major sources of RO<sub>2</sub> radicals are much higher in the summer (e.g., Fuentes and Wang, 1999). This suggestion is consistent with the lower Δ<sup>17</sup>O ranges in summer reported here. A second possibility is that the nitrates were formed from some NO<sub>x</sub> that did not reach isotopic steady state with O<sub>3</sub> retaining some of its original signature (assumed to be Δ<sup>17</sup>O=0 ‰). Most studies have assumed that isotopic steady state is established between O<sub>3</sub> and NO<sub>2</sub> within a few minutes after emission of NO<sub>x</sub> from a combustion source – or at least, that nitrate formation is negligible before NO<sub>x</sub> isotopic equilibrium is reached. However, recent modeling by Michalski et al. (2014) suggests that isotopic equilibration of NO<sub>x</sub> with O<sub>3</sub> could take several minutes up to a few hours at the relatively low O<sub>3</sub> concentrations in rural Alberta. At the measured average wind speeds on site of 8-19 km hr<sup>-1</sup>, transit times from the nearest sources to observation sites are estimated to be 9-55 minutes. While the fraction of NO<sub>x</sub> converted to nitrate in this transit time may be small, these are large sources of NO<sub>x</sub> in an area with very low background nitrates. For example, a plume containing 10 ppb of NO<sub>2</sub> mixing with background air with 0.1 ppt of OH (Howell et al., 2014) would produce HNO<sub>3</sub> via R6 at a rate of 0.011 μg N m<sup>-3</sup> min<sup>-1</sup> 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<sub>3</sub> 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<sub>x</sub> that had not yet reached isotopic steady state with O<sub>3</sub>. These two mechanisms are not exclusive and could both contribute to lower NO<sub>x</sub> and therefore nitrate, Δ<sup>17</sup>O values.

An additional piece of evidence suggests that the NO<sub>x</sub> plumes themselves, rather than ambient conditions, are the source of low-Δ<sup>17</sup>O nitrates in these samples. There is a strong correlation between the total nitrate Δ<sup>17</sup>O values and the maturity of the plume as expressed by the NO<sub>2</sub> concentration divided by sum of HNO<sub>3</sub> and p-NO<sub>3</sub> concentrations (Fig. 5). This observation is consistent with the unequilibrated NO<sub>2</sub> hypothesis. However, it does not rule out the possible contribution of RO<sub>2</sub>, since VOC releases from the NO<sub>x</sub> sources could lead to elevated RO<sub>2</sub> concentrations in the plume.

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#### 4.2 Causes of shifts in HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences

A challenging question is why do the HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences shift seasonally (Fig. 3)? One factor that may influence the relationship between HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> is mass-dependent isotopic equilibrium between NH<sub>4</sub>NO<sub>3</sub> and HNO<sub>3</sub> (R10); however, this mechanism would result in higher δ<sup>18</sup>O in p-NO<sub>3</sub><sup>-</sup> and unchanged Δ<sup>17</sup>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<sub>2</sub>O<sub>5</sub> pathway is likely to produce more p-NO<sub>3</sub><sup>-</sup> than HNO<sub>3</sub>(g), which would result in a higher contribution from ozone and explain why δ<sup>18</sup>O and Δ<sup>17</sup>O values are both higher in p-NO<sub>3</sub><sup>-</sup>. A previous study addressing why p-NO<sub>3</sub><sup>-</sup> 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 δ<sup>18</sup>O and Δ<sup>17</sup>O values were lower in p-NO<sub>3</sub><sup>-</sup> than in HNO<sub>3</sub> (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<sub>3</sub> dry deposits to surfaces more rapidly than p-NO<sub>3</sub><sup>-</sup> (Zhang et al., 2009; Benedict et al., 2013), which would create the discussed isotopic shifts in the situation where NO<sub>2</sub> has low Δ<sup>17</sup>O values in a fresh plume. The first nitrates formed in the plume shortly after emission from the NO<sub>x</sub> source have low δ<sup>18</sup>O and Δ<sup>17</sup>O values, either because NO<sub>x</sub> has not yet reached isotopic steady state with O<sub>3</sub> or because it reacted with <sup>17</sup>O-poor RO<sub>2</sub> present in the plume due to VOC emissions. Those nitrates that form as p-NO<sub>3</sub><sup>-</sup> or that partition to p-NO<sub>3</sub><sup>-</sup> remain in the plume for longer than HNO<sub>3</sub>, which is removed from the plume rapidly upon contact with vegetation or other surfaces. As the plume travels, the NO<sub>x</sub> becomes more enriched, and the newly formed nitrates take on higher δ<sup>18</sup>O and Δ<sup>17</sup>O values. However, p-NO<sub>3</sub><sup>-</sup> collected further downwind will derive from a mixture of low-δ<sup>18</sup>O and -Δ<sup>17</sup>O p-NO<sub>3</sub><sup>-</sup> formed earlier, plus high-δ<sup>18</sup>O and -Δ<sup>17</sup>O p-NO<sub>3</sub><sup>-</sup> formed more recently, while HNO<sub>3</sub> will have a larger proportion formed more recently and will therefore have higher δ<sup>18</sup>O and Δ<sup>17</sup>O values. The fact that we find the lowest isotopic values in summer p-NO<sub>3</sub><sup>-</sup> 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<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences between cold and warm sampling periods – differential N<sub>2</sub>O<sub>5</sub> contribution resulting in higher Δ<sup>17</sup>O values in p-NO<sub>3</sub><sup>-</sup> than in HNO<sub>3</sub>, and differential deposition resulting in lower Δ<sup>17</sup>O values in p-NO<sub>3</sub><sup>-</sup> – would essentially compete against each other, with local conditions and chemistry influencing the results. In winter, when the N<sub>2</sub>O<sub>5</sub> pathway is most important, the first mechanism dominates, as supported by the observation that p-NO<sub>3</sub><sup>-</sup> concentrations are higher during that season (trend *i*). Conversely, in summer, when the N<sub>2</sub>O<sub>5</sub> 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 δ<sup>18</sup>O differences. For instance, kinetic fractionation may be involved in the production of trend *iii*.

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In summary, examining the isotopic relationship of HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> (Fig. 3), reveals the complexity of anthropogenic NO<sub>x</sub> oxidation mechanisms. The negative isotopic differences between p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> during warm months may reflect differential removal rates from plumes containing NO<sub>2</sub> temporarily low in <sup>17</sup>O.

#### 5 4.3 - Low δ<sup>18</sup>O and Δ<sup>17</sup>O trends in global w- and p-NO<sub>3</sub><sup>-</sup> - 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<sub>x</sub> 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<sub>3</sub> and oxidation through the well-known OH and N<sub>2</sub>O<sub>5</sub> oxidation paths. However, NO<sub>2</sub> not in isotopic equilibrium with O<sub>3</sub>, and/or NO reacted with RO<sub>2</sub> 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<sub>2</sub> and/or HO<sub>2</sub> 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?

15 The full Δ<sup>17</sup>O and δ<sup>18</sup>O ranges for p-NO<sub>3</sub><sup>-</sup>, w-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (between 13.8 and 20.5 ‰, 48.4 and 83.2 ‰; Table 4) compare well with the isotopic ranges obtained for bulk deposition NO<sub>3</sub><sup>-</sup> 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 δ<sup>18</sup>O and Δ<sup>17</sup>O values.

Previous work in the Athabasca region reported very low δ<sup>18</sup>O and near-zero Δ<sup>17</sup>O values for p-NO<sub>3</sub><sup>-</sup> 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<sub>2</sub>. Similar isotopic signatures are very likely produced in source emissions of NO<sub>x</sub> in the studied Edmonton and Vauxhall areas (e.g., CFPP, gas compressors, industries). This source signature may persist into p-NO<sub>3</sub> collected close to the sources. Within the first few hours in the atmosphere (less, in polluted areas), the NO<sub>x</sub> δ<sup>18</sup>O and Δ<sup>17</sup>O values rapidly increase due to isotope exchange with O<sub>3</sub> (R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub> and O<sub>3</sub> formation, Table 5; Michalski et al., 2014) and reach isotopic equilibrium. Though the e-folding lifetime for NO<sub>x</sub> oxidation to nitrates may be longer than these few hours, depending on the NO<sub>x</sub>/VOC ratio, only a fraction of the oxidized source NO<sub>x</sub> 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 Δ<sup>17</sup>O values within 12 km of the emission sites, and where direct stack emissions of p-NO<sub>3</sub><sup>-</sup> were ~5000 times lower than NO<sub>x</sub> emissions (Wang et al., 2012).

35 In a methodological test study, we obtained low values for w-NO<sub>3</sub><sup>-</sup> sampled near a high traffic volume highway in Ontario, Canada (Smirnov et al., 2012). Low δ<sup>18</sup>O and Δ<sup>17</sup>O values in atmospheric nitrates during warm months (65 and 20 ‰ or less,

Supprimé: the δ<sup>18</sup>O and Δ<sup>17</sup>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<sub>3</sub><sup>-</sup>,

Supprimé: The final isotopic values are derived from the O<sub>3</sub>-NO<sub>x</sub> (Leighton) cycle and competing oxidation by RO<sub>2</sub>, possibly not yet at isotopic steady state - followed by the OH and N<sub>2</sub>O<sub>5</sub> (O<sub>3</sub>) oxidation pathways in proportions that vary with the periods of sampling (Fig. 4).

Supprimé: likely

Supprimé: s

Supprimé: NO<sub>x</sub>

Supprimé: Δ

Supprimé: at disequilibrium with O<sub>3</sub>. ¶

Supprimé: 3

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

Supprimé: sampled

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Supprimé: 5

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Supprimé: different source types,

Supprimé: appear near the O<sub>2</sub>-end of the O<sub>2</sub>-O<sub>3</sub>-NO<sub>x</sub> line (Fig. 46)

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Supprimé: via many iterations of the photochemical NO<sub>x</sub>-O<sub>2</sub>-O<sub>3</sub> 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  $\delta^{18}\text{O}$  values in w- $\text{NO}_3^-$  from a polluted city (Fang et al., 2011), in p- $\text{NO}_3^-$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values in summer nitrates may reflect the involvement of air masses that include nitrates from oxidation of  $\text{NO}_2$  with light isotopes in plumes. In such cases, while not ruling out a higher contribution from  $\text{RO}_2$  oxidation of  $\text{NO}$ , it is also possible that significant portions of the collected nitrate were formed before the  $\text{NO}_x$ - $\text{O}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  may reflect relative proximity to anthropogenic N emitters in general. Further research work on plume  $\text{NO}_x$  to nitrates chemical mechanisms may help to validate this suggestion. In the future, the assumption of  $\text{NO}_x$  isotopic steady state with  $\text{O}_3$  should be explored, given recent findings (Michalski et al., 2014), the critical importance of  $\text{NO}_x$  isotope characteristics on resulting nitrate isotopic values (Alexander et al., 2009), and the suggestion regarding the evolution of  $\text{NO}_x$ - $\text{NO}_3^-$  signals in fresh anthropogenic plumes (present study).

## 5 Conclusion

The  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  from anthropogenic sources in central and southern Alberta, simultaneously collected with wind sector-based conditional sampling systems produced  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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 ( $\text{HNO}_3$ ) 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- $\text{NO}_3^-$  in these samples generally shows higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than  $\text{HNO}_3$  in the fall-winter period as the heterogeneous  $\text{N}_2\text{O}_5$  pathway favours the production of p- $\text{NO}_3^-$ . In contrast,  $\text{HNO}_3$  has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during warm periods, which we propose is due to faster dry deposition rates relative to p- $\text{NO}_3^-$  in the event that low- $\Delta^{17}\text{O}$   $\text{NO}_2$  is oxidized in the plume. The mechanisms conferring nitrate with relatively low isotopic values, whether oxidation before  $\text{NO}_x$ - $\text{O}_3$  equilibrium is reached or higher contributions from  $\text{RO}_2$ , 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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values may reflect nitrates produced from undifferentiated anthropogenic  $\text{NO}_x$  emissions.

Supprimé: favour  $\text{RO}_2$  reactions and/or

Supprimé:  $\text{NO}_x$

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

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Supprimé: five different

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

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

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

Supprimé: Moreover

Supprimé:  $\text{NO}_x$

Supprimé: before reaching isotopic steady state with  $\text{O}_3$

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Supprimé: p- $\text{NO}_3^-$

Supprimé: prone

Supprimé: happen

Future research should explore the assumption of NO<sub>x</sub> isotopic equilibration with O<sub>3</sub>, given the critical importance of NO<sub>x</sub> 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<sub>y</sub>, 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.

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**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 <sub>x</sub> sources; fertilizer plant largest NH <sub>3</sub> 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 <sub>3</sub> and NO <sub>x</sub> source, oil refinery major NO <sub>x</sub> source

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

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5 **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)	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$
<i>Teflon filters</i> p-NO <sub>3</sub> <sup>-</sup> (19)	2	1
<i>Nylon filters</i> HNO <sub>3</sub> (18)	1	0.7

10 **Table 3. Average oxygen isotopic ratios (‰) for NO<sub>3</sub><sup>-</sup> sampled as gas (HNO<sub>3</sub>), w (precipitation) and p (particulate matter) relative to VSMOW.**

Matrix Source	Gas			w			p		
	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$
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)	- (3)	63.1 (3)	24.5 (2)	- (3)	26.4 (3)			
City traffic	65.7 (3)	67.2 (2)	59.6 (3)	21.2 (3)	24.4 (2)	22.5 (3)			
<b>Mean</b>	<b>66.8</b>	<b>66.0</b>	<b>62.6</b>	<b>23.0</b>	<b>24.3</b>	<b>23.4</b>			

(n): number of sampling periods characterized



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

$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	Regional context	Location	Authors
<b>HNO<sub>3</sub></b>				
62.4-81.7	19.3-29.0	Various contaminated sites	Alberta, Canada	<i>This study</i>
<b>p-NO<sub>3</sub><sup>-</sup></b>				
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	<i>This study</i>
<b>w-NO<sub>3</sub><sup>-</sup></b>				
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	Smirnov 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	<i>This study</i>
<b>Undifferentiated and Bulk NO<sub>3</sub><sup>-</sup></b>				
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	<i>This study</i>

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<sub>3</sub> and p-NO<sub>3</sub> isotopic results.

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**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) $\text{O}_2 + \text{Q} \rightarrow \text{O} + \text{O} + \text{Q}$ ; $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$ ; $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	
(R2) $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3$ ; $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	
(R3) $\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO}$	(R4) $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$
(R5) $\text{NO}_2 + h\nu$ (sunlight) $\rightarrow \text{NO} + \text{O}$	
(R6) $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	(R7) $\text{NO}_2 + \text{NO}_3^- \rightleftharpoons \text{N}_2\text{O}_5$
	(R8) $\text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{surface}) \rightarrow 2\text{HNO}_3(\text{aq})^*$
(R9) $\text{HNO}_3(\text{g}) \rightleftharpoons \text{HNO}_3(\text{aq})^* \rightarrow \text{NO}_3^-(\text{aq})^* + \text{H}^+(\text{aq})$	
(R10) $\text{HNO}_3(\text{g}) + \text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_4\text{NO}_3(\text{s})$	
(R11) $\text{HNO}_3(\text{g}) + \text{CaCO}_3(\text{s}) \rightarrow \text{Ca}(\text{NO}_3)_2(\text{s}) + \text{HCO}_3^-$	
(R12) $\text{NO}_3^- + \text{HC}_2(\text{CH}_3)_2\text{S} \rightarrow \text{HNO}_3 + \text{products}$	

*Q* is a stable molecule of high energy; *M* is either O<sub>2</sub> or N<sub>2</sub>; RO<sub>2</sub> stands for both HO<sub>2</sub> and alkyl peroxy. HC stand for hydrocarbons. \*This aqueous nitrate may be on a particle.

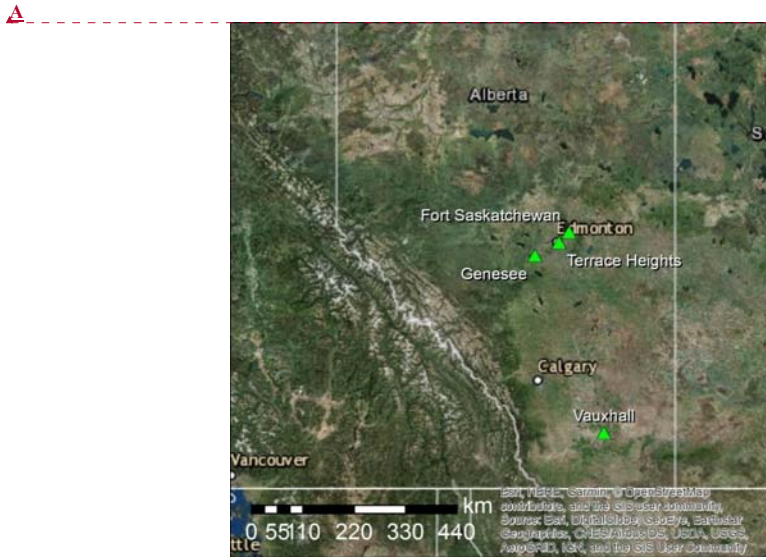
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Table 6. Correlations of NO<sub>3</sub><sup>-</sup> isotopic results (‰) with meteorological parameters and concentration (or ratio) of co-contaminants.

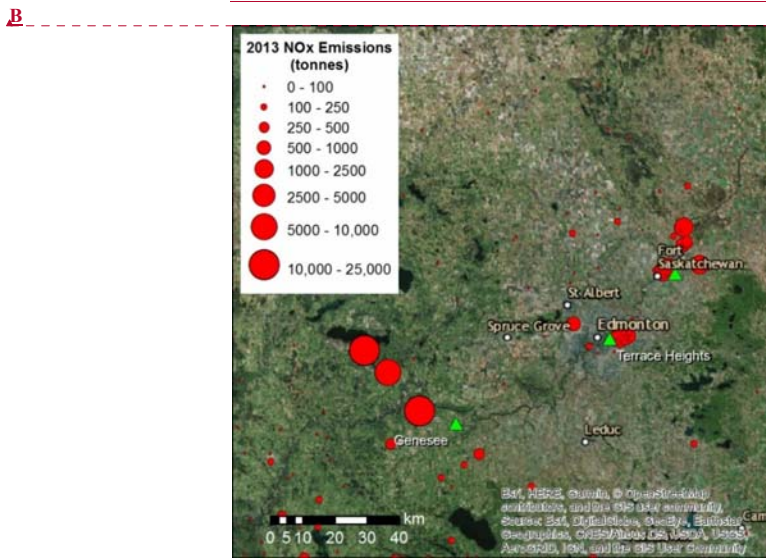
	Relative Humidity		Temperature		Daylight (fraction)		PM	SO <sub>2</sub>	O <sub>3</sub>	
	r	R <sup>2</sup>	r	R <sup>2</sup>	r	R <sup>2</sup>	r	r	r	R <sup>2</sup>
HNO <sub>3</sub>										
δ <sup>18</sup> O	<b>0.8</b>	0.59	-0.4		-0.3		0.1	0.0	-0.29	
n	8		15		15		13	13		13
Δ <sup>17</sup> O	0.6		<b>-0.5</b>	0.24	-0.4		0.4	0.3	-0.03	
n	8		15		15		13	13		13
p-NO <sub>3</sub> <sup>-</sup>										
δ <sup>18</sup> O	<b>0.9</b>	0.79	<b>-0.6</b>	0.34	<b>-0.6</b>	0.35	0.1	0.5	<b>-0.61</b>	0.38
n	7		15		15		12	12		12
Δ <sup>17</sup> O	<b>0.9</b>	0.73	<b>-0.6</b>	0.34	<b>-0.7</b>	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

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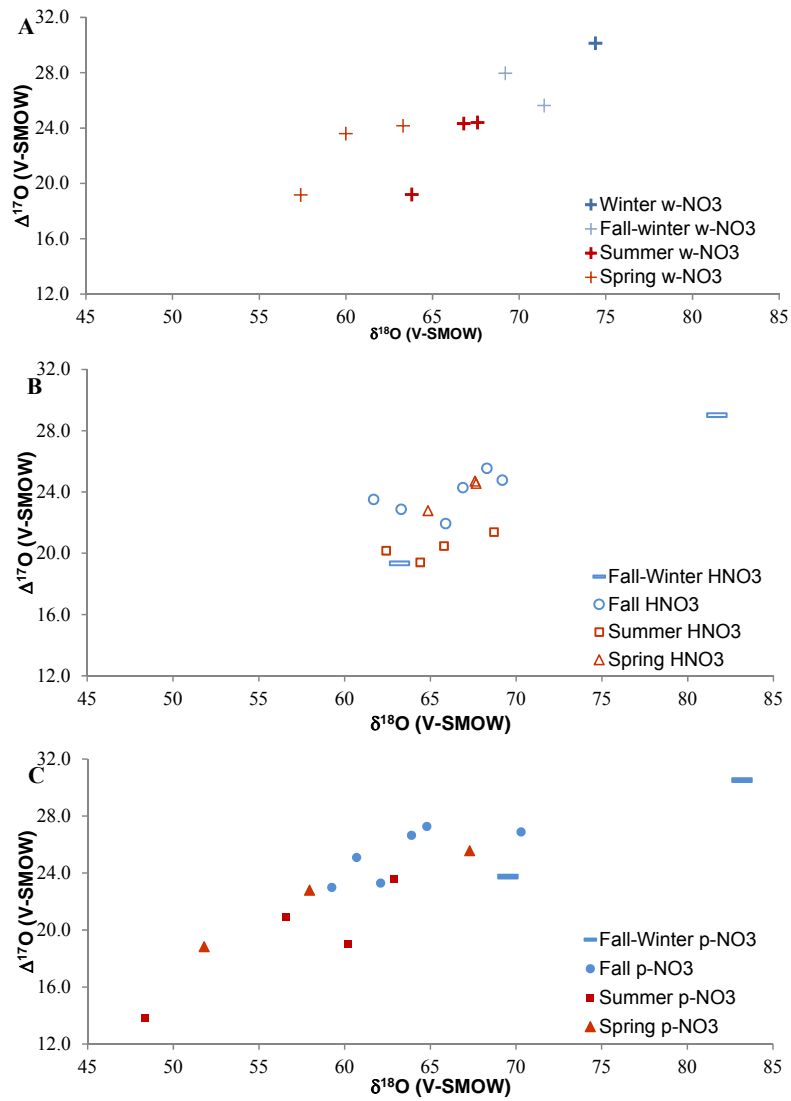


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5 **Figure 1.** Aerial images showing sampling sites (green triangles) in central and southern Alberta (A), and in the greater Edmonton area (B), along with emissions of NO<sub>x</sub> as tonnes of NO<sub>x</sub> reported to the National Pollutant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

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5 Figure 2: Triple O isotopic results (‰) obtained for simultaneously collected atmospheric HNO<sub>3</sub> (A), w-NO<sub>3</sub><sup>-</sup> (B) and p-NO<sub>3</sub><sup>-</sup> (C), in Alberta, identified by sampling periods (cold months - blue; warm months - red).

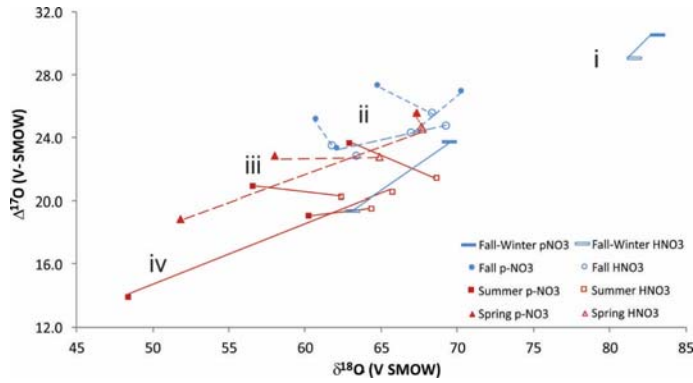


Figure 3: Line-connected  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values (‰) for simultaneously collected  $\text{HNO}_3$  (empty symbols) and  $\text{p-NO}_3^-$  (solid symbols) from cold (blue) and warm (red) sampling periods.

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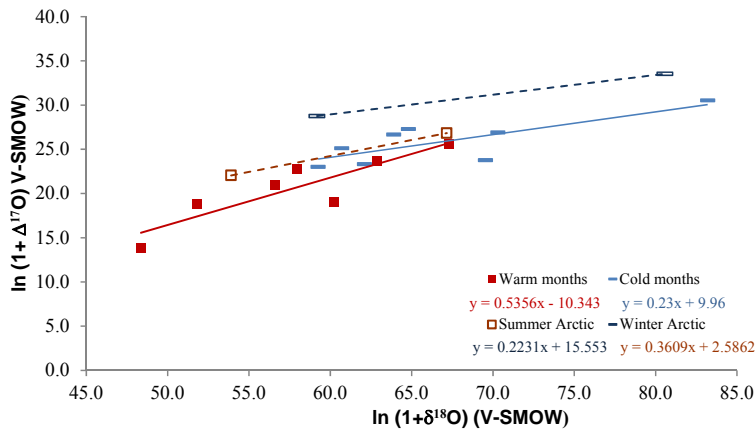
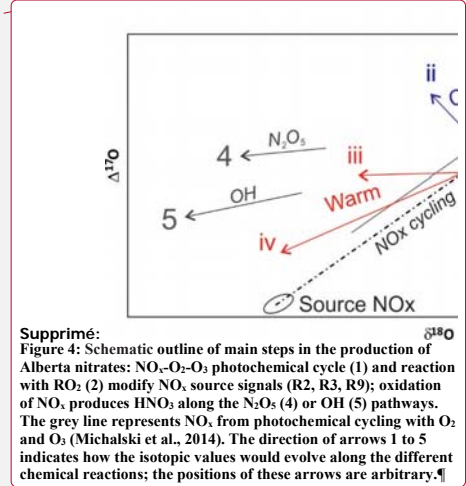


Figure 4: Isotopic results (‰) for  $\text{p-NO}_3^-$  identified by sampling periods (solid lines), compared with summer and winter trends obtained for Arctic sites (dashed lines; derived from  $\ln(1+\delta)$  in Morin et al., 2008).



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Figure 4: Schematic outline of main steps in the production of Alberta nitrates:  $\text{NO}_x\text{-O}_3\text{-O}_2$  photochemical cycle (1) and reaction with  $\text{RO}_2$  (2) modify  $\text{NO}_x$  source signals (R2, R3, R9); oxidation of  $\text{NO}_x$  produces  $\text{HNO}_3$  along the  $\text{N}_2\text{O}_5$  (4) or OH (5) pathways. The grey line represents  $\text{NO}_x$  from photochemical cycling with  $\text{O}_2$  and  $\text{O}_3$  (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. ¶

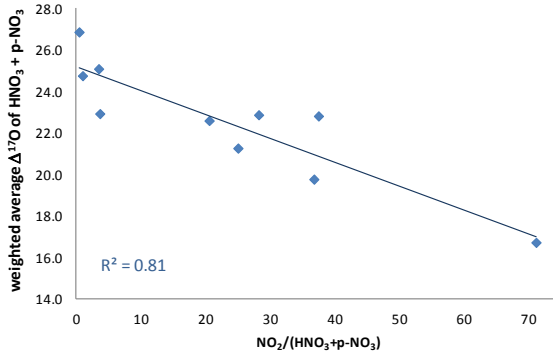


Figure 5: Weighted average  $\Delta^{17}\text{O}$  (‰) for the sum of dry nitrates as a function of  $\text{NO}_2$  concentration divided by  $\text{p-NO}_3$  plus  $\text{HNO}_3$  concentrations, a ratio indicative of the maturity of a plume.

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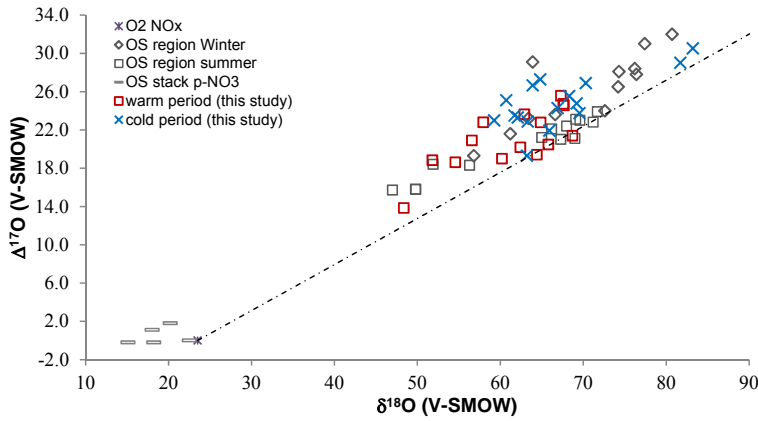


Figure 6: Isotopic ratios (‰) for atmospheric  $\text{p-NO}_3^-$ ,  $\text{w-NO}_3^-$  and  $\text{HNO}_3$  samples in cold and warm periods from central and southern Alberta (this study), compared with previously published winter and summer bulk and throughfall deposition samples from the oil sands (OS) region from northern Alberta (Proemse et al., 2013), and  $\text{p-NO}_3^-$  in-stack emissions data for an OS upgrader located in the same region (Proemse et al., 2012). The grey dotted line connects  $\text{NO}_x$  from theoretical combustion with  $\text{O}_2$  isotopic composition and at isotopic equilibrium with tropospheric  $\text{O}_3$  (Michalski et al., 2014).

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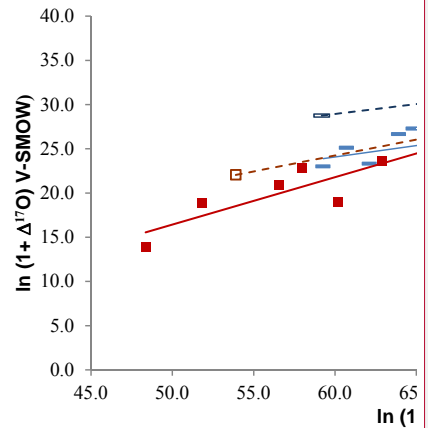


Figure 6: Isotopic results (‰) for  $\text{p-NO}_3^-$  identified by sampling periods (solid lines), compared with summer and winter trends obtained for Arctic sites (dashed lines; derived from  $\ln(1 + \delta)$  in Morin et al., 2008).

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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<sub>3</sub>/L (0.03 N-NO<sub>3</sub> umol/L). The concentration for NO and NO<sub>2</sub> collected with samplers of Maxxam Analytics were determined by Maxxam Analytics using an ion chromatograph.

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

The p-NO<sub>3</sub><sup>-</sup>, w-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> values co-vary when identified by source type in the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  space (Fig. 1). The isotopic range for a single source can be as large as 6 ‰ for  $\Delta^{17}\text{O}$  values and 19 ‰ for  $\delta^{18}\text{O}$  values in HNO<sub>3</sub>, 12 and 17 ‰ in w-NO<sub>3</sub><sup>-</sup>, and 7 and 21 ‰ in p-NO<sub>3</sub>. Each source type clearly exhibits nitrate  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  with a specific grouping. The CFPP w-NO<sub>3</sub><sup>-</sup> results show a range similar to the HNO<sub>3</sub> results, but lower  $\delta^{18}\text{O}$  values than the HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> groups. The few other precipitation samples show  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values generally higher than the p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> samples, again with exception of the chemical and metal industries.

The HNO<sub>3</sub> samples from a given source type tend to have a higher  $\delta^{18}\text{O}$  value for a given  $\Delta^{17}\text{O}$  value than p-NO<sub>3</sub><sup>-</sup> (or *vice versa*; Fig. 1). These observations suggest that the contribution of oxidation pathways leading to HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> are not identical, or that there is an isotope fractionation in the conversion of HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup>.

Regarding the potential for identifying nitrate sources, it appears that using  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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-  $\text{NO}_3$ ) or overlapping source results ( $\text{HNO}_3$ ; 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  $\text{NO}_x$  oxidation (Fig. 1; see Section 3.4). 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.

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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.

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The Alberta nitrate values do not fall on a single line but, rather, show a vertical extent in the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  sets as linear.

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Considering the relevant oxidation reactions shown in Table 5, anthropogenic atmospheric nitrates incorporate O atoms from three main molecules,  $\text{O}_2$  (via  $\text{RO}_2$  - R3, and possibly source  $\text{NO}_x$ - R1),  $\text{O}_3$  (via  $\text{NO}_2$ ,  $\text{NO}_3^-$  and  $\text{N}_2\text{O}_5$  - R2, R4, R7-R8) and  $\text{H}_2\text{O}$  (via OH, R5-R6). These molecules carry distinct isotopic signals that will partly determine the final  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of the nitrate products. The  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of  $\text{O}_2$  are 23.5 and 0 ‰, respectively. Anthropogenic emitters involving combustion ( $\text{O}_2$ ) may generate primary  $\text{NO}_x$  at or near sources that tend to carry low  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values (Zel'dovich, 1946; Lavoie et al., 1969). This primary  $\text{NO}_x$  (>90 % emitted as NO) cycles through  $\text{NO}$ - $\text{NO}_2$ - $\text{O}_3$ - $\text{NO}$  numerous times before it is removed in R6. OH typically has negative  $\delta^{18}\text{O}$  values and a  $\Delta^{17}\text{O}$  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  $\delta^{18}\text{O}$  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  $\text{H}_2\text{O}$  vapour (Walters and Michalski, 2016), we calculated that the  $\delta^{18}\text{O}$  values would range between -83 and -62 ‰. Peroxy radicals mostly derive from  $\text{O}_2$  at mid latitudes (Michalski et al., 2003; Morin et al., 2007; Alexander et al., 2009), but they have a non-zero  $\Delta^{17}\text{O}$  signal (1-2 ‰) due to the role of ozone in the  $\text{HO}_x$  cycle (Morin et al., 2011). However, their  $\delta^{18}\text{O}$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of bulk

O<sub>3</sub> 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<sub>x</sub> modelled at isotopic steady state with tropospheric O<sub>3</sub> yields 117 and 45 ‰ in δ<sup>18</sup>O and Δ<sup>17</sup>O, respectively (Michalski et al., 2014). This neglects the contribution of NO oxidation by RO<sub>2</sub> (R3), which will reduce the steady-state Δ<sup>17</sup>O and δ<sup>18</sup>O of NO<sub>x</sub> below the O<sub>3</sub>-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 δ<sup>18</sup>O values[AC2],[AC3]Amanda to revisit... (see section SM.1)

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Another argument supporting this interpretation is the strong correlation between Δ<sup>17</sup>O values and the maturity of a plume as expressed by the NO<sub>2</sub> content divided by sum of dry nitrates (Fig. 6). The results reflect the higher content of O<sub>3</sub>-derived O in dry nitrates from mature plumes, i.e., with relatively low NO<sub>2</sub> 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.

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

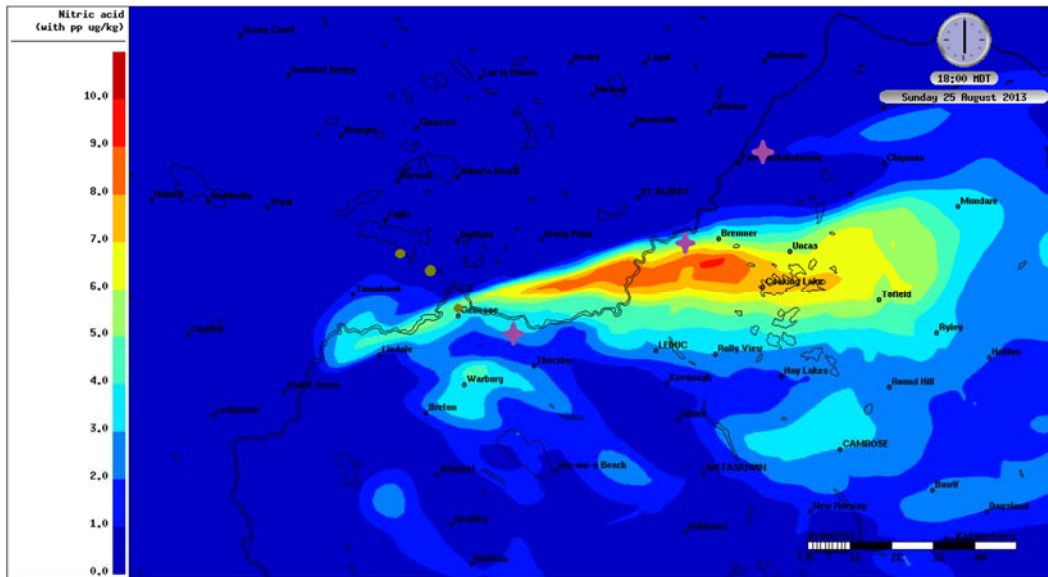
Comment 2: Intro: I think the introduction could use a better framework. If speciating  $\text{HNO}_3(\text{g})$  and  $\text{p-NO}_3^-$  is a main motivation of this study (however likely not achieved), then I think the introduction needs to have a better critical analysis of  $\text{HNO}_3(\text{g})$  and  $\text{p-NO}_3^-$  dynamics in the atmosphere. What might  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  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.

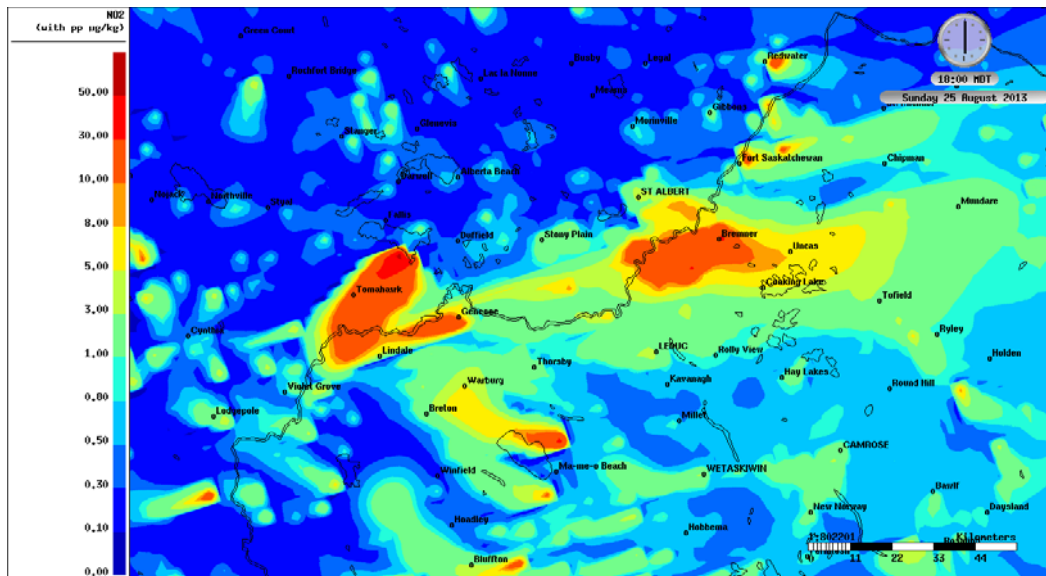
REPLY – We have modified the introduction to better illustrate the motivation for the research.

Change in manuscript: « In the past, due to sampling challenges,  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  were generally collected together (without differentiation). Therefore, no studies have separately and simultaneously collected and analyzed the  $\text{HNO}_3$  and  $\text{p-NO}_3^-$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values, and discussed these isotopic characteristics of nitrate collected downwind of anthropogenic emitters. While  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  can be in equilibrium (e.g. if  $\text{p-NO}_3^-$  is in the form of solid  $\text{NH}_4\text{NO}_3$ ), 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  $\text{NO}_x$  oxidation to nitrate and nitrate lifetime should be considered. Based on these lifetimes, how much of the sampled nitrate reasonable originated from  $\text{NO}_x$  oxidized from the upwind region? Was the emitted  $\text{NO}_x$  converted to nitrate from these emission regions are is the sampled nitrate a mixture of “background” nitrate originated from  $\text{NO}_x$  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  $\mu\text{g N m}^{-3}$ , 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<sub>3</sub> and HNO<sub>3</sub> 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<sub>2</sub> 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  $\mu\text{g N}/\text{m}^3$  for both  $\text{HNO}_3$  and  $p\text{-NO}_3^-$  (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  $\text{NO}_x$  converted to nitrate in this transit time may be small, these are large sources of  $\text{NO}_x$  in an area with very low background nitrates. For example, a plume containing 10 ppb of  $\text{NO}_2$  mixing with background air with 0.1 ppt of OH (Howell et al., 2014) would produce  $\text{HNO}_3$  via R6 at a rate of  $0.011\mu\text{g N m}^{-3} \text{min}^{-1}$  at  $T = 7^\circ\text{C}$  (Burkholder et al., 2015), or an equivalent amount of a typical sample in 10 minutes. Even if equilibration with  $\text{O}_3$  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 ( $\text{HNO}_3$  and  $p\text{-NO}_3^-$ ) was actually achieved with the sampling filter pack method. The problem, as the authors have pointed out, that the collected  $p\text{-NO}_3^-$  can easily volatilize as  $\text{HNO}_3$  that is collected on the filter designated for  $\text{HNO}_3(\text{g})$  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  $p\text{-NO}_3^-$  to play a major role on their results because  $p\text{-NO}_3^-$  isotope ratios are higher during winter than during summer and that the difference between  $p\text{-NO}_3^-$  and  $\text{HNO}_3$  is opposite than expected, but this is not proper justification. First, I wonder what the expected  $p\text{-NO}_3^-$  and  $\text{HNO}_3$  isotope difference is? This process is likely driven by an equilibrium effect rather than a kinetic effect since the volatilization of  $p\text{-NO}_3^-$  as  $\text{HNO}_3$  is due to the system being at non-equilibrium. I think this would change the authors expectation that the difference  $p\text{-NO}_3^-$  and  $\text{HNO}_3$  is driven by a kinetic effect (I assumed this was the authors assumption). Additionally, which “isotopic ratios” did the authors use to evaluate the  $p\text{-NO}_3^-$  and  $\text{HNO}_3$  difference? I’m assuming mass-dependent  $_{18}\text{O}$  but this information is not provided in text. Also, suggesting that this filter pack method has previously been used for

isotopic analysis of p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (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 elaborate 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 HNO<sub>3</sub>(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  $\Delta^{17}\text{O}$  values, this mass-dependent process would not create the observed HNO<sub>3</sub>-pNO<sub>3</sub> 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<sub>3</sub>) 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<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub> on the Teflon filter, <3% breakthrough of HNO<sub>3</sub> from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub><sup>-</sup> and positive bias in HNO<sub>3</sub> 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<sub>3</sub> 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<sub>2</sub> (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<sub>4</sub>NO<sub>3</sub> 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<sub>3</sub><sup>-</sup> isotopic ratios (δ<sup>17</sup>O and δ<sup>18</sup>O) to be generally higher during winter than during summer (see Section 3.4). Moreover, the p-NO<sub>3</sub><sup>-</sup> minus HNO<sub>3</sub> 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 δ<sup>15</sup>N values in NH<sub>3</sub> and NH<sub>4</sub>; 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 <sup>17</sup>O anomaly; therefore, Δ<sup>17</sup>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 NO<sub>2</sub><sup>-</sup> was minor say 5% relative to NO<sub>3</sub><sup>-</sup>, due to its rapid exchange with water below pH of 10, this could have artificially lowered the measured  $\delta^{17}\text{O}$  of the interpreted HNO<sub>3</sub>(g) or p-NO<sub>3</sub><sup>-</sup>. As an example, a 5% NO<sub>2</sub><sup>-</sup> contribution would have lowered the  $\delta^{17}\text{O}$  of the targeted nitrate (assuming  $\delta^{17}\text{O} = 30\text{‰}$  by 1.5‰ and could be the primary driver behind the  $\delta^{17}\text{O}$  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  $\delta^{17}\text{O}$  definition ( $\ln(1+d^{17}\text{O}/1000)-0.516*\ln(1+d^{18}\text{O}/1000)$ ) impact the authors comparison to data using the more commonly used linear  $\delta^{17}\text{O}$  definition ( $d^{17}\text{O}-0.52*d^{18}\text{O}$ ) (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<sub>3</sub> 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<sub>3</sub>/L (0.03 N-NO<sub>3</sub> 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 ( $\text{NO}_2^-$ ) using a custom-made cadmium column. The final preparation step involved using sodium azide to ultimately produce  $\text{N}_2\text{O}$  (McIlvin and Altabet, 2005; Smirnov et al., 2012). All extracted  $\text{N}_2\text{O}$  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; Smirnov 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  $\delta_{18}\text{O}$  +  $\delta_{17}\text{O}$  “source effect”. Their collections were from polluted air masses not direct stack emissions, such that  $\delta_{18}\text{O}$  and  $\delta_{17}\text{O}$  should effectively be wiped of any “source effect” due to the rapid equilibration of  $\text{NO}_x$  and its oxidants. The authors suggest in 3.2, that due to elevated  $\delta_{18}\text{O}$  +  $\delta_{17}\text{O}$  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  $\text{NO}_x$  oxidation cycling and post  $\text{NO}_2$  reactions would have altered  $\delta_{18}\text{O}$  +  $\delta_{17}\text{O}$  rather than a source derived  $\delta_{18}\text{O}$  +  $\delta_{17}\text{O}$  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  $\delta_{18}\text{O}$  and  $\delta_{17}\text{O}$  relationships appear linear despite the author’s claim to the contrary. Can the authors include regression statistics so that their argument is supported quantitatively 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  $\delta_{17}\text{O}$  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  $\delta^{17}\text{O}$  ranges? The authors indicate that the  $\delta^{17}\text{O}$  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  $\text{N}_2\text{O}_5$  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  $\delta^{17}\text{O}$  of  $\text{NO}_2$  is not equal to the asymmetrical  $\text{O}_3$  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  $\delta^{17}\text{O}$  of  $\text{NO}_2$ . Also, could the authors compare their  $\delta^{17}\text{O}$  in this region with the global  $\delta^{17}\text{O}$  model?

REPLY – The goal of the calculation was to constrain the source  $\text{NO}_2$   $\Delta^{17}\text{O}$  values based on those of nitrates, and it is not clear what the reviewer is suggesting. Use an approximate value of  $\text{NO}_2$   $\Delta^{17}\text{O}$  to calculate the contributions from the different  $\text{NO}_2$  oxidation pathways in different samples? That would require assuming the  $\text{NO}_2$   $\Delta^{17}\text{O}$  value was constant, which would also be unrealistic. The contribution of  $\text{RO}_2$  oxidation of NO is discussed in the paragraph following the calculation. The nitrate  $\Delta^{17}\text{O}$  are compared with the global model in sub-section 3.5;  $\text{NO}_2$   $\Delta^{17}\text{O}$  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  $\text{NO}_x$  and atmospheric lifetime of nitrate. I find it hard to believe any of the interpretation on  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  differences between p- $\text{NO}_3^-$  and  $\text{HNO}_3(\text{g})$  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  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  interpretation 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- $\text{NO}_3^-$   $\Delta^{17}\text{O}$  values were roughly correlated with the weighted average  $\Delta^{17}\text{O}$  values of p- $\text{NO}_3^-$  and  $\text{HNO}_3$  in samples covering the same time periods, consistent with scavenging of both  $\text{HNO}_3$  and p- $\text{NO}_3^-$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values (‰) for simultaneously collected  $\text{HNO}_3$  (empty symbols) and  $\text{p-NO}_3^-$  (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  $\text{HNO}_3$ ,  $\text{p-NO}_3^-$  and their isotopic compositions isn't surprising (particularly phase separation) due to the well-established thermodynamic equilibrium of  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  that determines this phase separation. This point however, directly contradicts that authors claim that reaction pathways (i.e.  $\text{NO}_2 + \text{OH}$  vs  $\text{N}_2\text{O}_5$  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  $\delta^{18}\text{O}$  values, but not the  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}$  values. The simplest explanation for this observation should be  $\text{NO}$  oxidation contributions from  $\text{RO}_2$ . 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  $\text{p-NO}_3$  in early plumes characterized by  $\Delta^{17}\text{O}$  values lower relative to those of  $\text{HNO}_3$  due to differential depositional rates. The  $\text{RO}_2$  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  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$  values with important implications multiple communities. (B) Additionally, challenging the assumption of  $\text{NO}_x$  isotopic steady state with  $\text{O}_3$  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 interchangeable".

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  $\text{NO}_x$  isotopes not at steady state with  $\text{O}_3$  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  $\Delta^{17}\text{O}$  values in non-winter p- $\text{NO}_3^-$ . 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.

Changes in manuscript: (A) in the abstract: « Recent laboratory experiments suggest that the isotopic equilibrium between  $\text{NO}_2$  (the main precursor of  $\text{NO}_3^-$ ) and  $\text{O}_3$  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- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  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  $\text{HNO}_3$  with  $\Delta^{17}\text{O}$  values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample  $\text{HNO}_3$  and p- $\text{NO}_3^-$ , and co-collect w- $\text{NO}_3^-$ . 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  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  from anthropogenic sources in central and southern Alberta, simultaneously collected with wind sector-based conditional sampling systems produced  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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 ( $\text{HNO}_3$ ) 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- $\text{NO}_3^-$  in these samples generally shows

higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than  $\text{HNO}_3$  in the fall-winter period as the heterogeneous  $\text{N}_2\text{O}_5$  pathway favours the production of  $\text{p-NO}_3^-$ . In contrast,  $\text{HNO}_3$  has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during warm periods, which we propose is due to faster dry deposition rates relative to  $\text{p-NO}_3^-$  in the event that low- $\Delta^{17}\text{O}$   $\text{NO}_2$  is oxidized in the plume. The mechanisms conferring nitrate with relatively low isotopic values, whether oxidation before  $\text{NO}_x\text{-O}_3$  equilibrium is reached or higher contributions from  $\text{RO}_2$ , 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.

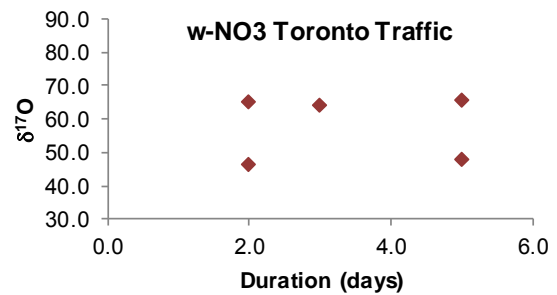
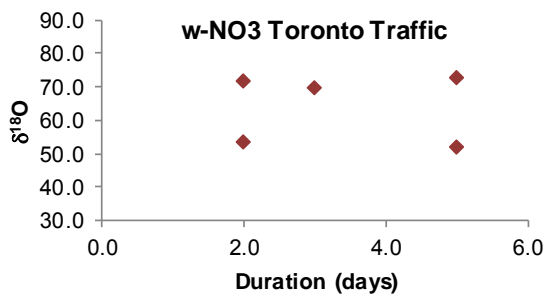
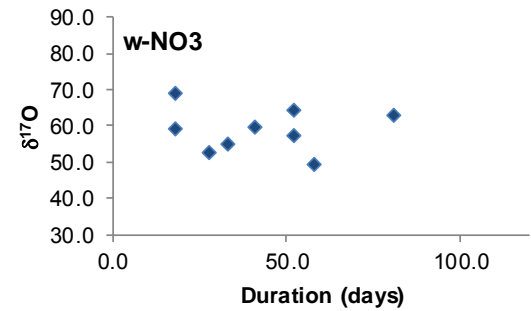
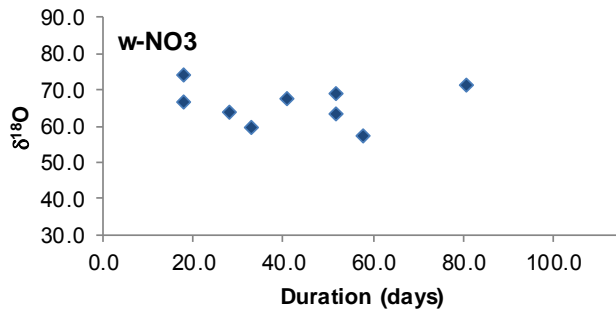
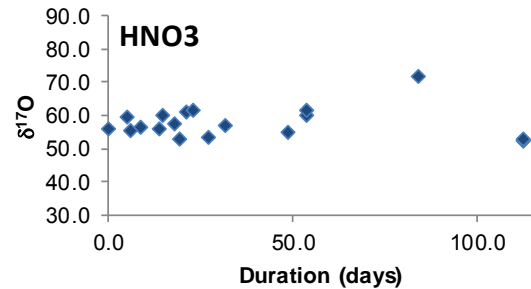
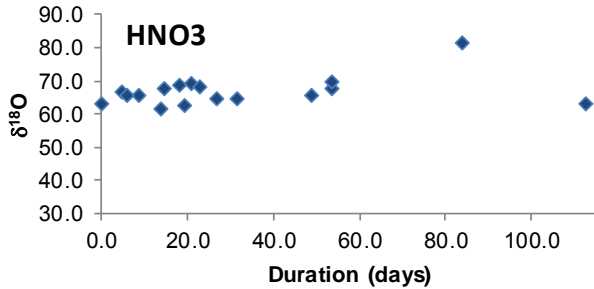
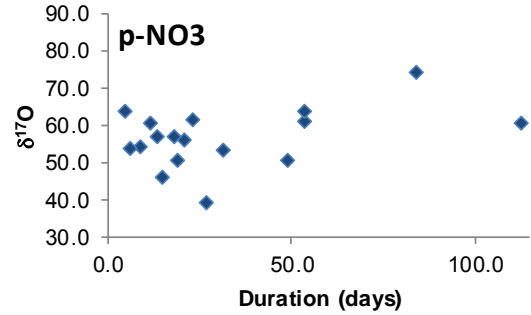
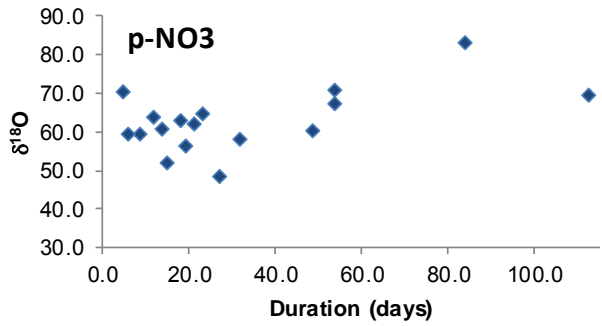
3-The authors points out "very few" air masses passed over other sources outside the targeted ones in the preceding 24 hours. For those that did, are they removed from the analysis? Why is this data not shown- as it seems relevant.

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  $\text{p-NO}_3$  and  $\text{HNO}_3$ :  $\text{p-NO}_3$  would have higher  $\delta^{18}\text{O}$  values than  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  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 (Smirnov 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 pNO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub>. 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<sub>3</sub><sup>-</sup> and HNO<sub>3</sub>...»

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<sub>3</sub><sup>-</sup>, 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 (O<sub>2</sub>) may generate primary NO<sub>x</sub> 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 restructuring 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  $\Delta^{17}\text{O}$  values of NO<sub>2</sub> from which the observed HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> 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  $\Delta^{17}\text{O}$  values of NO<sub>2</sub> 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<sub>3</sub> has a deposition velocity consistently higher than that of p-NO<sub>3</sub> (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  $\Delta^{17}\text{O}$  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  $\text{HNO}_3$  and p- $\text{NO}_3$ .

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  $^{15}\text{N}/^{14}\text{N}$  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  $\delta^{15}\text{N}$  values of all N-species investigated ( $\text{NH}_3/\text{NH}_4$  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  $\delta^{15}\text{N}$  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  $\text{NO}_x$  oxidation pathways and the  $\text{NO}_x/\text{HNO}_3/\text{p-NO}_3$  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  $\Delta^{17}\text{O}$  values in  $\text{HNO}_3$ , simultaneously sampled with  $\text{p-NO}_3$ . 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  $\text{NO}_x\text{-O}_3$ , 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 section 4. We have also modified the introduction to better express the rationale: « While  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  can be in equilibrium (e.g. if  $\text{p-NO}_3^-$  is in the form of solid  $\text{NH}_4\text{NO}_3$ ), 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,  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values were suggested to be useful to apportion the contribution of emission sources to regional atmospheric nitrate loads. However, the signals of precursor  $\text{NO}_x$  emitted from the same sources may quickly get modified through isotopic equilibration with  $\text{O}_3$ , 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  $\Delta^{17}\text{O}$  values previously suggested as indicative of anthropogenic emissions are characterizing anthropogenic emissions, generally speaking. Do low  $\Delta^{17}\text{O}$  values reflect a larger role of  $\text{RO}_2$  in the oxidation of anthropogenic  $\text{NO}_x$  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  $\text{NO}_3^-$  samples are not yet widespread. Also rare are the nitrate  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of field samples downwind from  $\text{NO}_x$ -emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). The few existing studies have chiefly characterized w- $\text{NO}_3^-$  or the sum of p- $\text{NO}_3^-$  and  $\text{HNO}_3$  (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  $\text{NO}_x$ ,  $\text{O}_3$  concentrations, photo-dissociation rates such  $\text{JNO}_2$  and/or modeling.

Reply: (A) We significantly shortened all text parts related to the individual anthropogenic emissions. We have used  $\text{O}_3$  and  $\text{NO}_x$  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  $\text{jNO}_2$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  have the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages, but not the highest w- $\text{NO}_3^-$  values; chemical industries show the lowest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages for w- and p- $\text{NO}_3^-$ , but not for  $\text{HNO}_3$ . 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-NO<sub>3</sub> (Cheng et al., 2012) and HNO<sub>3</sub> collection efficiency (Appel et al., 1980) on filters. Actually, such samplings artefacts can alternatively be an argument to explain the tight correlation observed between HNO<sub>3</sub>/p-NO<sub>3</sub> isotopes and RH (Table6). It is also surprising to see the use of filter pack system to differentiate p-NO<sub>3</sub> and HNO<sub>3</sub> 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-NO<sub>3</sub> by H<sub>2</sub>SO<sub>4</sub> acidification or gain of HNO<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> is likely volatilized p-NO<sub>3</sub>, 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<sub>3</sub> δ<sup>18</sup>O values low relative to p-NO<sub>3</sub> 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 Δ<sup>17</sup>O signals, so it cannot explain the correlations between RH and Δ<sup>17</sup>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<sub>3</sub>) on a Nylasorb nylon filter, and gaseous ammonia on a citric acid-coated Whatman 41 filter. The Teflon-nylon filter method for p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub> on the Teflon filter, <3% breakthrough of HNO<sub>3</sub> from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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  $p\text{-NO}_3^-$  and positive bias in  $\text{HNO}_3$  under hot ( $> 25\text{ }^\circ\text{C}$ ) and dry conditions, particularly in high ambient concentrations (e.g., Appel et al., 1981). However, other field studies have shown no significant differences in  $\text{HNO}_3$  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  $\text{HNO}_2$  (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  $\text{NH}_4\text{NO}_3$  for samples with mean temperatures below  $5\text{ }^\circ\text{C}$ , 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  $\text{NO}_x/\text{O}_3$  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  $p\text{-NO}_3^-$ , but not with  $\text{HNO}_3$  (Table 6). We now provide all the data, including available  $\text{O}_3$  and  $\text{NO}_x$  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 HNO<sub>3</sub> 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 not claim this is a novel interpretation. However, this aspect is crucial for estimating the isotopic signals of precursor NO<sub>x</sub>, and for further explaining the causes for the changes in isotopic differences between pNO<sub>3</sub> and HNO<sub>3</sub>.

As mentioned in reply to point 5, as well as in the text, the mentioned sampling artefacts cannot cause the observed  $\Delta^{17}\text{O}$  differences between pNO<sub>3</sub> and HNO<sub>3</sub>. 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 HNO<sub>3</sub> being enriched or depleted as function of season and with respect to p-NO<sub>3</sub>. In figure 3, there is few cases where summer p-NO<sub>3</sub> have higher  $\delta^{17}\text{O}$  than HNO<sub>3</sub>. It is thus difficult to understand why authors want to explain the greater  $\delta^{17}\text{O}$  of HNO<sub>3</sub> in summer over p-NO<sub>3</sub>. Furthermore, the discussion falls short to give an acceptable explanation (lines 10 to 25 of page 11).

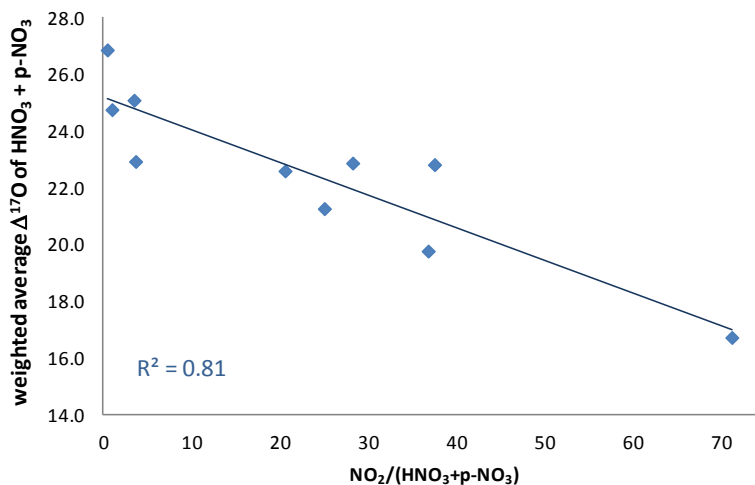
Reply: The data on Fig. 3 show clearly both positive and negative values of  $\Delta^{17}\text{O}_{(\text{HNO}_3)} - \Delta^{17}\text{O}_{(\text{pNO}_3)}$ , with a somewhat positive trend with temperature. While we hypothesize that negative values may be due to the larger contribution of the N<sub>2</sub>O<sub>5</sub>+H<sub>2</sub>O heterogeneous reaction to p-NO<sub>3</sub>, 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  $\Delta^{17}\text{O}$  values in HNO<sub>3</sub> is that the deposition of HNO<sub>3</sub> is greater than the one of p-NO<sub>3</sub>, a difference in rates that is much stronger during summer than winter. This mechanism combined with the NO<sub>x</sub>-O<sub>3</sub> 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 NO<sub>2</sub> is not in isotopic equilibrium with O<sub>3</sub> in summer is odd. First if equilibrium is not reached, it should be amplified in winter, not in summer when O<sub>3</sub> is at max (Angle et al., 1989) and photolysis at its peak.

The point is taken, though O<sub>3</sub> 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<sub>x</sub> 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  $\Delta^{17}\text{O}$  values (weighted average) as a function of NO<sub>2</sub> concentration divided by p-NO<sub>3</sub> plus HNO<sub>3</sub> concentrations). The relationship is strong ( $r^2=0.81$ ) and supports our interpretation: the more mature is a plume (low NO<sub>2</sub> concentration), the higher are the  $\Delta^{17}\text{O}$  values in the nitrates, i.e. the higher is the O<sub>3</sub>-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<sub>3</sub><sup>-</sup> 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<sup>17</sup>O values and the maturity of a plume as expressed by the NO<sub>2</sub> content divided by sum of dry nitrates (Fig. 6). The results reflect the higher content of O<sub>3</sub>-derived O in dry nitrates from mature plumes, i.e., with relatively low NO<sub>2</sub> contents. »



**Figure 5:** Weighted Δ<sup>17</sup>O average (‰) for the sum of dry nitrates as a function of NO<sub>2</sub> concentration divided by p-NO<sub>3</sub> plus HNO<sub>3</sub> concentrations, a ratio indicative of the maturity of a plume.

12- Moreover, NO<sub>2</sub> is the precursor of HNO<sub>3</sub> and p-NO<sub>3</sub>, if not in equilibrium it should impact equally HNO<sub>3</sub> and p-NO<sub>3</sub>. To twist this basic idea, the authors claim that HNO<sub>3</sub> is faster scavenged from the atmosphere than p-NO<sub>3</sub> 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<sub>3</sub> is HNO<sub>3</sub>. Additionally, we refer the reader again to the articles cited in the original manuscript showing higher dry deposition rates for HNO<sub>3</sub> (Zhang et al 2009; Benedict et al., 2013).

Changes in manuscript: none required.

13- Neither the authors tested the hypothesis that NO<sub>2</sub> is indeed not in equilibrium with O<sub>3</sub>. If Michalski et al. (2014) showed that the time-scale for equilibrium is strongly dependent on local sunlight conditions and NO<sub>x</sub>/O<sub>3</sub> 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 NO<sub>2</sub> to reach its isotopic equilibrium composition? or unrealistic O/O<sub>3</sub>/NO/NO<sub>2</sub> ratios after model initialization since chemical steady state will be reached in min and will radically change the NO<sub>2</sub>/O<sub>3</sub> ratio?). In another study, Morin et al. (2011) using a true atmospheric model modeled <sub>17</sub>O of NO<sub>2</sub> using different realistic atmospheric conditions and environments. They showed that NO<sub>2</sub> is largely at isotopic equilibrium except during few night hours but with little impact on prognosticated <sub>17</sub>O 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 NO<sub>x</sub> emissions and they used a 24-hour model spin up before reporting isotopic composition of NO<sub>2</sub>. Therefore, their modeling results are not comparable with the nitrates collected within minutes to hours of fresh NO<sub>x</sub> 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 NO<sub>x</sub>-NO<sub>3</sub> 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 NO<sub>x</sub>-NO<sub>3</sub> isotopic disequilibrium.

Considering that this article represents the first investigation of simultaneously sampled nitrates in precipitation, gas and particulate forms for their  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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?

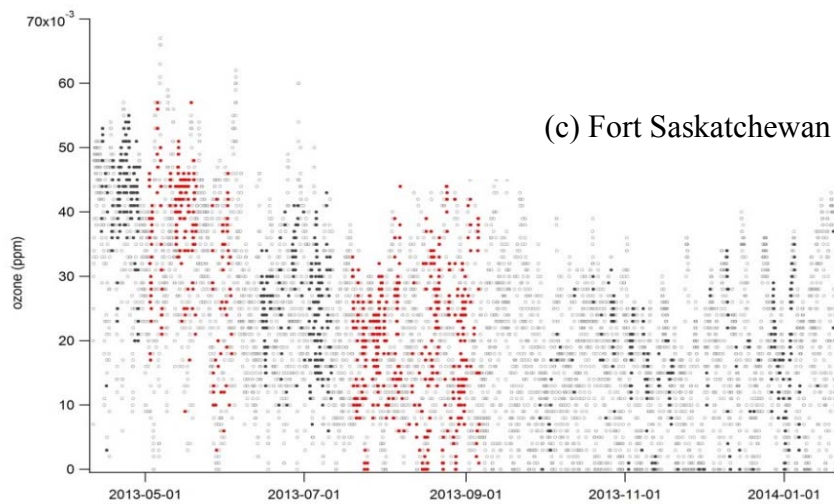
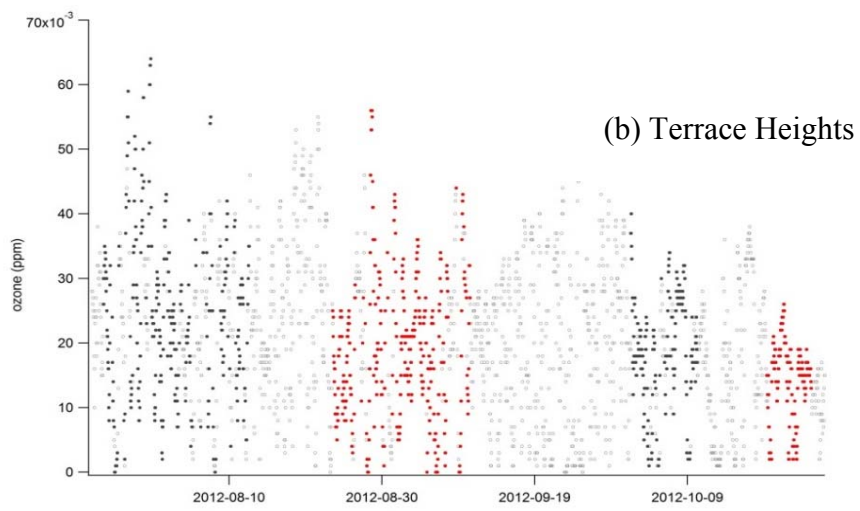
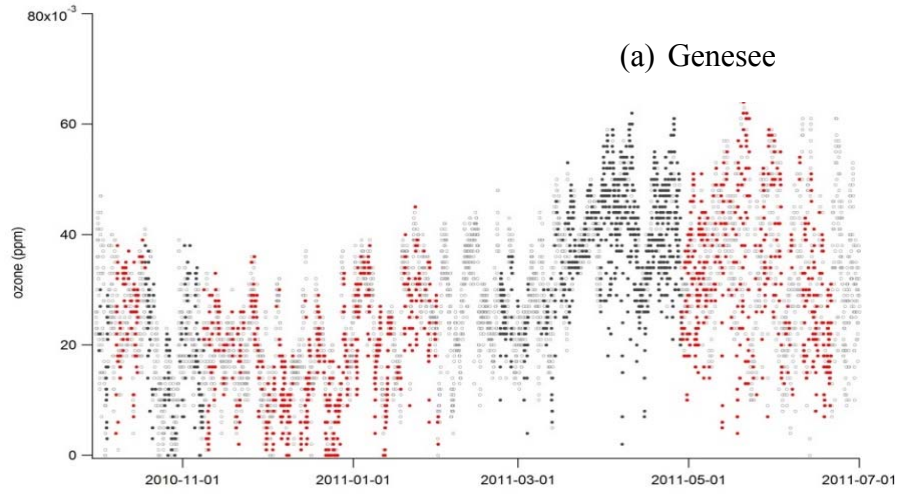
Reply: We judge pertinent suggesting an interpretation for these correlations as they relate to reactions summarized in Table 5. The text describing this interpretation is short, and it is now placed with the results and interpretation section (3), right after the interpretation in terms of oxidation 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 O<sub>3</sub>, NO<sub>x</sub> and jNO<sub>2</sub> 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<sub>3</sub>, NO<sub>x</sub> and jNO<sub>2</sub> would be meaningful in interpreting these integrated and intermittent samples, which is why we used average values over the sampling times for O<sub>3</sub> and NO<sub>x</sub> 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<sub>2</sub> is discussed in point 4. Graphs of the O<sub>3</sub> 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<sub>x</sub>, we decided the comparison with NO<sub>x</sub> 5 km away was problematic and removed it. However, NO<sub>2</sub> data measured on-site now appear reported where available.





[Changes in manuscript](#): 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 NO<sub>2</sub> with O<sub>3</sub>) has now become a certainty (line 6 page 13).

REPLY: Good point. The previous sentence was : « However, NO<sub>2</sub> not in isotopic equilibrium with O<sub>3</sub>, and/or NO reacted with RO<sub>2</sub> significantly influenced the overall results.»

Changes in manuscript: sub-section 4.2, p. 12, line 25: *However, NO<sub>2</sub> not in isotopic equilibrium with O<sub>3</sub>, and/or NO reacted with RO<sub>2</sub> may have significantly influenced the overall results.»*

17-Finally, the idea that low values of  $\delta^{17}\text{O}$  can be linked to the rapid oxidation of anthropogenic NO<sub>x</sub> is attractive but would have merited more investigation such as following for example the NO<sub>x</sub>/NO<sub>3</sub>- 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<sub>2</sub> 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<sub>2</sub> concentrations only at 3 of the 4 sites, both in the Edmonton urban area.

We have plotted the  $\delta^{17}\text{O}$  values (weighed average) of p-NO<sub>3</sub> and HNO<sub>3</sub> as a function of NO<sub>2</sub> concentrations / (p-NO<sub>3</sub> plus HNO<sub>3</sub> concentrations), and there is clear inverse correlation. In other words, when NO<sub>2</sub> is high (low nitrates in early plume), the  $\delta^{17}\text{O}$  values are low, and when NO<sub>2</sub> is low (late plumes), the nitrates  $\delta^{17}\text{O}$  values are high. These NO<sub>2</sub> 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)

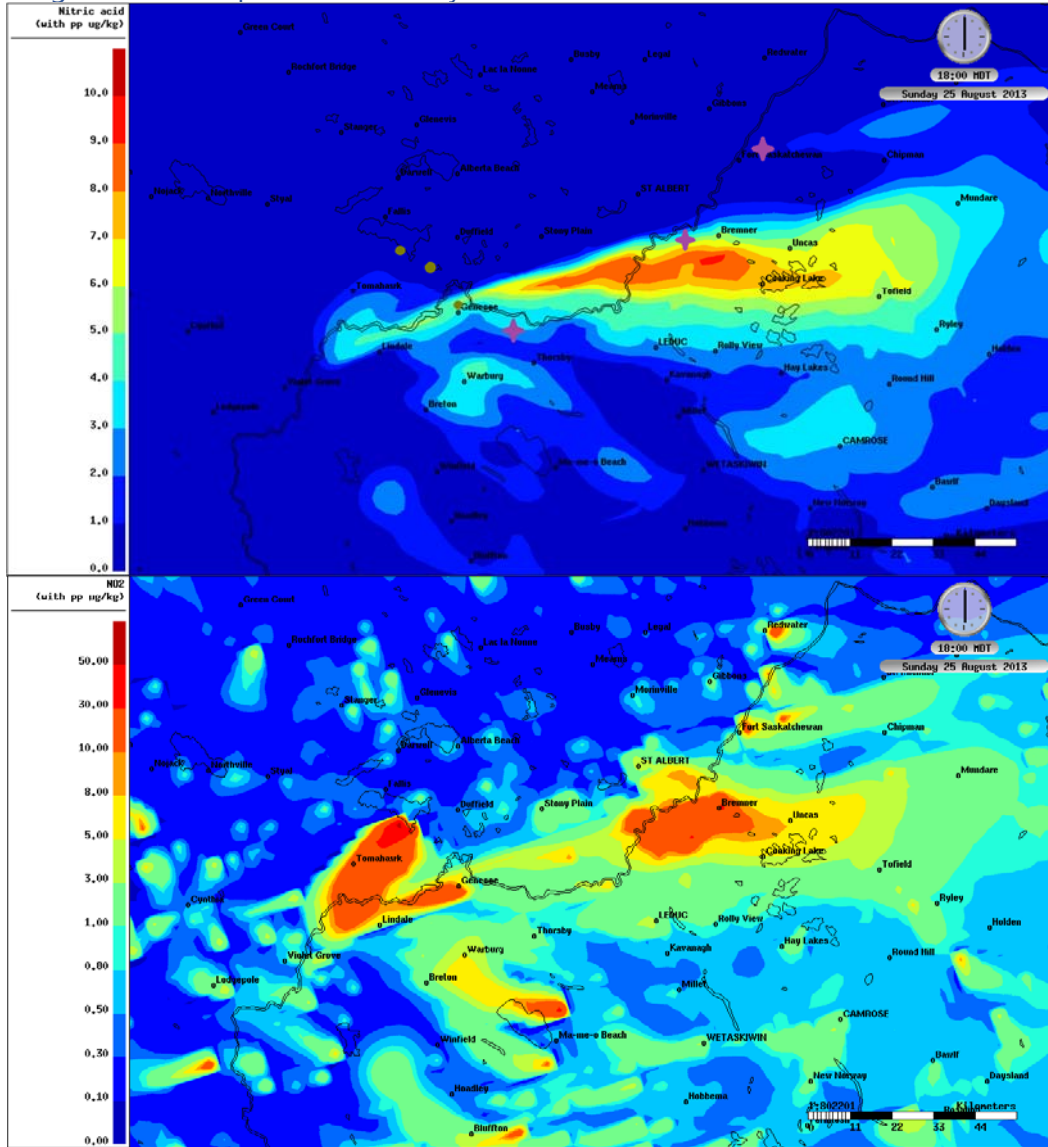
REPLY- We mean 'New and novel' implying that the data is QA/QC checked, i.e., valid.

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 NO<sub>x</sub>, nitrate (or any other tracers, CO, O<sub>3</sub>) 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  $\mu\text{g N m}^{-3}$ , 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<sub>3</sub> and HNO<sub>3</sub> 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 NO<sub>2</sub> 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: The title is changed to “The  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\mu\text{g N/m}^3$  for both  $\text{HNO}_3$  and  $p\text{-NO}_3^-$  (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 O<sub>3</sub>.

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<sub>3</sub> 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<sub>x</sub>, we decided the comparison with NO<sub>x</sub> 5 km away was problematic and removed it. However, NO<sub>2</sub> 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 HNO<sub>3</sub> are used in the most remote regions of world (eg Antarctica, Jourdain and Legrand, 2002, Legrand et al., 2017). Denuders that are operational at 1m<sup>3</sup>/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  $p\text{-NO}_3$  and 2nd nylon filter for HNO<sub>3</sub>) is not the reference set up used to separate  $p\text{-NO}_3$  and HNO<sub>3</sub>. It is a set up used mainly to collect total nitrate. The difference in  $\text{NO}_3^-$  between  $p\text{-NO}_3$  and HNO<sub>3</sub> 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 HNO<sub>3</sub> 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, Norway EMEP/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  $\delta^{17}\text{O}$  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  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  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  $\delta^{17}\text{O}$  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  $\delta^{17}\text{O}$   $\text{HNO}_3$  and p- $\text{NO}_3$  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  $\text{NO}$  and  $\text{NO}_2$  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  $\text{HNO}_3$  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- $\text{NO}_3$  and  $\text{HNO}_3$ ) 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  $\text{HNO}_3$  and p- $\text{NO}_3$   $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  values (as well as  $\delta^{15}\text{N}$  in  $\text{NH}_3$  and p- $\text{NH}_4$ ), and their pattern with temperature, to judge whether this was strongly affecting the results. We did not draw conclusions about the artifact based on  $\Delta^{17}\text{O}$  values, just stated that mass-dependent volatilization would not affect the  $\Delta^{17}\text{O}$  value, which is correct. While the reviewer does suggest a possible mechanism that would affect  $\Delta^{17}\text{O}$  values (exchange with  $\text{H}_2\text{O}$  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  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ . In any case, this scenario would similarly influence p- $\text{NO}_3$  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<sub>3</sub>) on a Nylasorb nylon filter, and gaseous ammonia on a citric acid-coated Whatman 41 filter. The Teflon-nylon filter method for p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub> on the Teflon filter, <3% breakthrough of HNO<sub>3</sub> from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub><sup>-</sup> and positive bias in HNO<sub>3</sub> 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<sub>3</sub> 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<sub>2</sub> (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<sub>4</sub>NO<sub>3</sub> 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 <sup>17</sup>O anomaly; therefore, Δ<sup>17</sup>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 Δ<sup>17</sup>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 Δ<sup>17</sup>O and δ<sup>18</sup>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  $\delta^{17}\text{O}$  difference between p-NO<sub>3</sub> and HNO<sub>3</sub> with season (fig3). In summer, two out of four have  $\delta^{17}\text{O}$  nitrate >  $\delta^{17}\text{O}$  HNO<sub>3</sub> 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- HNO<sub>3</sub> is formed from non-equilibrated NO<sub>x</sub>/O<sub>3</sub> system and 2- HNO<sub>3</sub> is faster scavenged. I can propose the formation of lower  $\delta^{17}\text{O}$  p-NO<sub>3</sub> by the heterogeneous reaction  $2\text{NO}_2 + \text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{ads}) + \text{HONO}$  (Finlayson-Pitts, 2009), or higher  $\delta^{17}\text{O}$  HNO<sub>3</sub> by  $\text{NO}_3 + \text{RH} \rightarrow \text{HNO}_3$  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 NO<sub>x</sub>-O<sub>3</sub> 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 O<sub>3</sub> vs NO<sub>x</sub>). Yet ozone formation is the only reaction creating  $\delta^{17}\text{O}$ -excess, and since chemical steady state is quickly reached, equilibrium of  $\delta^{17}\text{O}$  among all species can't be reached faster than O<sub>3</sub> own equilibrium time in Michalski's model. Clearly, the limiting step in Michalski's model to propagate  $\delta^{17}\text{O}$  is ozone formation and not NO<sub>x</sub>/O<sub>3</sub> interaction. If ozone is in isotopic equilibrium, any new population of NO<sub>2</sub> formed by O<sub>3</sub>+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 NO<sub>2</sub> versus flux of NO<sub>2</sub> to reach equilibrium. Isotopic abundance has nothing to do here. Let's imagine that O<sub>3</sub> is already in isotopic equilibrium, further formation/destruction have no effect on ozone <sup>17</sup>O. Let's imagine further that NO<sub>x</sub> and O<sub>3</sub> are in chemical/isotopic equilibrium (new O<sub>3</sub> formed has the same isotopic composition than consumed O<sub>3</sub> as O<sub>3</sub> isotope is controlled by pressure and temperature only). Suddenly, a new pool of NO is emitted. NO will be converted to NO<sub>2</sub> by O<sub>3</sub> contained in the surrounding atmosphere upon mixing and thus NO<sub>2</sub> will be formed at the rate of the Leighton cycle in this system. The characteristic time of the isotopic transfer from O<sub>3</sub> to NO<sub>2</sub> 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 O<sub>3</sub> so that O<sub>3</sub> stays constant. The characteristic time, Tau, at which the non-equilibrated isotopic NO<sub>x</sub> reservoir is replaced by the isotopic equilibrated NO<sub>2</sub> is simply twice the size of NO<sub>2</sub> reservoir divided by the speed of Leighton cycle, either NO+O<sub>3</sub> reaction or JNO<sub>2</sub> depending on the chemistry context, as one of these reactions is the limiting step. Using Michalski first simulations, NO = 23 ppbv (assumed NO<sub>2</sub>/NO<sub>x</sub> = 0.3 for fresh plume), NO<sub>2</sub> = 10 ppbv, O<sub>3</sub> = 50 ppbv and k = 2e-14 molecules cm<sup>-3</sup> s<sup>-1</sup>, J = 0,007 s; then Tau = 2/J = 4,8 min. In 20 min NO<sub>2</sub> is at 98 % in isotopic equilibrium. Using Michalski second simulations NO<sub>2</sub> = 0,03ppb, NO=0,003 ppb (assumed NO<sub>2</sub>/NO<sub>x</sub> = 0.9 for remote place), O<sub>3</sub> = 5 ppb, Tau = 2 [NO<sub>2</sub>]/(k[NO][O<sub>3</sub>]) = 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 NO<sub>x</sub> are recycled through the BrO + NO and not NO+O<sub>3</sub> reaction. In a more rural situation (Rohrer et al., 1998), NO<sub>2</sub> = 1,4 ppb, NO = 0,3 ppb, O<sub>3</sub> = 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 NO<sub>2</sub> 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<sub>x</sub> that had been converted to nitrate and therefore "frozen" in Δ<sup>17</sup>O at the point of conversion, contributions from unequilibrated NO<sub>x</sub> 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<sub>2</sub>-O<sub>3</sub>

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<sub>2</sub> could also give a similar result, as has been previously hypothesized. However, since the possibility of incomplete NO<sub>x</sub> equilibration retained in nitrate field samples was a new idea supported by winter data when RO<sub>2</sub> cannot play significantly, NO<sub>x</sub>-O<sub>3</sub> 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<sub>x</sub> converted to nitrate in this transit time may be small, these are large sources of NO<sub>x</sub> in an area with very low background nitrates. For example, a plume containing 10 ppb of NO<sub>2</sub> mixing with background air with 0.1 ppt of OH (Howell et al., 2014) would produce HNO<sub>3</sub> via R6 at a rate of 0.011 μg N m<sup>-3</sup> min<sup>-1</sup> at T = 7 °C (Burkholder et al., 2015), or an equivalent amount of a typical sample in 10 minutes. Even if equilibration with O<sub>3</sub> 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<sub>3</sub> and oxidation through the well-known OH and N<sub>2</sub>O<sub>5</sub> oxidation paths. However, NO<sub>2</sub> not in isotopic equilibrium with O<sub>3</sub>, and/or NO reacted with RO<sub>2</sub> 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- HNO<sub>3</sub> has a different <sup>17</sup>O composition than p-NO<sub>2</sub> and 2- NO<sub>x</sub> 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 $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of atmospheric nitrates **simultaneously collected downwind of anthropogenic sources** – Implications for polluted air masses

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10 **Abstract.** There are clear motivations for better understanding the atmospheric processes that transform nitrogen (N) oxides ( $\text{NO}_x$ ) emitted from anthropogenic sources into nitrates ( $\text{NO}_3^-$ ), two of them being that  $\text{NO}_3^-$  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 ( $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ ) are frequently applied to infer the chemical pathways leading to the observed mass independent isotopic anomalies from interaction with  $^{17}\text{O}$ -rich ozone ( $\text{O}_3$ ). Recent laboratory experiments suggest that the isotopic equilibrium between  $\text{NO}_2$  (the main precursor of  $\text{NO}_3^-$ ) and  $\text{O}_3$  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  $\text{NO}_3^-$  in precipitation (w- $\text{NO}_3^-$ ) and in particulate (p- $\text{NO}_3^-$ ) 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  $\text{HNO}_3$  with  $\Delta^{17}\text{O}$  values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample  $\text{HNO}_3$  and p- $\text{NO}_3^-$ , and co-collect w- $\text{NO}_3^-$ . The nitrates are from various distances (<1 to >125 km) downwind of different anthropogenic emitters, and consequently from varying time lapses after emission.

25 The separate collection of nitrates shows that the  $\text{HNO}_3$   $\delta^{18}\text{O}$  ranges are distinct from those of w- and p- $\text{NO}_3^-$ . Interestingly, the  $\Delta^{17}\text{O}$  differences between p- $\text{NO}_3^-$  and  $\text{HNO}_3$  shift from positive during cold sampling periods to negative during warm periods. The low p- $\text{NO}_3^-$   $\Delta^{17}\text{O}$  values observed during warm periods may partly derive from the involvement of  $^{17}\text{O}$ -depleted peroxy radicals ( $\text{RO}_2$ ) oxidizing  $\text{NO}$  during that season. Another possibility is that nitrates derive from  $\text{NO}_x$  that has not yet reached isotopic equilibrium with  $\text{O}_3$ . However, these mechanisms, individually or together, cannot explain the observed p- $\text{NO}_3^-$  minus  $\text{HNO}_3$  isotopic changes. We propose differences in dry depositional rates, faster for  $\text{HNO}_3$ , as a mechanism for the observed shifts. Larger proportions of p- $\text{NO}_3^-$  formed via the  $\text{N}_2\text{O}_5$  pathway would explain the opposite fall-winter patterns. Our results show that the separate  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  isotopic signals can be used to further our understanding of  $\text{NO}_x$  oxidation and deposition. Future research should investigate all tropospheric nitrate species as well as  $\text{NO}_x$  to refine our understanding of nitrate distribution worldwide and to develop effective emission reduction strategies.

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Supprimé: simultaneously collected

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Supprimé: distribution of wet (w- $\text{NO}_3^-$ ), particulate (p- $\text{NO}_3^-$ ), and the sum of p- $\text{NO}_3^-$  and gaseous  $\text{HNO}_3$ ,

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Supprimé: while the gaseous form ( $\text{HNO}_3$ ) has never been separately characterized for  $^{17}\text{O}$ .

Supprimé: recent laboratory experiments suggest that the reveal time lapses between emission of  $\text{NO}_x$ ... isotopic equilibrium between  $\text{NO}_2$  (the main precursors... of  $\text{NO}_3^-$ ) and its isotopic equilibrium with  $\text{O}_3$  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... nitrates may be formed near emission sources with lower isotopic values than those at equilibrium... formed further downwind. Equally important, Previous research studies have investigated characterization of f... indeed, previously published field measurements of oxygen isotopes in  $\text{NO}_3^-$  in precipitation (w- $\text{NO}_3^-$ ... and in particulate (p- $\text{NO}_3^-$ ) ... [1]

Supprimé: or p- $\text{NO}_3^-$  +  $\text{HNO}_3$  from non-polluted or polluted air masses, and inferred seasonal changes in the dominance of oxidation pathways to account for higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values in winter relative to summer.

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Supprimé: polluted... if studies have deployed systems allowing collection of... samples specific to targeted emission ... [2]

Supprimé: pathways... isotopic signature due to moving... hanging wind directions, or separately characterized gaseous  $\text{HNO}_3$  with  $\Delta^{17}\text{O}$  values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample  $\text{HNO}_3$  and p- $\text{NO}_3^-$ , and co-collect w- $\text{NO}_3^-$ . The nitrates are from various distances (<1 to >125 km) downwind from... five ... [3]

Supprimé: five different... anthropogenic sources ... [4]

Supprimé: Overall, the w- and p- $\text{NO}_3^-$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values show expected differences between cold and warm seasons, but only the  $\Delta^{17}\text{O}$  values of  $\text{HNO}_3$  follow this pattern.

Supprimé: the... those of w- and p- $\text{NO}_3^-$  patterns... Interestingly, the  $\Delta^{17}\text{O}$  differences between p- $\text{NO}_3^-$  and  $\text{HNO}_3$  shifts... from positive during cold sampling periods to negative during warm periods. The very ... [5]

Supprimé: The summer pattern... may be... partly derive ue to... from the... involvement of  $^{17}\text{O}$ -depleted peroxy radicals ( $\text{RO}_2$ ) oxidizing  $\text{NO}$  during that season. Another possibility is that the presence of nitrates derived... from  $\text{NO}_x$  that has not yet reached isotopic equilibrium with  $\text{O}_3$ ... However, these mechanisms, individually or together, cannot explain the observed p- $\text{NO}_3^-$  minus  $\text{HNO}_3$  isotopic changes. We propose and subsequent ... [6]

Supprimé: valid... mechanism for the observed shifts. Subsequent increased renewal of  $\text{HNO}_3$  in the plume, with higher  $\Delta^{17}\text{O}$  values in newly formed  $\text{HNO}_3$  as  $\text{NO}_x$ - $\text{O}_3$  equilibrate with time. ... [7]

Supprimé: while the l... larger proportions of p- $\text{NO}_3^-$  formed via the  $\text{N}_2\text{O}_5$  pathway would can... explain the opposite fall-winter patterns. Very low p- $\text{NO}_3^-$   $\Delta^{17}\text{O}$  values observed during warm months may be due to this non-equilibrated  $\text{NO}_x$ , though contribution from  $\text{RO}_2$  oxidation remains a possibility. ... our results show that the separate  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  isotopic signals of  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  are not interchangeable and that their differences... can be used to further our understanding of  $\text{NO}_x$  oxidation and deposition. Future research should investigate all tropospheric nitrate species as well as  $\text{NO}_x$  to refine our understanding of nitrate distribution worldwide and to develop effective emission reduction strategies.¶ ... [8]

## 1 Introduction

Anthropogenic NO<sub>x</sub> (NO and NO<sub>2</sub>) emissions are oxidized to nitrate in the atmosphere in the form of gaseous, wet or particulate forms, HNO<sub>3</sub> being one of the main precursors of p-NO<sub>3</sub><sup>-</sup>. 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<sub>3</sub>, HNO<sub>3</sub> and w-NO<sub>3</sub>).

Triple oxygen isotopes ( $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ ), have been used to decipher atmospheric oxidation pathways of NO<sub>x</sub> leading to ambient nitrate. Michalski et al. (2003) performed the first measurement of  $\delta^{17}\text{O}$  values in atmospheric nitrate. The authors found nitrate highly enriched in  $^{18}\text{O}$  and  $^{17}\text{O}$ , likely due to the transfer of anomalous oxygen atoms from ozone (O<sub>3</sub>) via the NO<sub>x</sub>-ozone photochemical cycle and oxidation to nitrate. During its formation, O<sub>3</sub> inherits abnormally high  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values through mass independent fractionation. The specific  $\delta^{17}\text{O}$  departure from the terrestrial mass dependent fractionation line, named the  $^{17}\text{O}$  anomaly, is often expressed as  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.517 \times \delta^{18}\text{O}$  (Thiemens, 1999). Further investigations suggested that the  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values of w-NO<sub>3</sub><sup>-</sup> and p-NO<sub>3</sub><sup>-</sup> reflect several reactions taking place after the atmospheric emission of NO<sub>x</sub>, i.e., atmospheric oxidation pathways transforming NO<sub>x</sub> 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  $\delta^{18}\text{O}$  differences in w-NO<sub>3</sub><sup>-</sup> 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; Smirnov et al., 2012), transfer of the ozone  $^{17}\text{O}$  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<sub>3</sub><sup>-</sup> samples are not yet widespread. Also rare are the nitrate  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of field samples downwind from NO<sub>x</sub>-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). The few existing studies have chiefly characterized w-NO<sub>3</sub><sup>-</sup> or the sum of p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (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<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> were generally collected together (without differentiation). Therefore, no studies have separately and simultaneously collected and analyzed the HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup>  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values, and discussed these isotopic characteristics of nitrate collected downwind of anthropogenic emitters. While HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> can be in equilibrium (e.g. if p-NO<sub>3</sub><sup>-</sup> is in the form of solid NH<sub>4</sub>NO<sub>3</sub>), this is not always the case, for example, if nitrate is

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Supprimé: Elliott et al. (2009) measured  $\delta^{18}\text{O}$ , but not  $\Delta^{17}\text{O}$ , in United States CASTNET (Clean Air Status and Trends Network) samples of simultaneously-collected p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> as well as in nearby NTN (National Trends Network) precipitation samples.

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Supprimé: (Proemse et al., 2013) Even rarer are the nitrate  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of field samples downwind from NO<sub>x</sub>-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). In those studies,  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values were suggested to be useful to apportion the contribution of emission sources to regional atmospheric nitrate loads.

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Supprimé: However, the signals of precursor NO<sub>x</sub> emitted from the same sources may quickly get modified through isotopic equilibration with O<sub>3</sub>, so that the original source signals may be difficult to recognize.

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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<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> as well as w-NO<sub>3</sub><sup>-</sup> downwind of the source types. The objective of this work was to assess the atmospheric NO<sub>x</sub> reaction pathways and determine processes responsible for the distribution of HNO<sub>3</sub>, and w- and p-NO<sub>3</sub><sup>-</sup> in a mid-latitude region.

## 2 Methodology

### 2.1 Regional context

While national reported NO<sub>x</sub> 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 PM<sub>2.5</sub> (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<sub>x</sub> 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<sub>3</sub><sup>-</sup>, HNO<sub>3</sub> and w-NO<sub>3</sub><sup>-</sup>) 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

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Supprimé: Importantly, the rate of HNO<sub>3</sub> production depends on the atmospheric NO<sub>x</sub> amounts and production rates of oxidizing agents (e.g., O<sub>3</sub>, OH, RO<sub>2</sub>; see section 3.3), and further down the chain of reactions, atmospheric HNO<sub>3</sub> participates in forming p-NO<sub>3</sub><sup>-</sup> 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 NO<sub>x</sub>-O<sub>3</sub> isotopic disequilibrium. It is clear our working hypothesis is that

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While national reported NO<sub>x</sub> 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 PM<sub>2.5</sub> (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<sub>x</sub> emissions in Canada, and the area of southern Alberta, characterized by dense gas compressor station and agricultural emissions, have never been investigated. ¶

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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<sub>x</sub> 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<sub>3</sub>) 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<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub> on the Teflon filter, <3% breakthrough of HNO<sub>3</sub> from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> 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<sub>3</sub><sup>-</sup> and positive bias in HNO<sub>3</sub> 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<sub>3</sub> 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<sub>2</sub> (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<sub>4</sub>NO<sub>3</sub> 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.

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After the first five sample periods, an experimental active sampling system for NO<sub>2</sub> and NO<sub>x</sub> 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<sub>2</sub>, and one- or two-stage filter pack containing two identical Maxxam Analytics' impregnated filters designed to collect NO<sub>x</sub> (mostly NO due to upstream collection of NO<sub>2</sub>). Oxygen isotopes in NO<sub>2</sub> and NO<sub>x</sub> 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.

Here we report on oxygen isotopes in the simultaneously sampled HNO<sub>3</sub> and p-NO<sub>3</sub>, along with co-sampled w-NO<sub>3</sub> 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.

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.

### 2.3 Analytical procedures

Nitric acid from nylon filters were extracted using 10 mL of 0.01M solution of NaCl. Particulate-NO<sub>3</sub> 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.

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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<sub>3</sub>/L (0.03 N-NO<sub>3</sub> 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  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  ratios of HNO<sub>3</sub>, w-NO<sub>3</sub><sup>-</sup>, and p-NO<sub>3</sub><sup>-</sup>, along with the  $\delta^{15}\text{N}$  values of NH<sub>3</sub>, w-NH<sub>4</sub><sup>+</sup>, p-NH<sub>4</sub><sup>+</sup> and NO<sub>x</sub> (all N isotopic results are in Savard et al., 2017). The present article deals solely with the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values obtained for the three nitrate species. We treated the samples using the chemical conversion and thermal decomposition of N<sub>2</sub>O protocols, providing the ability to simultaneously analyze low-concentration N- and O-containing species (Smirnov 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  $\mu\text{mol NO}_3/\text{L}$ ). Therefore, not all samples could be diluted to produce volumes sufficient for reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub> and subsequent conversion to N<sub>2</sub>O, the final product before isotope analysis. Samples with an initial concentration below 2.3  $\mu\text{mol/L}$  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<sub>2</sub><sup>-</sup>) using a custom-made cadmium column. The final preparation step involved using sodium azide to ultimately produce N<sub>2</sub>O (McIlvin and Altabet, 2005; Smirnov et al., 2012). All extracted N<sub>2</sub>O 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; Smirnov et al., 2012). The utilized approach allows the spectrum of  $\delta^{15}\text{N}$ ,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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<sub>2</sub>O. The laboratory analytical precision (average of replicates) determined during the present study was 0.6 ‰ for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values in gaseous (n=12) and solid nitrates (n=20). For w-NO<sub>3</sub><sup>-</sup>, analytical replicates gave 0.6 and 0.5 ‰, for  $\delta^{18}\text{O}$  (n=3) and  $\delta^{17}\text{O}$  (n=4) values, respectively. The  $\Delta^{17}\text{O}$  values are defined as  $\ln(1+\delta^{17}\text{O}/1000) - 0.516 \times \ln(1+\delta^{18}\text{O}/1000)$ , relative to Vienna Standard Mean Ocean Water (VSMOW).

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### 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  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\text{NH}_4\text{NO}_3$  on the particle filter into  $\text{HNO}_3$  and  $\text{NH}_3$ , 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- $\text{NO}_3^-$  isotopic ratios ( $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) to be generally higher during winter than during summer (see Section 3.4). Moreover, the p- $\text{NO}_3^-$  minus  $\text{HNO}_3$  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  $\delta^{15}\text{N}$  values in  $\text{NH}_3$  and  $\text{NH}_4$ ; 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  $^{17}\text{O}$  anomaly; therefore,  $\Delta^{17}\text{O}$  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- $\text{NO}_3^-$  and  $\text{HNO}_3$  (Elliott et al., 2009).

#### 3.2 Concentrations and isotopic ratios of nitrates in Alberta samples

The range of  $\text{HNO}_3$  concentrations measured by the filters (from 0.01 to 0.15  $\mu\text{g N/m}^3$ ; average of 0.06) are slightly lower than those of p- $\text{NO}_3^-$  (from 0.02 to 0.35  $\mu\text{g N/m}^3$ ; 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  $\mu\text{g N/m}^3$  for  $\text{HNO}_3$  and from 0.007 to 0.45  $\mu\text{g N/m}^3$  for p- $\text{NO}_3^-$  (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

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northern Alberta border revealed similar average concentrations of 0.02  $\mu\text{g N/m}^3$  for both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  (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  $\text{w-NO}_3^-$  samples was 0.15 – 0.48  $\text{mg N/L}$ . 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  $\text{mg N/L}$ , while at the most polluted site in southern Ontario (Longwoods) the volume-weighted mean concentration was approximately 0.3  $\text{mg N/L}$  (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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of  $\text{HNO}_3$  (gas),  $\text{w-}$  and  $\text{p-NO}_3^-$  show no apparent systematic ordering (Table 3; Tables SM-1 and 2), in contrast to what was found for  $\delta^{15}\text{N}$  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  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  have the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages, but not the highest  $\text{w-NO}_3^-$  values; chemical industries show the lowest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  averages for  $\text{w-}$  and  $\text{p-NO}_3^-$ , but not for  $\text{HNO}_3$ . Though the number of samples were limited,  $\text{w-NO}_3^-$   $\Delta^{17}\text{O}$  values were roughly correlated with the weighted average  $\Delta^{17}\text{O}$  values of  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  in samples covering the same time periods, consistent with scavenging of both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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  $\text{NO}_x$  cycling and oxidation (nitrate derived through combustion in  $\text{O}_2$  would show  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of 23.5 and 0 ‰, respectively). When examining the existing  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data for  $\text{w-}$  and  $\text{p-NO}_3^-$  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  $\delta^{18}\text{O}$  range of atmospheric  $\text{NO}_3^-$  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  $\text{NO}_3^-$  samples are scarce (Table 4). The  $\text{HNO}_3$  range documented here is within the broad spectrum of  $\text{p-NO}_3^-$  values compiled for remote to contaminated sites. Elliott et al. (2009) reported  $\text{HNO}_3$  oxygen results for  $\delta^{18}\text{O}$  values only, with a range of +51.6 to +94.0 ‰ (mean of 77.4), with simultaneously-sampled  $\text{p-NO}_3^-$   $\delta^{18}\text{O}$  values between +45.2 and +92.7 ‰ (mean of 75.2). Those ranges are broader than the  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  values obtained in the present study.

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

The  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  ranges for  $\text{HNO}_3$  identified by sampling period are narrower than those of the simultaneously collected  $\text{p-NO}_3^-$  (Fig. 2; Table SM-1), suggesting that there are additional mechanisms affecting  $\text{HNO}_3$ , or that  $\text{p-NO}_3^-$  is derived from different pathways with more variation in isotopic signatures. Overall, the  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  results for  $\text{HNO}_3$ ,  $\text{w-NO}_3^-$  and  $\text{p-NO}_3^-$

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The  $\text{p-NO}_3^-$ ,  $\text{w-NO}_3^-$  and  $\text{HNO}_3$  values co-vary when identified by source type in the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  space (Fig. 1). The isotopic range for a single source can be as large as 6 ‰ for  $\Delta^{17}\text{O}$  values and 19 ‰ for  $\delta^{18}\text{O}$  values in  $\text{HNO}_3$ , 12 and 17 ‰ in  $\text{w-NO}_3^-$ , and 7 and 21 ‰ in  $\text{p-NO}_3^-$ . Each source type clearly exhibits nitrate  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  with a specific grouping. The CFPP  $\text{w-NO}_3^-$  results show a range similar to the  $\text{HNO}_3$  results, but lower  $\delta^{18}\text{O}$  values than the  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  groups. The few other precipitation samples show  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values generally higher than the  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  samples, again with exception of the chemical and metal industries. ¶

¶ The  $\text{HNO}_3$  samples from a given source type tend to have a higher  $\delta^{18}\text{O}$  value for a given  $\Delta^{17}\text{O}$  value than  $\text{p-NO}_3^-$  (or vice versa; Fig. 1). These observations suggest that the contribution of oxidation pathways leading to  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  are not identical, or that there is an isotope fractionation in the conversion of  $\text{HNO}_3$  to  $\text{p-NO}_3^-$ . ¶

¶ Regarding the potential for identifying nitrate sources, it appears that using  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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 ( $\text{p-}$  and  $\text{w-NO}_3^-$ ) or overlapping source results ( $\text{HNO}_3$ ; 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  $\text{NO}_x$  oxidation (Fig. 1; see [10]). 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]

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clearly show higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during cold periods relative to warm periods (Fig. 2), with the exception of  $\text{HNO}_3$   $\delta^{18}\text{O}$  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  $0^\circ\text{C}$  (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- $\text{NO}_3^-$ .

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,  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) is produced through reactions of air  $\text{N}_2$  with atmospheric  $\text{O}_2$  at high temperatures (reactions R1; Table 5). Then,  $\text{NO}_x$  cycles between  $\text{NO}$  and  $\text{NO}_2$  through a series of reactions involving sunlight (R5),  $\text{O}_3$  (R2, R4), and peroxy ( $\text{HO}_2$ ) or alkyl peroxy ( $\text{RO}_2$ ) radicals (R3; Morin et al., 2007; Fang et al., 2011; Michalski et al., 2014; here we use  $\text{RO}_2$  to refer collectively to  $\text{HO}_2$  and  $\text{RO}_2$ ).

The oxidation of  $\text{NO}_x$  (specifically  $\text{NO}_2$ ) to  $\text{HNO}_3$  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,  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  (R8),  $\text{HNO}_3$  is likely to be retained on the reaction particle as p- $\text{NO}_3^-$  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  $\text{NO}_3^-$  with hydrocarbons (R12) since they are predicted to have a minimal contribution to nitrate formation in this region (Alexander et al., 2009). Finally,  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of w- and p- $\text{NO}_3^-$  formed during summer are lower than those during winter due to higher contribution from the  $\text{N}_2\text{O}_5$  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- $\text{NO}_3^-$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data presented here follow the same patterns for warm and cold months (Fig. 2). In contrast, the less commonly studied  $\text{HNO}_3$  shows similar  $\delta^{18}\text{O}$  values during warm and cold seasons, but summer  $\Delta^{17}\text{O}$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  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  $\text{HNO}_3$  and p- $\text{NO}_3^-$  samples (n of w- $\text{NO}_3^-$  too low) with meteorological and air quality parameters measured routinely at nearby monitoring stations where available (Table SM-3). We found that the p- $\text{NO}_3^-$  and  $\text{HNO}_3$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values correlate with RH, with p- $\text{NO}_3^-$  values showing stronger statistical links than  $\text{HNO}_3$  (Table 6). The  $\text{N}_2\text{O}_5$  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- $\text{NO}_3^-$   $\delta^{18}\text{O}$ , p- $\text{NO}_3^-$   $\Delta^{17}\text{O}$ , and  $\text{HNO}_3$   $\Delta^{17}\text{O}$ . These negative links likely arise since

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$N_2O_5$  is more stable under cold conditions, leading to a higher contribution of R8. The stronger links with  $p\text{-NO}_3^-$  may be due to R8 taking place on surfaces (such as particles) with liquid water, which is likely to retain the  $\text{HNO}_3$  as  $p\text{-NO}_3^-$  rather than release it to the gas phase. Therefore, in winter, R8 may contribute more to  $p\text{-NO}_3^-$  than to  $\text{HNO}_3(\text{g})$ . Moreover, the highest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values for both  $p\text{-NO}_3^-$  and  $\text{HNO}_3$  were found for fall-winter samples collected at high RH (76 %) and low temperature ( $-10^\circ\text{C}$ ). In contrast, the lowest  $p\text{-NO}_3^-$  isotopic values were found for samples with similar proportions of  $\text{HNO}_3$  and  $p\text{-NO}_3^-$ , and sampled during moderately humid (60-63 %) and warm ( $8\text{-}20^\circ\text{C}$ ) periods. The accompanying shift in isotopic differences between  $p\text{-NO}_3^-$  and  $\text{HNO}_3$ , will help infer the mechanisms dominating during the cold and warm periods (Section 4.2).

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Concentrations of oxidants, co-contaminants (e.g.,  $\text{SO}_4^-$  aerosols) and  $\text{NO}_x$  influence the dominance and rates of the discussed reactions (Brown et al., 2006; Michalski et al., 2014). However, while temperature, RH and  $\text{O}_3$  are well captured within a 5 km radius, other pollutant measurements like continuous  $\text{SO}_2$ ,  $\text{PM}_{2.5}$  and  $\text{NO}_x$  can have large gradients near sources, therefore it is not surprising that no correlations were found with  $\text{SO}_2$  or  $\text{PM}_{2.5}$  measured at sites 4-5 km away (Table 6). Surprisingly, only the  $p\text{-NO}_3^-$   $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  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  $\text{HNO}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values.

Supprimé: For instance, high  $\text{NO}_x/\text{O}_3$  ratios do not favor NO oxidation by peroxy radicals ( $\text{RO}_2$  family) with typically low isotopic values, explaining the positive link between  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values with  $\text{NO}_x/\text{O}_3$  ratios (Table 6).

### 3.5 Comparison with high-latitude $p\text{-NO}_3^-$

An interesting aspect of the Alberta  $p\text{-NO}_3^-$  cold-period  $\Delta^{17}\text{O}$  ranges is that they compare relatively well with the range obtained for the Canadian Arctic (Fig. 4), during winter, when nighttime conditions and the  $\text{N}_2\text{O}_5$  pathway prevail without interruption (Morin et al., 2008; for comparison with  $\text{HNO}_3$  values see Fig. SM-4). This observation supports the suggestion that the  $\text{N}_2\text{O}_5$  pathway produces around 90 % of nitrates during mid-latitude cold months (Michalski et al., 2003; Section 4.1). The  $\delta^{18}\text{O}$  ranges of cold months are similar in Alberta and in the Arctic. This similarity goes against previous suggestions that at higher latitudes, nitrate  $\delta^{18}\text{O}$  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  $\text{N}_2\text{O}_5$  pathway during the Arctic winter (Fang et al., 2011).

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The  $\Delta^{17}\text{O}$  departure between the Alberta and Arctic winter parallel lines is about 3 ‰. Such difference is slightly larger than the one calculated for winter  $\text{NO}_3^-$  at 80 and 40°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  $\Delta^{17}\text{O}$  values is similar at the mid- and high-latitude 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  $\Delta^{17}\text{O}$  values of  $\text{NO}_x$  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  $\text{N}_2\text{O}_5$  pathways during summer and winter, respectively. Finally, the

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$\Delta^{17}\text{O}$  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 $\text{HNO}_3$ and $\text{p-NO}_3^-$

As far as the isotopic characteristics are concerned, an important feature to keep in mind is that the  $\text{HNO}_3$  of central and southern Alberta has distinct properties relative to simultaneously sampled  $\text{p-NO}_3^-$ . In practical terms, the relationships between the simultaneously sampled  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  are of four types (Fig. 3): (i)  $\text{HNO}_3$   $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  are both lower than  $\text{p-NO}_3^-$ ; (ii)  $\text{HNO}_3$  has lower  $\Delta^{17}\text{O}$  but higher  $\delta^{18}\text{O}$  values than  $\text{p-NO}_3^-$ ; (iii)  $\text{HNO}_3$  has higher  $\delta^{18}\text{O}$  values and similar  $\Delta^{17}\text{O}$  ones relative to  $\text{p-NO}_3^-$ ; and (iv)  $\text{HNO}_3$  has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than  $\text{p-NO}_3^-$  (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  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  in northeastern USA with similar seasonal changes of  $\delta^{18}\text{O}$  differences (no  $\Delta^{17}\text{O}$  measurement). The  $\text{HNO}_3$   $\delta^{18}\text{O}$  were generally similar or lower than the  $\text{p-NO}_3^-$  values during winter and fall, and slightly to much higher during spring and summer, with the spring and autumn  $\text{p-NO}_3^-$ - $\text{HNO}_3$  relationships being roughly intermediate between the winter and summer ones. The average  $\delta^{18}\text{O}$  difference of  $\text{p-NO}_3^-$  minus  $\text{HNO}_3$  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  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  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  $\text{NO}_x$  source.

## 4 Discussion

### 4.1 Estimation of $\Delta^{17}\text{O}$ values of $\text{NO}_x$ precursor to the studied nitrates - Highlighting oxidation mechanisms

In the present sub-section, we estimate the  $\Delta^{17}\text{O}$  values of  $\text{NO}_2$  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  $\text{N}_2\text{O}_5$  due to interaction with  $\text{O}_3$  (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  $\text{H}_2\text{O}$  (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  $\text{NO}_2$ , 1/6 from  $\text{O}_3$  and 1/6 from  $\text{H}_2\text{O}$ , while the second produces nitrates via R6 with 2 out of 3 O atoms coming from  $\text{NO}_2$  and 1/3 from OH (e.g., Michalski et al., 2003). Using these proportions with the Alberta  $\Delta^{17}\text{O}$  values of  $\text{p-NO}_3^-$  and  $\text{HNO}_3$  in weighted averages allows us to make a rough estimation of the maximum and minimum  $\Delta^{17}\text{O}$  values of  $\text{NO}_2$  oxidized to nitrates in the air masses sampled. The calculations assume the O from  $\text{O}_3$  contributes a signal of ~39 ‰ as was recently measured (Vicars et al., 2014) and that  $\Delta^{17}\text{O}$  of OH and  $\text{H}_2\text{O}$  are zero. The estimated  $\text{NO}_2$   $\Delta^{17}\text{O}$  values for fall-

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Supprimé: In the Alberta samples,  $\text{HNO}_3$  is present at such significant proportions, that if they had not been differentiated, the low end of the isotopic range obtained for  $\text{p-NO}_3^-$  would have been significantly higher in both  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  (Table 4, see undifferentiated category). Hence, a

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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<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> 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<sub>2</sub> Δ<sup>17</sup>O ranges indicate that the potential parent NO<sub>2</sub> had a smaller <sup>17</sup>O anomaly than O<sub>3</sub> (39 ‰; Vicars and Savarino, 2014) or NO<sub>2</sub> in isotopic equilibrium with O<sub>3</sub> alone (45 ‰; Michalski et al., 2014) in all possible scenarios.

Two mechanisms could be responsible for the Δ<sup>17</sup>O differences between these estimates and NO<sub>2</sub> in isotopic equilibrium with O<sub>3</sub>. One is the competition of R3 with R2 in oxidizing NO to NO<sub>2</sub>, since RO<sub>2</sub> will decrease the Δ<sup>17</sup>O values relative to an ozone-only equilibrium. The relative reaction rates of R2 and R3 have previously been presumed to control the NO<sub>2</sub> isotopic composition (e.g., Alexander et al., 2009) based on the assumption of isotopic steady state. A larger contribution of RO<sub>2</sub> is expected in the NO<sub>2</sub> precursors for summer relative to winter, since biogenic VOCs that are major sources of RO<sub>2</sub> radicals are much higher in the summer (e.g., Fuentes and Wang, 1999). This suggestion is consistent with the lower Δ<sup>17</sup>O ranges in summer reported here. A second possibility is that the nitrates were formed from some NO<sub>x</sub> that did not reach isotopic steady state with O<sub>3</sub> retaining some of its original signature (assumed to be Δ<sup>17</sup>O=0 ‰). Most studies have assumed that isotopic steady state is established between O<sub>3</sub> and NO<sub>2</sub> within a few minutes after emission of NO<sub>x</sub> from a combustion source – or at least, that nitrate formation is negligible before NO<sub>x</sub> isotopic equilibrium is reached. However, recent modeling by Michalski et al. (2014) suggests that isotopic equilibration of NO<sub>x</sub> with O<sub>3</sub> could take several minutes up to a few hours at the relatively low O<sub>3</sub> concentrations in rural Alberta. At the measured average wind speeds on site of 8-19 km hr<sup>-1</sup>, transit times from the nearest sources to observation sites are estimated to be 9-55 minutes. While the fraction of NO<sub>x</sub> converted to nitrate in this transit time may be small, these are large sources of NO<sub>x</sub> in an area with very low background nitrates. For example, a plume containing 10 ppb of NO<sub>2</sub> mixing with background air with 0.1 ppt of OH (Howell et al., 2014) would produce HNO<sub>3</sub> via R6 at a rate of 0.011 μg N m<sup>-3</sup> min<sup>-1</sup> 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<sub>3</sub> 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<sub>x</sub> that had not yet reached isotopic steady state with O<sub>3</sub>. These two mechanisms are not exclusive and could both contribute to lower NO<sub>x</sub> and therefore nitrate, Δ<sup>17</sup>O values.

An additional piece of evidence suggests that the NO<sub>x</sub> plumes themselves, rather than ambient conditions, are the source of low-Δ<sup>17</sup>O nitrates in these samples. There is a strong correlation between the total nitrate Δ<sup>17</sup>O values and the maturity of the plume as expressed by the NO<sub>2</sub> concentration divided by sum of HNO<sub>3</sub> and p-NO<sub>3</sub> concentrations (Fig. 5). This observation is consistent with the unequilibrated NO<sub>2</sub> hypothesis. However, it does not rule out the possible contribution of RO<sub>2</sub>, since VOC releases from the NO<sub>x</sub> sources could lead to elevated RO<sub>2</sub> concentrations in the plume.

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Supprimé: TThe extent of the Δ<sup>17</sup>O difference between the spring-summer and fall-winter HNO<sub>3</sub> clusters (Fig. 2B) likely reflects various combinations degrees of involvement of the invoked se two mechanisms. (Myrick et al., 1994) Δ<sup>17</sup>O reaching the sampling site older than when the plume is emitted within the boundary layer

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#### 4.2 Causes of shifts in HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences

A challenging question is why do the HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences shift seasonally (Fig. 3)? One factor that may influence the relationship between HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> is mass-dependent isotopic equilibrium between NH<sub>4</sub>NO<sub>3</sub> and HNO<sub>3</sub> (R10); however, this mechanism would result in higher δ<sup>18</sup>O in p-NO<sub>3</sub><sup>-</sup> and unchanged Δ<sup>17</sup>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<sub>2</sub>O<sub>5</sub> pathway is likely to produce more p-NO<sub>3</sub><sup>-</sup> than HNO<sub>3</sub>(g), which would result in a higher contribution from ozone and explain why δ<sup>18</sup>O and Δ<sup>17</sup>O values are both higher in p-NO<sub>3</sub><sup>-</sup>. A previous study addressing why p-NO<sub>3</sub><sup>-</sup> 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 δ<sup>18</sup>O and Δ<sup>17</sup>O values were lower in p-NO<sub>3</sub><sup>-</sup> than in HNO<sub>3</sub> (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<sub>3</sub> dry deposits to surfaces more rapidly than p-NO<sub>3</sub><sup>-</sup> (Zhang et al., 2009; Benedict et al., 2013), which would create the discussed isotopic shifts in the situation where NO<sub>2</sub> has low Δ<sup>17</sup>O values in a fresh plume. The first nitrates formed in the plume shortly after emission from the NO<sub>x</sub> source have low δ<sup>18</sup>O and Δ<sup>17</sup>O values, either because NO<sub>x</sub> has not yet reached isotopic steady state with O<sub>3</sub> or because it reacted with <sup>17</sup>O-poor RO<sub>2</sub> present in the plume due to VOC emissions. Those nitrates that form as p-NO<sub>3</sub><sup>-</sup> or that partition to p-NO<sub>3</sub><sup>-</sup> remain in the plume for longer than HNO<sub>3</sub>, which is removed from the plume rapidly upon contact with vegetation or other surfaces. As the plume travels, the NO<sub>x</sub> becomes more enriched, and the newly formed nitrates take on higher δ<sup>18</sup>O and Δ<sup>17</sup>O values. However, p-NO<sub>3</sub><sup>-</sup> collected further downwind will derive from a mixture of low-δ<sup>18</sup>O and -Δ<sup>17</sup>O p-NO<sub>3</sub><sup>-</sup> formed earlier, plus high-δ<sup>18</sup>O and -Δ<sup>17</sup>O p-NO<sub>3</sub><sup>-</sup> formed more recently, while HNO<sub>3</sub> will have a larger proportion formed more recently and will therefore have higher δ<sup>18</sup>O and Δ<sup>17</sup>O values. The fact that we find the lowest isotopic values in summer p-NO<sub>3</sub><sup>-</sup> 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<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> isotopic differences between cold and warm sampling periods – differential N<sub>2</sub>O<sub>5</sub> contribution resulting in higher Δ<sup>17</sup>O values in p-NO<sub>3</sub><sup>-</sup> than in HNO<sub>3</sub>, and differential deposition resulting in lower Δ<sup>17</sup>O values in p-NO<sub>3</sub><sup>-</sup> – would essentially compete against each other, with local conditions and chemistry influencing the results. In winter, when the N<sub>2</sub>O<sub>5</sub> pathway is most important, the first mechanism dominates, as supported by the observation that p-NO<sub>3</sub><sup>-</sup> concentrations are higher during that season (trend *i*). Conversely, in summer, when the N<sub>2</sub>O<sub>5</sub> 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 δ<sup>18</sup>O differences. For instance, kinetic fractionation may be involved in the production of trend *iii*.

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In summary, examining the isotopic relationship of HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup> (Fig. 3), reveals the complexity of anthropogenic NO<sub>x</sub> oxidation mechanisms. The negative isotopic differences between p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> during warm months may reflect differential removal rates from plumes containing NO<sub>2</sub> temporarily low in <sup>17</sup>O.

#### 5 4.3 - Low δ<sup>18</sup>O and Δ<sup>17</sup>O trends in global w- and p-NO<sub>3</sub><sup>-</sup> - 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<sub>x</sub> 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<sub>3</sub> and oxidation through the well-known OH and N<sub>2</sub>O<sub>5</sub> oxidation paths. However, NO<sub>2</sub> not in isotopic equilibrium with O<sub>3</sub>, and/or NO reacted with RO<sub>2</sub> 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<sub>2</sub> and/or HO<sub>2</sub> 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?

15 The full Δ<sup>17</sup>O and δ<sup>18</sup>O ranges for p-NO<sub>3</sub><sup>-</sup>, w-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (between 13.8 and 20.5 ‰, 48.4 and 83.2 ‰; Table 4) compare well with the isotopic ranges obtained for bulk deposition NO<sub>3</sub><sup>-</sup> 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 δ<sup>18</sup>O and Δ<sup>17</sup>O values.

Previous work in the Athabasca region reported very low δ<sup>18</sup>O and near-zero Δ<sup>17</sup>O values for p-NO<sub>3</sub><sup>-</sup> 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<sub>2</sub>. Similar isotopic signatures are very likely produced in source emissions of NO<sub>x</sub> in the studied Edmonton and Vauxhall areas (e.g., CFPP, gas compressors, industries). This source signature may persist into p-NO<sub>3</sub> collected close to the sources. Within the first few hours in the atmosphere (less, in polluted areas), the NO<sub>x</sub> δ<sup>18</sup>O and Δ<sup>17</sup>O values rapidly increase due to isotope exchange with O<sub>3</sub> (R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub> and O<sub>3</sub> formation, Table 5; Michalski et al., 2014) and reach isotopic equilibrium. Though the e-folding lifetime for NO<sub>x</sub> oxidation to nitrates may be longer than these few hours, depending on the NO<sub>x</sub>/VOC ratio, only a fraction of the oxidized source NO<sub>x</sub> 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 Δ<sup>17</sup>O values within 12 km of the emission sites, and where direct stack emissions of p-NO<sub>3</sub><sup>-</sup> were ~5000 times lower than NO<sub>x</sub> emissions (Wang et al., 2012).

35 In a methodological test study, we obtained low values for w-NO<sub>3</sub><sup>-</sup> sampled near a high traffic volume highway in Ontario, Canada (Smirnov et al., 2012). Low δ<sup>18</sup>O and Δ<sup>17</sup>O values in atmospheric nitrates during warm months (65 and 20 ‰ or less,

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Supprimé: The final isotopic values are derived from the O<sub>3</sub>-NO<sub>x</sub> (Leighton) cycle and competing oxidation by RO<sub>2</sub>, possibly not yet at isotopic steady state - followed by the OH and N<sub>2</sub>O<sub>5</sub> (O<sub>3</sub>) oxidation pathways in proportions that vary with the periods of sampling (Fig. 4).

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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  $\delta^{18}\text{O}$  values in w- $\text{NO}_3^-$  from a polluted city (Fang et al., 2011), in p- $\text{NO}_3^-$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values in summer nitrates may reflect the involvement of air masses that include nitrates from oxidation of  $\text{NO}_2$  with light isotopes in plumes. In such cases, while not ruling out a higher contribution from  $\text{RO}_2$  oxidation of  $\text{NO}_2$ , it is also possible that significant portions of the collected nitrate were formed before the  $\text{NO}_x$ - $\text{O}_3$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  may reflect relative proximity to anthropogenic N emitters in general. Further research work on plume  $\text{NO}_x$  to nitrates chemical mechanisms may help to validate this suggestion. In the future, the assumption of  $\text{NO}_x$  isotopic steady state with  $\text{O}_3$  should be explored, given recent findings (Michalski et al., 2014), the critical importance of  $\text{NO}_x$  isotope characteristics on resulting nitrate isotopic values (Alexander et al., 2009), and the suggestion regarding the evolution of  $\text{NO}_x$ - $\text{NO}_3^-$  signals in fresh anthropogenic plumes (present study).

## 5 Conclusion

The  $\text{HNO}_3$ , w- $\text{NO}_3^-$  and p- $\text{NO}_3^-$  from anthropogenic sources in central and southern Alberta, simultaneously collected with wind sector-based conditional sampling systems produced  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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 ( $\text{HNO}_3$ ) 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- $\text{NO}_3^-$  in these samples generally shows higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values than  $\text{HNO}_3$  in the fall-winter period as the heterogeneous  $\text{N}_2\text{O}_5$  pathway favours the production of p- $\text{NO}_3^-$ . In contrast,  $\text{HNO}_3$  has higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values during warm periods, which we propose is due to faster dry deposition rates relative to p- $\text{NO}_3^-$  in the event that low- $\Delta^{17}\text{O}$   $\text{NO}_2$  is oxidized in the plume. The mechanisms conferring nitrate with relatively low isotopic values, whether oxidation before  $\text{NO}_x$ - $\text{O}_3$  equilibrium is reached or higher contributions from  $\text{RO}_2$ , 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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values may reflect nitrates produced from undifferentiated anthropogenic  $\text{NO}_x$  emissions.

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

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Future research should explore the assumption of NO<sub>x</sub> isotopic equilibration with O<sub>3</sub>, given the critical importance of NO<sub>x</sub> 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<sub>y</sub>, 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.

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**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 <sub>x</sub> sources; fertilizer plant largest NH <sub>3</sub> 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 <sub>3</sub> and NO <sub>x</sub> source, oil refinery major NO <sub>x</sub> source

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

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5 **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)	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$
<i>Teflon filters</i> p-NO <sub>3</sub> <sup>-</sup> (19)	2	1
<i>Nylon filters</i> HNO <sub>3</sub> (18)	1	0.7

10 **Table 3. Average oxygen isotopic ratios (‰) for NO<sub>3</sub><sup>-</sup> sampled as gas (HNO<sub>3</sub>), w (precipitation) and p (particulate matter) relative to VSMOW.**

Matrix Source	Gas			w			p		
	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$
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)	- (3)	63.1 (3)	24.5 (2)	- (3)	26.4 (3)			
City traffic	65.7 (3)	67.2 (2)	59.6 (3)	21.2 (3)	24.4 (2)	22.5 (3)			
<b>Mean</b>	<b>66.8</b>	<b>66.0</b>	<b>62.6</b>	<b>23.0</b>	<b>24.3</b>	<b>23.4</b>			

(n): number of sampling periods characterized

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

$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	Regional context	Location	Authors
<b>HNO<sub>3</sub></b>				
62.4-81.7	19.3-29.0	Various contaminated sites	Alberta, Canada	<i>This study</i>
<b>p-NO<sub>3</sub><sup>-</sup></b>				
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	<i>This study</i>
<b>w-NO<sub>3</sub><sup>-</sup></b>				
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	Smirnov 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	<i>This study</i>
<b>Undifferentiated and Bulk NO<sub>3</sub><sup>-</sup></b>				
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	<i>This study</i>

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<sub>3</sub> and p-NO<sub>3</sub> isotopic results.

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**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) $\text{O}_2 + \text{Q} \rightarrow \text{O} + \text{O} + \text{Q}$ ; $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$ ; $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	
(R2) $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3$ ; $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	
(R3) $\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO}$	
	(R4) $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$
(R5) $\text{NO}_2 + h\nu$ (sunlight) $\rightarrow \text{NO} + \text{O}$	
(R6) $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	(R7) $\text{NO}_2 + \text{NO}_3^- \rightleftharpoons \text{N}_2\text{O}_5$
	(R8) $\text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{surface}) \rightarrow 2\text{HNO}_3(\text{aq})^*$
(R9) $\text{HNO}_3(\text{g}) \rightleftharpoons \text{HNO}_3(\text{aq})^* \rightarrow \text{NO}_3^-(\text{aq})^* + \text{H}^+(\text{aq})$	
(R10) $\text{HNO}_3(\text{g}) + \text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_4\text{NO}_3(\text{s})$	
(R11) $\text{HNO}_3(\text{g}) + \text{CaCO}_3(\text{s}) \rightarrow \text{Ca}(\text{NO}_3)_2(\text{s}) + \text{HCO}_3^-$	
(R12) $\text{NO}_3^- + \text{HC}(\text{CH}_3)_2\text{S} \rightarrow \text{HNO}_3 + \text{products}$	

*Q* is a stable molecule of high energy; *M* is either O<sub>2</sub> or N<sub>2</sub>; *RO*<sub>2</sub> stands for both HO<sub>2</sub> and alkyl peroxy. *HC* stand for hydrocarbons. \*This aqueous nitrate may be on a particle.

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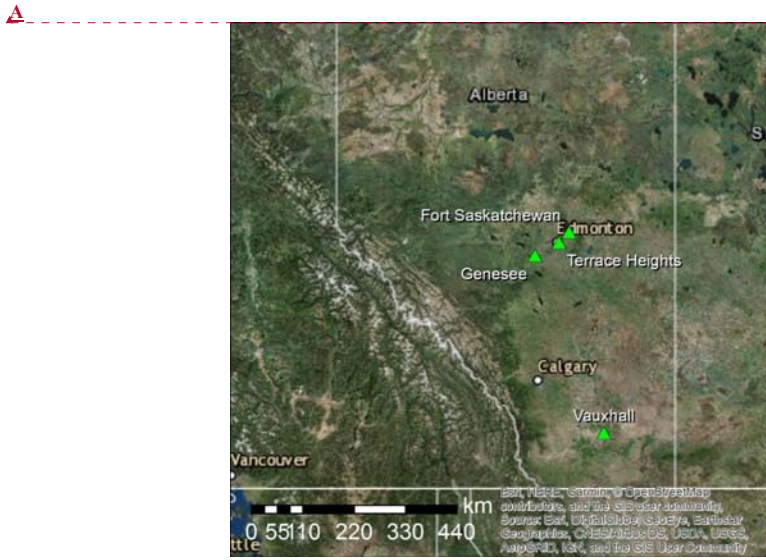
Table 6. Correlations of NO<sub>3</sub><sup>-</sup> isotopic results (‰) with meteorological parameters and concentration (or ratio) of co-contaminants.

	Relative Humidity		Temperature		Daylight (fraction)		PM	SO <sub>2</sub>	O <sub>3</sub>	
	r	R <sup>2</sup>	r	R <sup>2</sup>	r	R <sup>2</sup>	r	r	r	R <sup>2</sup>
HNO <sub>3</sub>										
δ <sup>18</sup> O	<b>0.8</b>	0.59	-0.4		-0.3		0.1	0.0	-0.29	
n	8		15		15		13	13		13
Δ <sup>17</sup> O	0.6		<b>-0.5</b>	0.24	-0.4		0.4	0.3	-0.03	
n	8		15		15		13	13		13
p-NO <sub>3</sub> <sup>-</sup>										
δ <sup>18</sup> O	<b>0.9</b>	0.79	<b>-0.6</b>	0.34	<b>-0.6</b>	0.35	0.1	0.5	<b>-0.61</b>	0.38
n	7		15		15		12	12		12
Δ <sup>17</sup> O	<b>0.9</b>	0.73	<b>-0.6</b>	0.34	<b>-0.7</b>	0.44	0.0	0.5	-0.47	
n	7		15		15		12	12		12

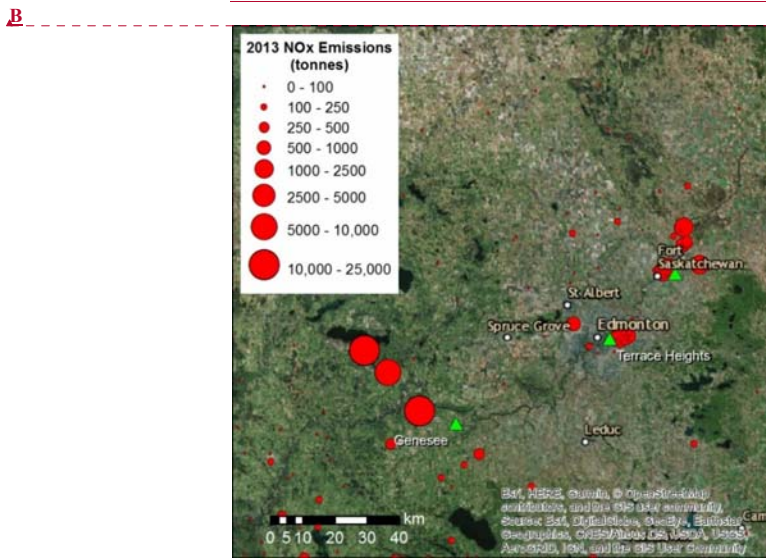
In **bold** are the significant correlation coefficients, equal or above the 95 % significance value

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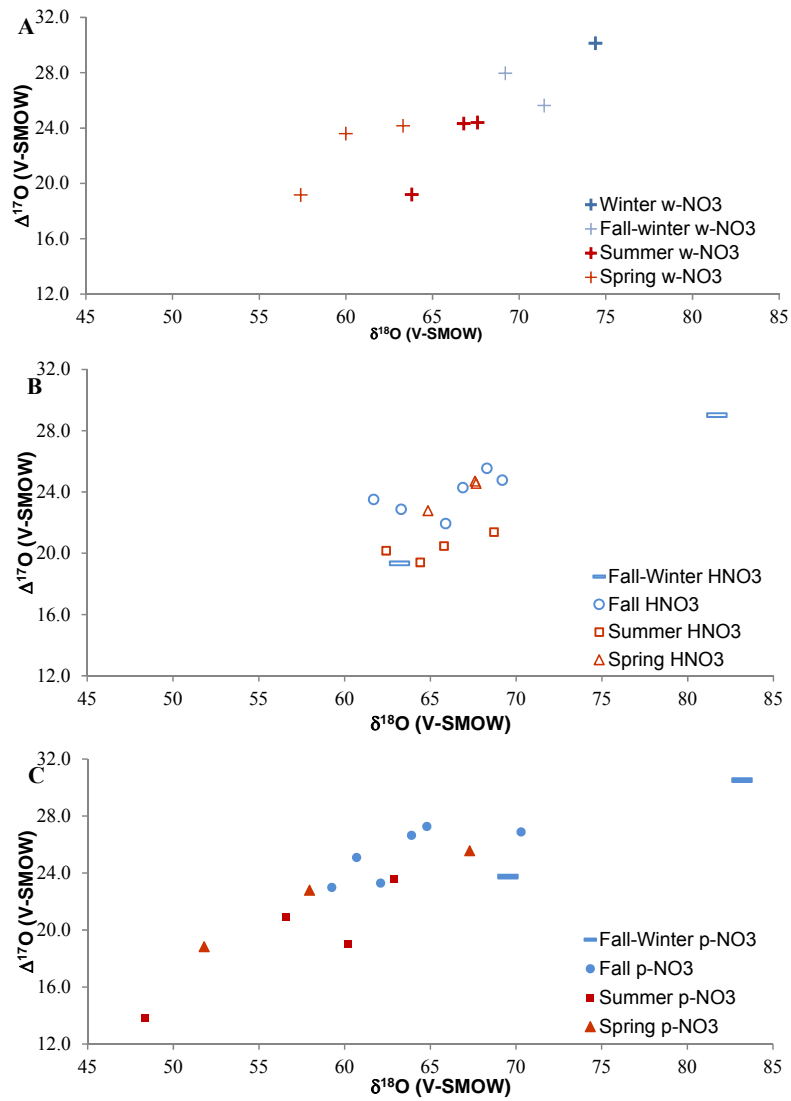


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5 **Figure 1.** Aerial images showing sampling sites (green triangles) in central and southern Alberta (A), and in the greater Edmonton area (B), along with emissions of NO<sub>x</sub> as tonnes of NO<sub>x</sub> reported to the National Pollutant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

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5 Figure 2: Triple O isotopic results (‰) obtained for simultaneously collected atmospheric HNO<sub>3</sub> (A), w-NO<sub>3</sub><sup>-</sup> (B) and p-NO<sub>3</sub><sup>-</sup> (C), in Alberta, identified by sampling periods (cold months - blue; warm months - red).

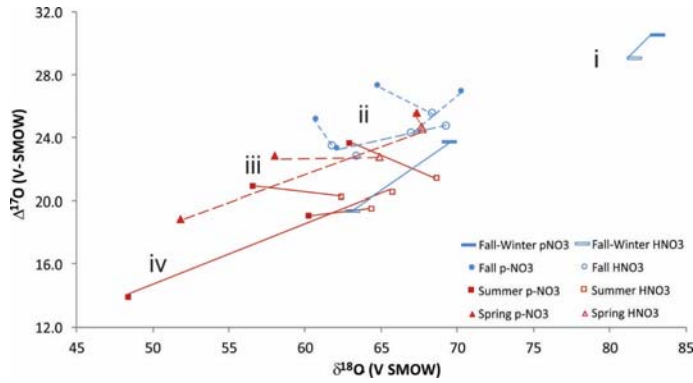


Figure 3: Line-connected  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values (‰) for simultaneously collected  $\text{HNO}_3$  (empty symbols) and  $\text{p-NO}_3^-$  (solid symbols) from cold (blue) and warm (red) sampling periods.

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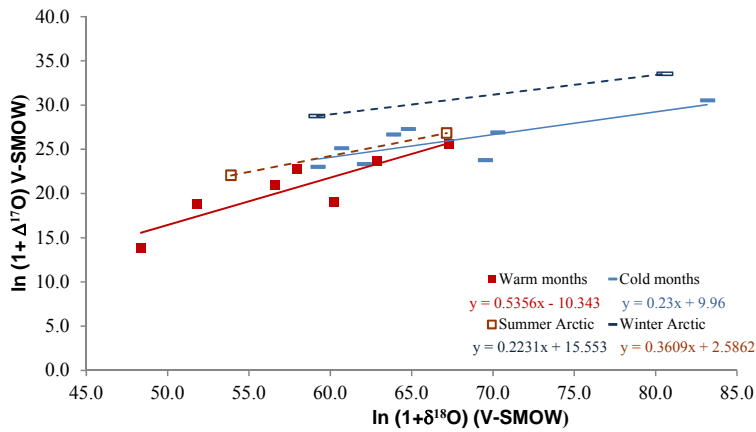
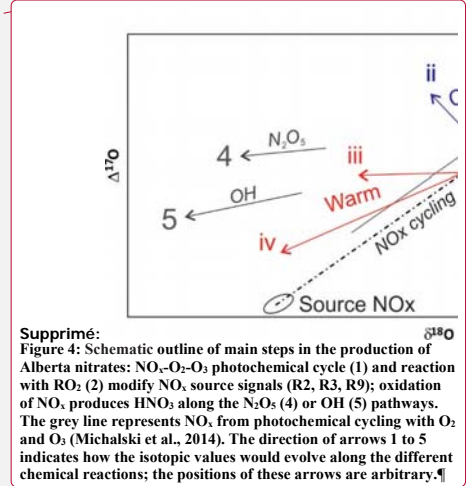


Figure 4: Isotopic results (‰) for  $\text{p-NO}_3^-$  identified by sampling periods (solid lines), compared with summer and winter trends obtained for Arctic sites (dashed lines; derived from  $\ln(1+\delta)$  in Morin et al., 2008).



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Figure 4: Schematic outline of main steps in the production of Alberta nitrates:  $\text{NO}_x\text{-O}_3\text{-O}_3$  photochemical cycle (1) and reaction with  $\text{RO}_2$  (2) modify  $\text{NO}_x$  source signals (R2, R3, R9); oxidation of  $\text{NO}_x$  produces  $\text{HNO}_3$  along the  $\text{N}_2\text{O}_5$  (4) or OH (5) pathways. The grey line represents  $\text{NO}_x$  from photochemical cycling with  $\text{O}_2$  and  $\text{O}_3$  (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. ¶

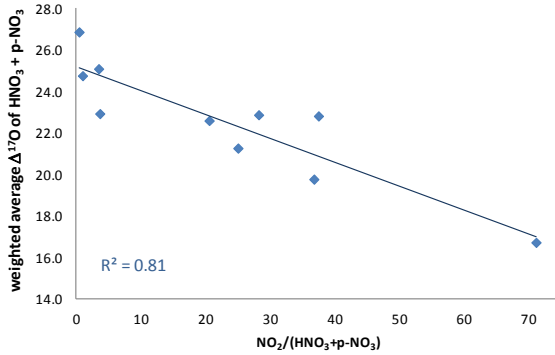


Figure 5: Weighted average  $\Delta^{17}\text{O}$  (‰) for the sum of dry nitrates as a function of  $\text{NO}_2$  concentration divided by  $\text{p-NO}_3$  plus  $\text{HNO}_3$  concentrations, a ratio indicative of the maturity of a plume.

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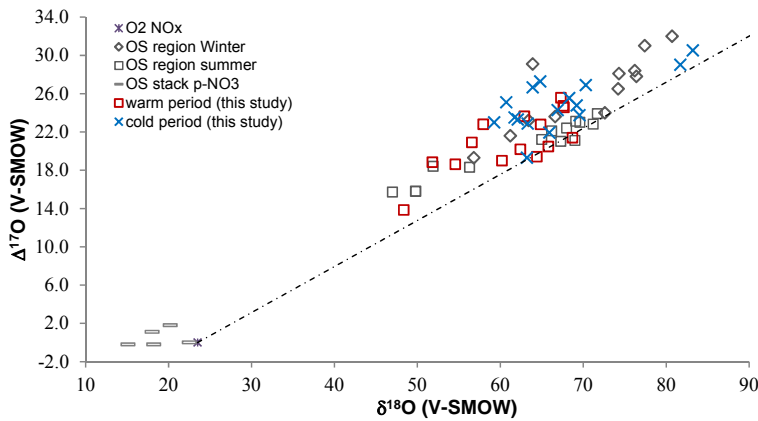


Figure 6: Isotopic ratios (‰) for atmospheric  $\text{p-NO}_3^-$ ,  $\text{w-NO}_3^-$  and  $\text{HNO}_3$  samples in cold and warm periods from central and southern Alberta (this study), compared with previously published winter and summer bulk and throughfall deposition samples from the oil sands (OS) region from northern Alberta (Proemse et al., 2013), and  $\text{p-NO}_3^-$  in-stack emissions data for an OS upgrader located in the same region (Proemse et al., 2012). The grey dotted line connects  $\text{NO}_x$  from theoretical combustion with  $\text{O}_2$  isotopic composition and at isotopic equilibrium with tropospheric  $\text{O}_3$  (Michalski et al., 2014).

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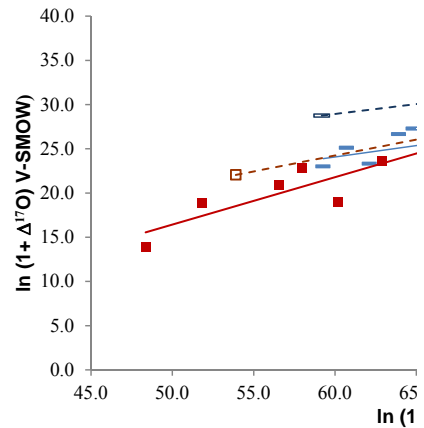


Figure 6: Isotopic results (‰) for  $\text{p-NO}_3^-$  identified by sampling periods (solid lines), compared with summer and winter trends obtained for Arctic sites (dashed lines; derived from  $\ln(1 + \delta)$  in Morin et al., 2008).

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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<sub>3</sub>/L (0.03 N-NO<sub>3</sub> umol/L). The concentration for NO and NO<sub>2</sub> collected with samplers of Maxxam Analytics were determined by Maxxam Analytics using an ion chromatograph.

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

The p-NO<sub>3</sub><sup>-</sup>, w-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> values co-vary when identified by source type in the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  space (Fig. 1). The isotopic range for a single source can be as large as 6 ‰ for  $\Delta^{17}\text{O}$  values and 19 ‰ for  $\delta^{18}\text{O}$  values in HNO<sub>3</sub>, 12 and 17 ‰ in w-NO<sub>3</sub><sup>-</sup>, and 7 and 21 ‰ in p-NO<sub>3</sub>. Each source type clearly exhibits nitrate  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  with a specific grouping. The CFPP w-NO<sub>3</sub><sup>-</sup> results show a range similar to the HNO<sub>3</sub> results, but lower  $\delta^{18}\text{O}$  values than the HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> groups. The few other precipitation samples show  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values generally higher than the p-NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> samples, again with exception of the chemical and metal industries.

The HNO<sub>3</sub> samples from a given source type tend to have a higher  $\delta^{18}\text{O}$  value for a given  $\Delta^{17}\text{O}$  value than p-NO<sub>3</sub><sup>-</sup> (or *vice versa*; Fig. 1). These observations suggest that the contribution of oxidation pathways leading to HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> are not identical, or that there is an isotope fractionation in the conversion of HNO<sub>3</sub> to p-NO<sub>3</sub><sup>-</sup>.

Regarding the potential for identifying nitrate sources, it appears that using  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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<sub>3</sub>) or overlapping source results (HNO<sub>3</sub>; 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<sub>x</sub> oxidation (Fig. 1; see Section 3.4). 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.

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The Alberta nitrate values do not fall on a single line but, rather, show a vertical extent in the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  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<sub>2</sub> (via RO<sub>2</sub> - R3, and possibly source NO<sub>x</sub>- R1), O<sub>3</sub> (via NO<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O<sub>5</sub> - R2, R4, R7-R8) and H<sub>2</sub>O (via OH, R5-R6). These molecules carry distinct isotopic signals that will partly determine the final  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of the nitrate products. The  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of O<sub>2</sub> are 23.5 and 0 ‰, respectively. Anthropogenic emitters involving combustion (O<sub>2</sub>) may generate primary NO<sub>x</sub> at or near sources that tend to carry low  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values (Zel'dovich, 1946; Lavoie et al., 1969). This primary NO<sub>x</sub> (>90 % emitted as NO) cycles through NO-NO<sub>2</sub>-O<sub>3</sub>-NO numerous times before it is removed in R6. OH typically has negative  $\delta^{18}\text{O}$  values and a  $\Delta^{17}\text{O}$  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  $\delta^{18}\text{O}$  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<sub>2</sub>O vapour (Walters and Michalski, 2016), we calculated that the  $\delta^{18}\text{O}$  values would range between -83 and -62 ‰. Peroxy radicals mostly derive from O<sub>2</sub> at mid latitudes (Michalski et al., 2003; Morin et al., 2007; Alexander et al., 2009), but they have a non-zero  $\Delta^{17}\text{O}$  signal (1-2 ‰) due to the role of ozone in the HO<sub>x</sub> cycle (Morin et al., 2011). However, their  $\delta^{18}\text{O}$  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  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of bulk



O<sub>3</sub> 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<sub>x</sub> modelled at isotopic steady state with tropospheric O<sub>3</sub> yields 117 and 45 ‰ in δ<sup>18</sup>O and Δ<sup>17</sup>O, respectively (Michalski et al., 2014). This neglects the contribution of NO oxidation by RO<sub>2</sub> (R3), which will reduce the steady-state Δ<sup>17</sup>O and δ<sup>18</sup>O of NO<sub>x</sub> below the O<sub>3</sub>-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 δ<sup>18</sup>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 Δ<sup>17</sup>O values and the maturity of a plume as expressed by the NO<sub>2</sub> content divided by sum of dry nitrates (Fig. 6). The results reflect the higher content of O<sub>3</sub>-derived O in dry nitrates from mature plumes, i.e., with relatively low NO<sub>2</sub> 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  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of atmospheric nitrates ~~simultaneously collected downwind of anthropogenic sources – Implications for polluted air masses~~

Supprimé: simultaneously collected

Supprimé: from

5 Martine M. Savard<sup>1\*</sup>, Amanda Cole<sup>2</sup>, Robert Vet<sup>2</sup>, Anna Smirnoff<sup>1</sup>

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

#	Site	Deployment	Collection	Days	Sampling hours	Mean (total for pooled) air volume (m <sup>3</sup> )	p-NO <sub>3</sub> <sup>-</sup>				HNO <sub>3</sub>				Daylight fraction (sunrise to sunset)	NO <sub>2</sub> in sample train* (ug N/m <sup>2</sup> )		
							Mean (total for pooled) loading (ug N)	Air conc (ug N/m <sup>2</sup> )	δ <sup>18</sup> O (‰)	δ <sup>17</sup> O (‰)	Δ <sup>17</sup> O (‰)	Mean (total for pooled) loading (ug N)	Air conc (ug N/m <sup>3</sup> )	δ <sup>18</sup> O (‰)			δ <sup>17</sup> O (‰)	Δ <sup>17</sup> O (‰)
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<sub>2</sub> filters where breakthrough <15%. Sum of NO<sub>2</sub> 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.**

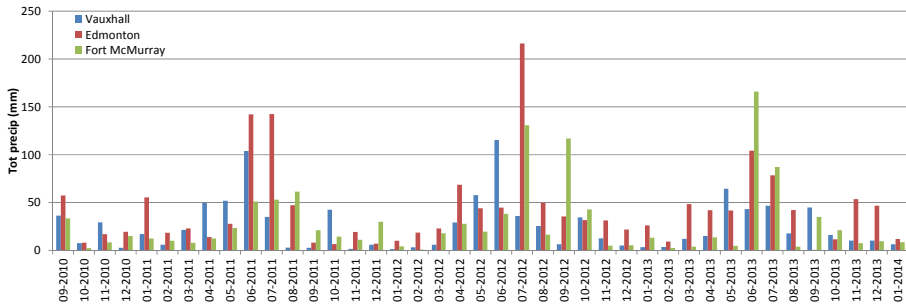
#	Site	Sampling duration			w-NO <sub>3</sub>			
		Deployment	End	Days	Concentration (mg N/L)	δ <sup>18</sup> O (‰)	δ <sup>17</sup> O (‰)	Δ <sup>17</sup> O (‰)
4	Genesee	2010-11-14	2011-01-06	49	0.18	69.2	64.3	28.0
4	Genesee	2011-01-06	2011-01-24	19	0.27	74.4	69.2	30.1
5	Genesee	2011-02-04	2011-04-28	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. Saskatchewan	2013-05-02	2013-06-05	33	0.46	60.0	55.1	23.6
16	F. Saskatchewan	2013-06-14	2013-07-11	27	0.30	63.8	52.7	19.2
18	F. Saskatchewan	2013-09-20	2014-01-20	122		71.4	63.1	25.6

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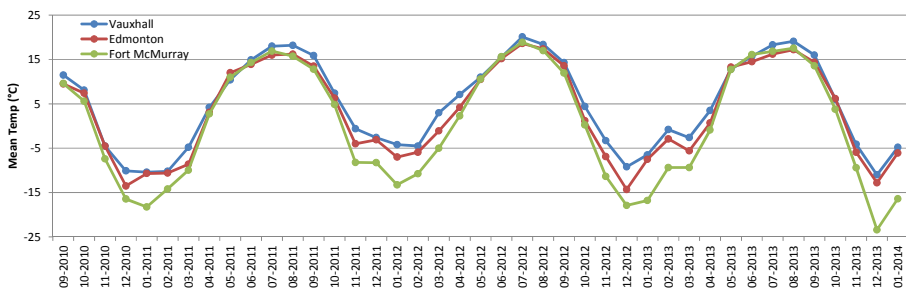
**Table SM-3. Sampling sites and other measured parameters.**

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 <sub>3</sub> (ppb)	SO <sub>2</sub> (ppb)	PM <sub>2.5</sub> (µg/m <sup>3</sup> )	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

A



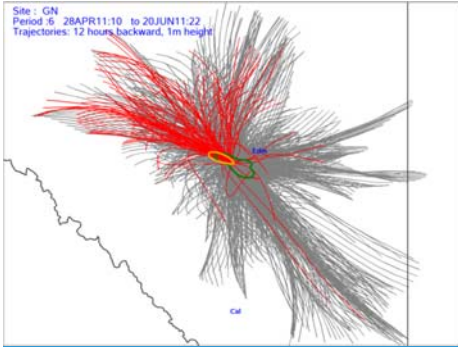
B



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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.

10



[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.](#)

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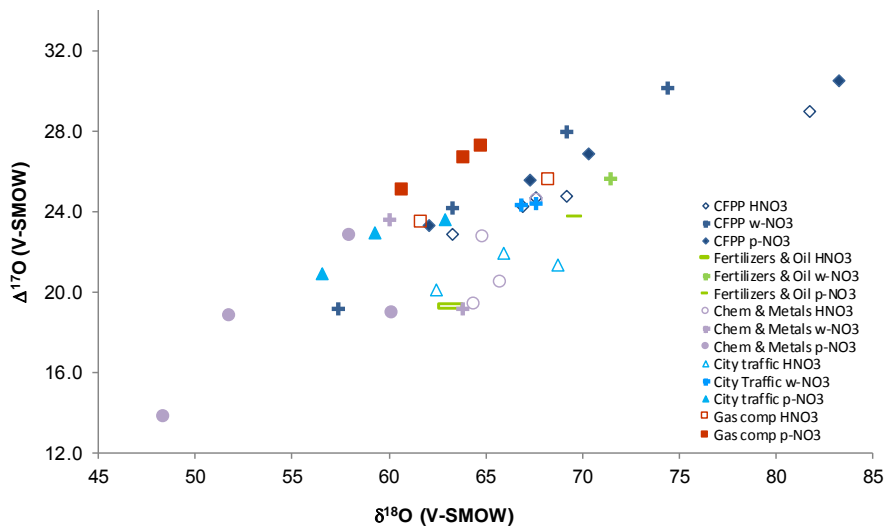


Figure SM-3. Triple oxygen isotopic results (‰) obtained for simultaneously sampled atmospheric HNO<sub>3</sub> (empty symbols), w-NO<sub>3</sub><sup>-</sup> (crosses) and p-NO<sub>3</sub><sup>-</sup> (full symbols) downwind of the various sources.

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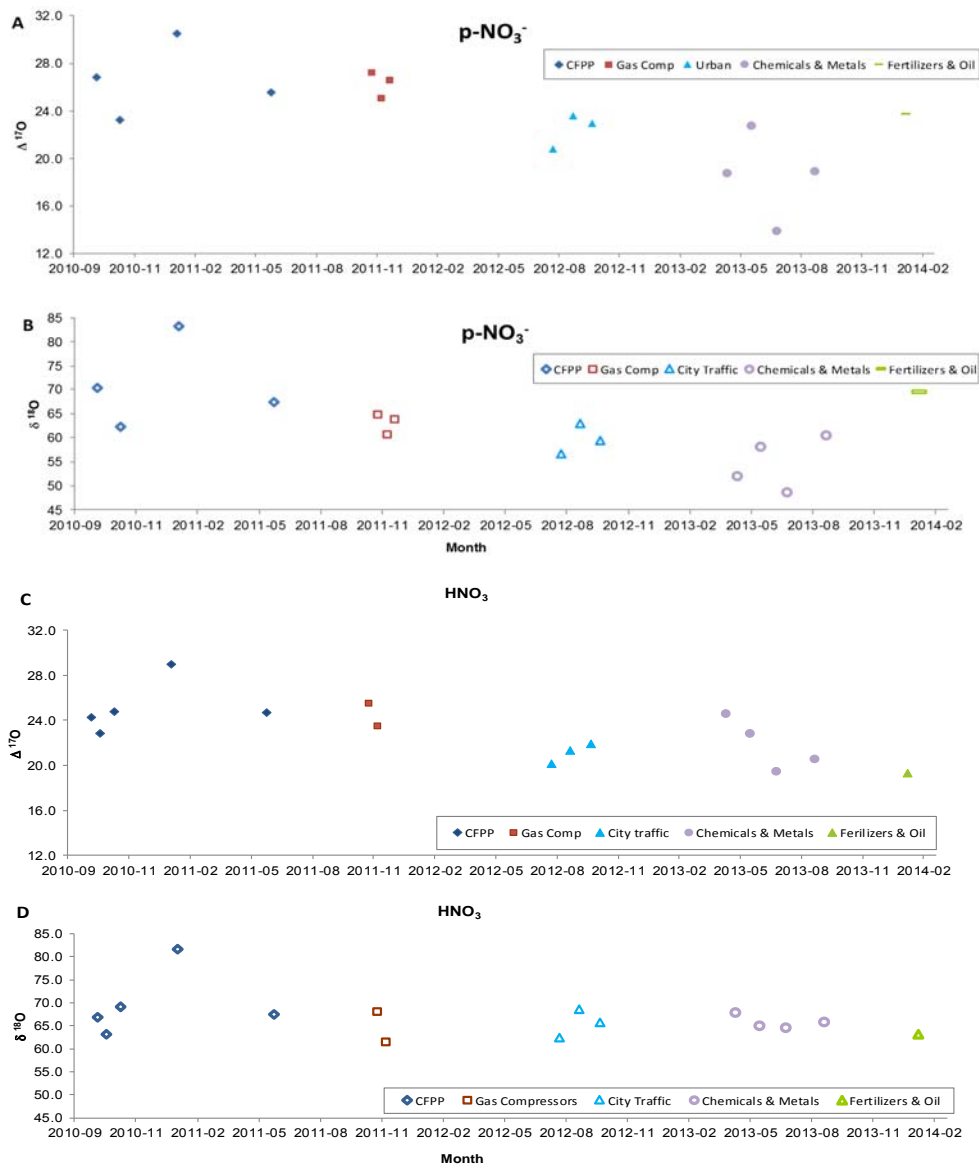


Figure SM-4. Oxygen isotopic variations as a function of sampling period labelled by emitter types:  $p\text{-NO}_3^-$  (A)  $\Delta^{17}\text{O}$  and (B)  $\delta^{18}\text{O}$  values; and  $\text{HNO}_3$  (C)  $\Delta^{17}\text{O}$  and (D)  $\delta^{18}\text{O}$  values.

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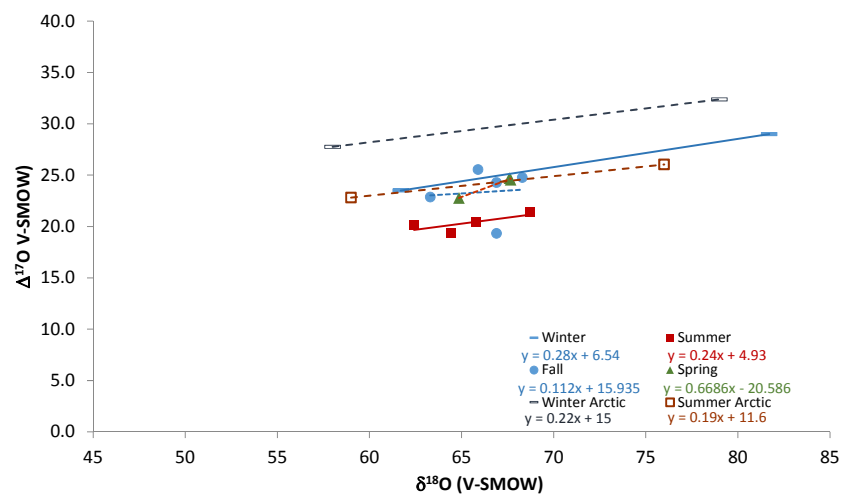


Figure SM-5. Triple oxygen isotopic (‰) results for  $\text{HNO}_3$  from Southern and central Alberta (solid symbols) and  $\text{p-NO}_3^-$  (empty symbols) for High Arctic (Morin et al., 2008).

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## Supplementary Material – ACP 1103

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

Supprimé: simultaneously collected

Supprimé: from

5 Martine M. Savard<sup>1\*</sup>, Amanda Cole<sup>2</sup>, Robert Vet<sup>2</sup>, Anna Smirnoff<sup>1</sup>

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

#	Site	Deployment	Collection	Days	Sampling hours	Mean (total for pooled) air volume (m <sup>3</sup> )	p-NO <sub>3</sub> <sup>-</sup>				HNO <sub>3</sub>				Daylight fraction (sunrise to sunset)	NO <sub>2</sub> in sample train* (ug N/m <sup>2</sup> )		
							Mean (total for pooled) loading (ug N)	Air conc (ug N/m <sup>2</sup> )	δ <sup>18</sup> O (‰)	δ <sup>17</sup> O (‰)	Δ <sup>17</sup> O (‰)	Mean (total for pooled) loading (ug N)	Air conc (ug N/m <sup>3</sup> )	δ <sup>18</sup> O (‰)			δ <sup>17</sup> O (‰)	Δ <sup>17</sup> O (‰)
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<sub>2</sub> filters where breakthrough <15%. Sum of NO<sub>2</sub> 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.**

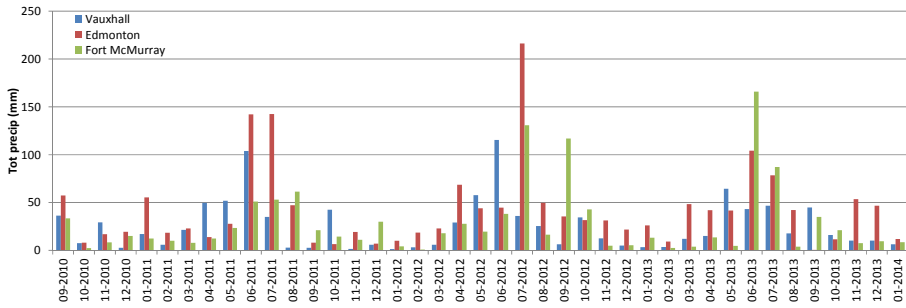
#	Site	Sampling duration			w-NO <sub>3</sub>			
		Deployment	End	Days	Concentration (mg N/L)	δ <sup>18</sup> O (‰)	δ <sup>17</sup> O (‰)	Δ <sup>17</sup> O (‰)
4	Genesee	2010-11-14	2011-01-06	49	0.18	69.2	64.3	28.0
4	Genesee	2011-01-06	2011-01-24	19	0.27	74.4	69.2	30.1
5	Genesee	2011-02-04	2011-04-28	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. Saskatchewan	2013-05-02	2013-06-05	33	0.46	60.0	55.1	23.6
16	F. Saskatchewan	2013-06-14	2013-07-11	27	0.30	63.8	52.7	19.2
18	F. Saskatchewan	2013-09-20	2014-01-20	122		71.4	63.1	25.6

Code de champ modifié

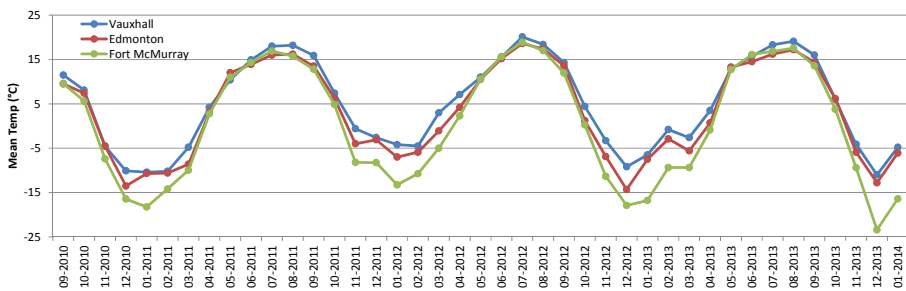
**Table SM-3. Sampling sites and other measured parameters.**

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 <sub>3</sub> (ppb)	SO <sub>2</sub> (ppb)	PM <sub>2.5</sub> (µg/m <sup>3</sup> )	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

A



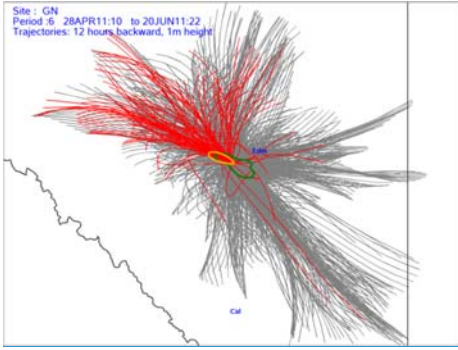
B



5

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.

10



[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.](#)

5



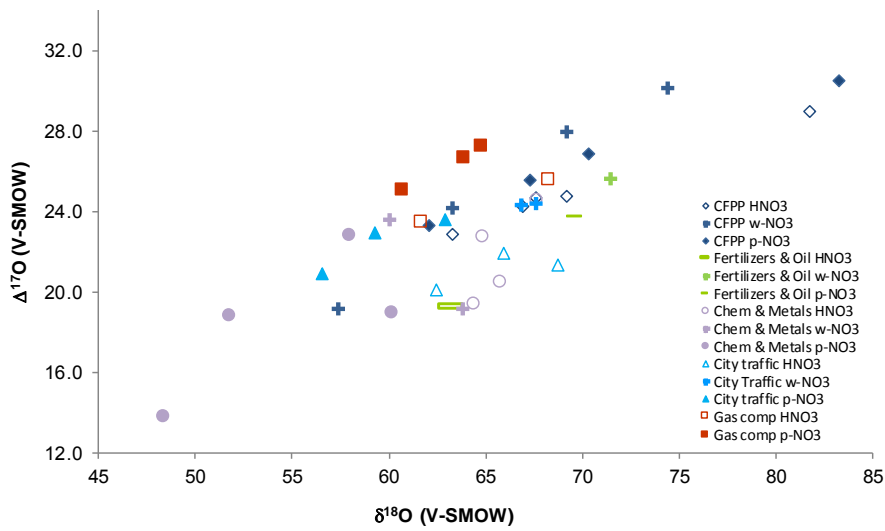


Figure SM-3. Triple oxygen isotopic results (‰) obtained for simultaneously sampled atmospheric HNO<sub>3</sub> (empty symbols), w-NO<sub>3</sub> (crosses) and p-NO<sub>3</sub> (full symbols) downwind of the various sources.

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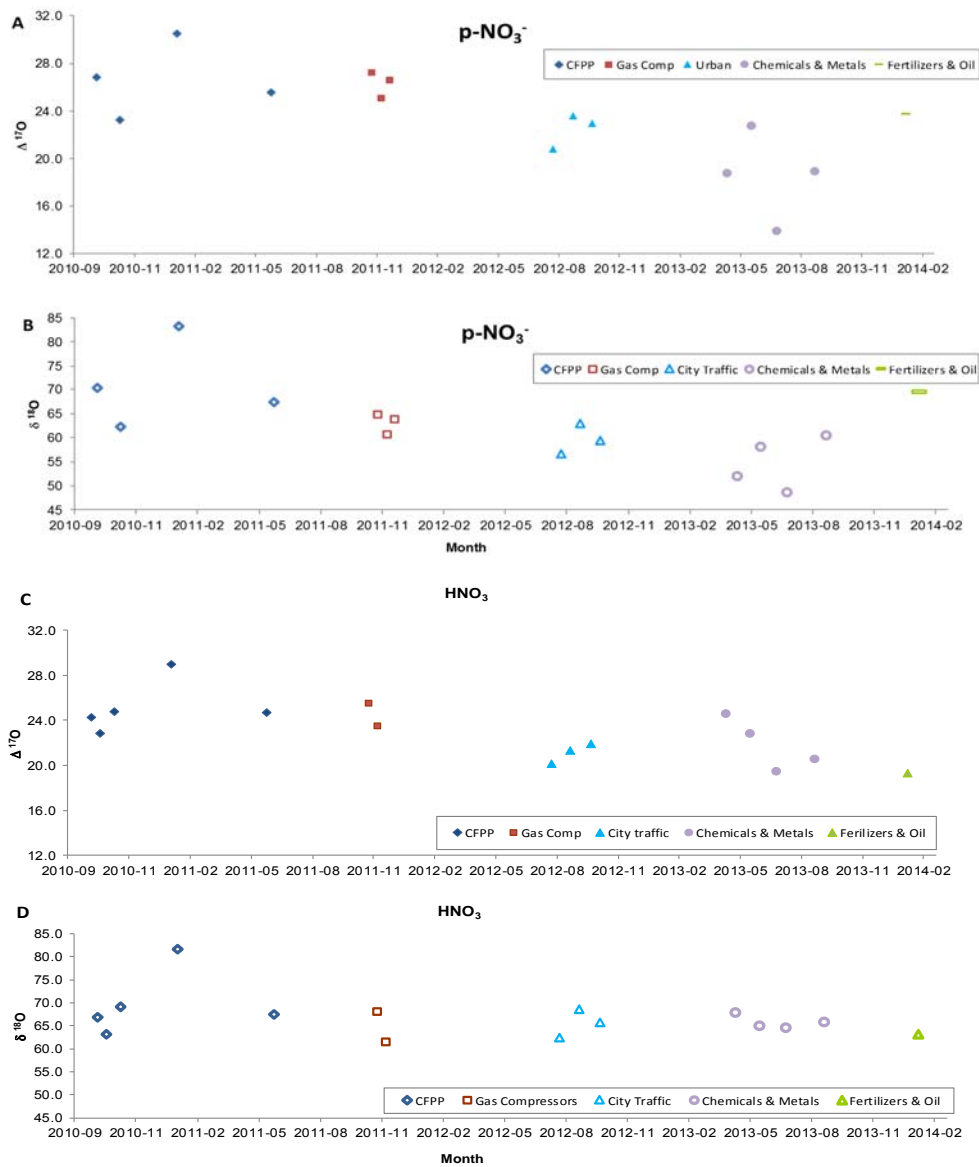


Figure SM-4. Oxygen isotopic variations as a function of sampling period labelled by emitter types:  $p\text{-NO}_3^-$  (A)  $\Delta^{17}\text{O}$  and (B)  $\delta^{18}\text{O}$  values; and  $\text{HNO}_3$  (C)  $\Delta^{17}\text{O}$  and (D)  $\delta^{18}\text{O}$  values.

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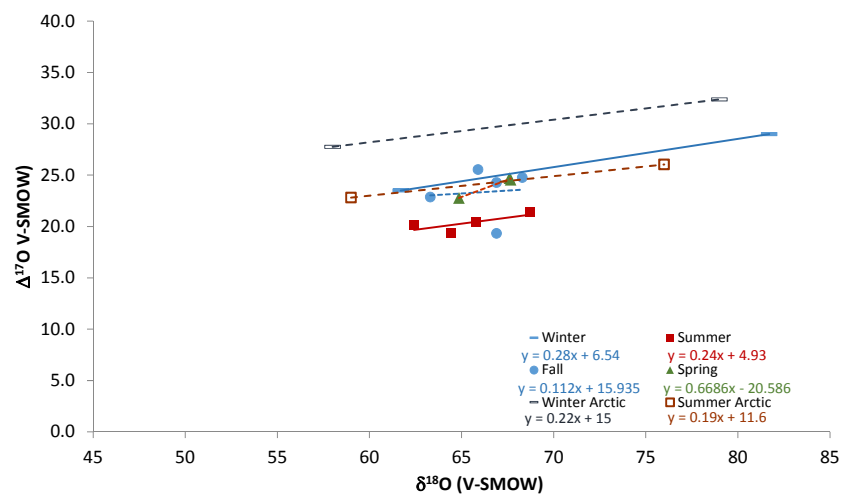


Figure SM-5. Triple oxygen isotopic (‰) results for  $\text{HNO}_3$  from Southern and central Alberta (solid symbols) and  $\text{p-NO}_3^-$  (empty symbols) for High Arctic (Morin et al., 2008).

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