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Abstract. There are clear motivations for better understanding the atmospheric processes that transform nitrogen (N) oxides (NOx) emitted from anthropogenic sources into nitrates (NO3-), two of them being that NO3- 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 (δ18O, Δ17O) are frequently applied to infer the chemical pathways leading to the observed mass independent isotopic anomalies from interaction with 17O-rich ozone (O3). Recent laboratory experiments suggest that the isotopic equilibrium between NO2 (the main precursor of NO3-) and O3 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 NO3- in precipitation (w-NO3-) and in particulate (p-NO3-) 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 HNO3 with Δ17O values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample HNO3 and p-NO3-, and co-collect w-NO3-. The nitrates are from various distances (<1 to >125 km) downwind of different anthropogenic emitters, and consequently from varying time lapses after emission.

The separate collection of nitrates shows that the HNO3 δ18O ranges are distinct from those of w- and p-NO3-. Interestingly, the Δ17O differences between p-NO3- and HNO3 shift from positive during cold sampling periods to negative during warm periods. The low p-NO3- Δ17O values observed during warm periods may partly derive from the involvement of 17O-depleted peroxy radicals (RO2) oxidizing NO during that season. Another possibility is that nitrates derive from NOx that has not yet reached isotopic equilibrium with O3. However, these mechanisms, individually or together, cannot explain the observed p-NO3 minus HNO3 isotopic changes. We propose differences in dry depositional rates, faster for HNO3, as a mechanism for the observed shifts. Larger proportions of p-NO3- formed via the N2O5 pathway would explain the opposite fall-winter patterns. Our results show that the separate HNO3, w-NO3- and p-NO3- isotopic signals can be used to further our understanding of NOx oxidation and deposition. Future research should investigate all tropospheric nitrate species as well as NOx to refine our understanding of nitrate distribution worldwide and to develop effective emission reduction strategies.
1 Introduction

Anthropogenic NOx (NO and NO2) emissions are oxidized to nitrate in the atmosphere in the form of gaseous, wet or particulate forms, HNO3 being one of the main precursors of p-NO3-. 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-NO3, HNO3 and w-NO3).

Triple oxygen isotopes (δ18O and δ17O) have been used to decipher atmospheric oxidation pathways of NOx leading to ambient nitrate. Michalski et al. (2003) performed the first measurement of δ17O values in atmospheric nitrate. The authors found nitrate highly enriched in 18O and 17O, likely due to the transfer of anomalous oxygen atoms from ozone (O3) via the NOx-ozone photochemical cycle and oxidation to nitrate. During its formation, O3 inherits abnormally high δ18O and δ17O values through mass independent fractionation. The specific δ17O departure from the terrestrial mass dependent fractionation line, named the 17O anomaly, is often expressed as Δ17O = δ17O -0.517 x δ18O (Thiemens, 1999). Further investigations suggested that the δ18O and δ17O values of w-NO3- and p-NO3 reflect several reactions taking place after the atmospheric emission of NOx, i.e., atmospheric oxidation pathways transforming NOx 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 δ18O differences in w-NO3 samples (less variable and lower values during summer) have been interpreted to be due to changes in these chemical pathways (Hastings et al., 2003). Modeling and validation based on sparse existing data provide hope regarding a global understanding of atmospheric nitrate (Alexander et al., 2009), however, further measurements need to be done on the ground, particularly at mid-latitudes.

Additional studies dealing with triple oxygen isotope characterizations have addressed questions of methodology (Kaiser et al., 2007; Smirnoff et al., 2012), transfer of the ozone 17O 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 NO3- samples are not yet widespread. Also rare are the nitrate δ18O and Δ17O values of field samples downwind from NOx-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). The few existing studies have chiefly characterized w-NO3- or the sum of p-NO3- and HNO3 (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, HNO3 and p-NO3- were generally collected together (without differentiation). Therefore, no studies have separately and simultaneously collected and analyzed the HNO3 and p-NO3- δ18O and Δ17O values, and discussed these isotopic characteristics of nitrate collected downwind of anthropogenic emitters. While HNO3 and p-NO3- can be in equilibrium (e.g. if p-NO3- is in the form of solid NH4NO3), 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 HNO₃ and p-NO₃⁻ as well as w-NO₃⁻ downwind of the source types. The objective of this work was to assess the atmospheric NOₓ reaction pathways and determine processes responsible for the distribution of HNO₃, and w- and p-NO₃⁻ in a mid-latitudinal region.

2 Methodology

2.1 Regional context

While national reported NOₓ emissions in Canada declined steadily from 2000 to 2015, emissions in the Province of Alberta have remained relatively constant since 2004 (Environment and Climate Change Canada, 2016). Pioneering work was accomplished measuring nitrate on emitted PM2.5 (particulate matter less than 2.5 µm) and in bulk and throughfall precipitation samples (wet and some dry deposition on ion exchange resin collectors) collected at or downwind of the Athabasca oil-sands mining operations in northern Alberta (Proemse et al., 2012; Proemse et al., 2013). However, the Edmonton area in central Alberta, known to generate the highest NOₓ 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-NO₃⁻, HNO₃ and w-NO₃⁻) 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
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 NOx 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 (HNO3) on a Nylasorb nylon filter, and gaseous ammonia on a citric acid-coated Whatman 41 filter (all 47 mm). The Teflon-nylon filter method for p-NO$_3^-$ and HNO3 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 HNO3 on the Teflon filter, <3% breakthrough of HNO3 from the nylon filter with loadings more than three times higher than reported here, and blanks for p-NO$_3^-$ and HNO3 of approximately 0.2 μg N per filter (Anlauf et al., 1985; Anlauf et al., 1986). Intercomparisons with more labor-intensive methods, such as tunable diode laser absorption spectroscopy and annular denuder-filter pack systems, have shown evidence of some volatilization of ammonium nitrate from the Teflon filter leading to a negative bias in p-NO$_3^-$ and positive bias in HNO3 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 HNO3 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 HNO2 (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$_4$NO3 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.
After the first five sample periods, an experimental active sampling system for NO\textsubscript{2} and NO\textsubscript{x} was added downstream of the three-stage filter pack. This system consisted of one or two custom cartridges packed with Maxxam Analytics’ resin to selectively collect NO\textsubscript{2}, and one- or two-stage filter pack containing two identical Maxxam Analytics’ impregnated filters designed to collect NO\textsubscript{x} (mostly NO due to upstream collection of NO\textsubscript{2}). Oxygen isotopes in NO\textsubscript{2} and NO\textsubscript{x} were not measured since we could not rule out oxygen isotope exchange during the extraction process, however, concentrations meeting the QC criteria (Savard et al., 2017) are presented for reference in Table SM-1.

Here we report on oxygen isotopes in the simultaneously sampled HNO\textsubscript{3} and p-NO\textsubscript{3}\textsuperscript{-}, along with co-sampled w-NO\textsubscript{3}\textsuperscript{-} 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\textsubscript{3} from Teflon filters were extracted in two portions of 6 mL of ultrapure water (ELGA). To reduce possible evaporation, filters were placed in an ultrasonic bath with ice. The extractions were performed during one hour and samples were left for 48 hours in a fridge to insure the complete extractions. The solutions were decanted and a small portion (1-2 mL) was used to determine concentrations. The remaining extracts were stored in the fridge for subsequent isotope analysis. The blanks from both filters were treated the same way.
Concentration of nitrates in Teflon and Nylon filter extracts, and in precipitation samples were determined at the Institut national de la recherche scientifique – Eau, Terre, Environnement (INRS-ETE). The determinations used an automated QuikChem 8000 FIA+ analyzer (Lachat Instruments), equipped with an ASX-260 series autosampler. The detection limit for the method with sulfanilamide (# 31-107-04-1-A) was 0.03 µmol/L of NO₃⁻-N. Nitrite concentrations were also measured in the extracts. Nitrite concentrations above the detection limit (1.1 µmol/L of NO₂⁻-N) were found in a handful of samples at Terrace Heights. These samples were excluded from the reported data.

We characterized the δ¹⁷O, δ¹⁸O and δ¹⁵N ratios of HNO₃, w-NO₃⁻, and p-NO₃⁻, along with the δ¹⁵N values of NH₃, w-NH₄, p-NH₄ and NO₃ (all N isotopic results are in Savard et al., 2017). The present article deals solely with the δ¹⁸O and Δ¹⁷O values obtained for the three nitrate species. We treated the samples using the chemical conversion and thermal decomposition of N₂O protocols, providing the ability to simultaneously analyze low-concentration N- and O-containing species (Smirnoff et al., 2012).

A notable challenge in the analysis of the filter-based atmospheric samples is their small extraction volumes. Only 10-12 mL of extract solution were normally available for the measurement of concentrations and isotopic analysis. In addition, the concentrations of these low volume samples were also low (7.1-21.4 µmol/L of NO₃⁻-N). Therefore, not all samples could be diluted to produce volumes sufficient for reduction of NO₃ to NO₂ and subsequent conversion to N₂O, the final product before isotope analysis. Samples with an initial concentration below 2.3 µmol/L could not be treated individually and were combined to produce volumes sufficient for analyses (same sampling period but combination of collected parallel samples).

The preparation steps involved conversion of nitrate-containing samples into nitrite (NO₂⁻) using a custom-made cadmium column. The final preparation step involved using sodium azide to ultimately produce N₂O (McIlvin and Altabet, 2005; Smirnoff et al., 2012). All extracted N₂O was analyzed using a pre-concentrator (PreCon, Thermo Finnigan MAT) including a furnace with ‘gold’ wires, online with an Isotope Ratio Mass Spectrometer (Delta V Plus, Thermo Electron; Kaiser et al., 2007; Smirnoff et al., 2012). The utilized approach allows the spectrum of δ¹⁵N, δ¹⁷O and δ¹⁸O 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 N₂O. The laboratory analytical precision (average of replicates) determined during the present study was 0.6 ‰ for δ¹⁸O and δ¹⁷O values in gaseous (n=12) and solid nitrates (n=20). For w-NO₃⁻, analytical replicates gave 0.6 and 0.5 ‰, for δ¹⁸O (n=3) and δ¹⁷O (n=4) values, respectively. The Δ¹⁷O values are defined as ln (1+δ¹⁷O) − 0.516 x ln (1+δ¹⁸O), relative to Vienna Standard Mean Ocean Water (VSMOW).
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 δ17O and δ18O 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 NH4NO3 on the particle filter into HNO3 and NH3, 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-NO3− isotopic values (δ17O and δ18O) to be generally higher during winter than during summer (see sub-section 3.4). Moreover, the p-NO3− δ18O minus HNO3 δ18O differences are negative during summer (see sub-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 δ15N values in NH3 and NH4; 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 17O anomaly; therefore, Δ17O 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-NO3− and HNO3 (Elliott et al., 2009).

3.2 Concentrations and isotopic ratios of nitrates in Alberta samples

The range of HNO3-N concentrations measured by the filters (from 0.01 to 0.15 µg/m3; average of 0.06) are slightly lower than those of p-NO3−-N (from 0.02 to 0.35 µg/m3; average of 0.12). For context, the median concentrations at all CAPMoN sites, which represent non-urban areas across Canada, range from 0.02 to 0.25 µg/m3 for HNO3-N and from 0.007 to 0.45 µg/m3 for p-NO3−-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
northern Alberta border revealed similar average concentrations of 0.02 μg/m³ of NO₃⁻-N for both HNO₃ and p-NO₃⁻ (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 NO₃⁻-N concentrations of the w-NO₃⁻ samples was 10.71 – 34.29 μmol/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 5.00 μmol/L of NO₃⁻-N, while at the most polluted site in southern Ontario (Longwoods) the volume-weighted mean concentration was approximately 21.43 μmol/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 δ¹⁸O and Δ¹⁷O values of HNO₃ (gas), w- and p-NO₃⁻ show no apparent systematic ordering (Table 3; Tables SM-1 and 2), in contrast to what was found for δ¹⁵N 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 HNO₃ and p-NO₃⁻ have the highest δ¹⁸O and Δ¹⁷O averages, but not the highest delta values for w-NO₃⁻ values; chemical industries show the lowest δ¹⁸O and Δ¹⁷O averages for w- and p-NO₃, but not for HNO₃. Though the number of samples were limited, w-NO₃⁻ Δ¹⁷O values were roughly correlated with the weighted average Δ¹⁷O values of p-NO₃ and HNO₃ in samples covering the same time periods, consistent with scavenging of both HNO₃ and p-NO₃ 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 δ¹⁸O and Δ¹⁷O values range between +48.4 and +83.2 ‰, and between 13.8 and 30.5 ‰, respectively (Table 4; Table SM-1, Fig. SM-4). These ranges indicate that ozone partly transferred its isotopic anomaly to nitrates during NOx cycling and oxidation (nitrate derived through combustion in O₂ would show δ¹⁸O and Δ¹⁷O values of 23.5 and 0 ‰, respectively). When examining the existing δ¹⁸O and Δ¹⁷O data for w- and p-NO₃ 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 δ¹⁸O range of atmospheric NO₃⁻ 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 NO₃⁻ samples are scarce (Table 4). The HNO₃ range documented here is within the broad spectrum of p-NO₃⁻ values compiled for remote to contaminated sites. Elliott et al. (2009) reported HNO₃ oxygen results for δ¹⁸O values only, with a range of +51.6 to +94.0 ‰ (mean of 77.4), with simultaneously-sampled p-NO₃⁻ δ¹⁸O values between +45.2 and +92.7 ‰ (mean of 75.2). Those ranges are broader than the HNO₃ and p-NO₃⁻ values obtained in the present study.
3.3 The δ¹⁸O and Δ¹⁷O trends in nitrates from cold and warm sampling periods

The δ¹⁸O and Δ¹⁷O ranges for HNO₃ identified by sampling period are narrower than those of the simultaneously collected p-NO₃⁻ (Fig. 2; Table SM-1), suggesting that there are additional mechanisms affecting HNO₃, or that p-NO₃ is derived from different pathways with more variation in isotopic signatures. Overall, the Δ¹⁷O and δ¹⁸O results for HNO₃, w-NO₃⁻ and p-NO₃⁻ clearly show higher δ¹⁸O and Δ¹⁷O values during cold periods relative to warm periods (Fig. 2), with the exception of HNO₃ δ¹⁸O 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 °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-NO₃⁻.

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, NOₓ (NO and NO₂) is produced through reactions of air N₂ with atmospheric O₂ at high temperatures (reactions R1; Table 5). Then, NOₓ cycles between NO and NO₂ through a series of reactions involving sunlight (R5), O₃ (R2, R4), and peroxy (HO₂) or alkyl peroxy (RO₂) radicals (R3; Morin et al., 2007; Fang et al., 2011; Michalski et al., 2014; here we use RO₂ to refer collectively to HO₂ and RO₂).

The oxidation of NOₓ (specifically NO₂) to HNO₃ 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, N₂O₅ 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 N₂O₅ (R8), HNO₃ is likely to be retained on the reaction particle as p-NO₃⁻ 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 NO₃ with hydrocarbons (R12) since they are predicted to have a minimal contribution to nitrate formation in this region (Alexander et al., 2009). Finally, HNO₃ 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 δ¹⁸O and Δ¹⁷O values of w- and p-NO₃⁻ formed during summer are lower than those during winter due to higher contribution from the N₂O₅ 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-NO₃⁻ δ¹⁸O and Δ¹⁷O data presented here follow the same patterns for warm and cold months (Fig. 2). In contrast, the less commonly studied HNO₃ shows similar δ¹⁸O values during warm and cold seasons, but summer Δ¹⁷O 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 HNO₃ and p-NO₃⁻ 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 HNO₃ and p-NO₃ samples (n of w-NO₃ too low) with meteorological and air quality parameters measured routinely
at nearby monitoring stations where available (Table SM-3). We found that the p-NO$_3^-$ and HNO$_3$ $\delta^{18}$O and $\Delta^{17}$O values correlate with RH, with p-NO$_3^-$ values showing stronger statistical links than HNO$_3$ (Table 6). The N$_2$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-NO$_3^-$ $\delta^{18}$O, p-NO$_3^-$ $\Delta^{17}$O, and HNO$_3$ $\Delta^{17}$O. These negative links likely arise since N$_2$O$_5$ is more stable under cold conditions, leading to a higher contribution of R8. The stronger links with p-NO$_3^-$ may be due to R8 taking place on surfaces (such as particles) with liquid water, which is likely to retain the HNO$_3$ as p-NO$_3^-$ rather than release it to the gas phase. Therefore, in winter, R8 may contribute more to p-NO$_3^-$ than to HNO$_3$(g). Moreover, the highest $\delta^{18}$O and $\Delta^{17}$O values for both p-NO$_3^-$ and HNO$_3$ were found for fall-winter samples collected at high RH (76 %) and low temperature (-10°C). In contrast, the lowest p-NO$_3^-$ isotopic values were found for samples with similar proportions of HNO$_3$ and p-NO$_3^-$, and sampled during moderately humid (60-63 %) and warm (8-20°C) periods. The accompanying shift in $\delta^{18}$O and $\Delta^{17}$O differences between p-NO$_3^-$ and HNO$_3$, will help infer the mechanisms dominating during the cold and warm periods (Section 4.2).

Concentrations of oxidants, co-contaminants (e.g., SO$_4^-$_ aerosols) and NO$_x$ influence the dominance and rates of the discussed reactions (Brown et al., 2006; Michalski et al., 2014). However, while temperature, RH and O$_3$ are well captured within a 5 km radius, other pollutant measurements like continuous SO$_2$, PM$_{2.5}$ and NO$_x$ can have large gradients near sources, therefore it is not surprising that no correlations were found with SO$_2$ or PM$_{2.5}$ measured at sites 4-5 km away (Table 6). Surprisingly, only the p-NO$_3^-$$\Delta^{17}$O and $\delta^{18}$O values correlated with the fraction of each sample collected during daylight hours (i.e., between the sunrise and sunset times on the day at the middle of each sampling period, either at Edmonton or Lethbridge), which was expected for HNO$_3$ as well due to the daytime-only OH pathway. However, daylight hours do not take into account light intensity, which can influence significantly the oxidation rate through this pathway, and consequently both the $\delta^{18}$O and $\Delta^{17}$O values.

3.5 Comparison with high-latitude p-NO$_3^-$

An interesting aspect of the Alberta p-NO$_3^-$ cold-period $\Delta^{17}$O ranges is that they compare relatively well with the range obtained for the Canadian Arctic (Fig. 4), during winter, when nighttime conditions and the N$_2$O$_5$ pathway prevail without interruption (Morin et al., 2008; for comparison with HNO$_3$ values see Fig. SM-4). This observation supports the suggestion that the N$_2$O$_5$ pathway produces around 90 % of nitrates during mid-latitude cold months (Michalski et al., 2003; sub-section 4.1). The $\delta^{18}$O ranges of cold months are similar in Alberta and in the Arctic. This similarity goes against previous suggestions that at higher latitudes, nitrate $\delta^{18}$O annual means should be higher than at mid-latitudes due to local ambient conditions and atmospheric chemistry affecting the proportions of species involved in producing nitrate (Morin et al., 2009), namely, the sole influence of the N$_2$O$_5$ pathway during the Arctic winter (Fang et al., 2011).

The $\Delta^{17}$O departure between the Alberta and Arctic winter parallel lines is about 3 ‰. Such difference is slightly larger than the one calculated for winter NO$_3^-$ at 80 and 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}O values is similar at the mid- and high-latitudinal sites (about 6 \% here, and 5 \% in Morin et al., 2008). This similarity is likely coincidental as it may reflect the fact that within-plume chemistry may lower the \Delta^{17}O values of NO\textsubscript{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\textsubscript{2}O\textsubscript{5} pathways during summer and winter, respectively. Finally, the \Delta^{17}O averages for the Alberta summer and winter results approximately fits within ranges predicted for the studied area by global modeling (Alexander et al., 2009), suggesting that global modeling of nitrate distribution worldwide is promising.

3.6 Isotopic differences between HNO\textsubscript{3} and p-NO\textsubscript{3}⁻

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

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

The marked shifts in isotopic differences between the separately analyzed HNO\textsubscript{3} and p-NO\textsubscript{3}⁻ reported here likely reflect changes in the dominant reactions and processes leading to the production of the two nitrates (see sub-section 4.2). Analyzing them separately provides additional granularity that may be used to elucidate further details of the production and loss of nitrate species downwind from a NO\textsubscript{x} source.

4 Discussion

4.1 Estimation of \Delta^{17}O values of NO\textsubscript{x} precursor to the studied nitrates- Highlighting oxidation mechanisms

In the present sub-section, we estimate the \Delta^{17}O values of NO\textsubscript{2} involved during the production of the Alberta nitrates based on the observed nitrate values and discuss the implications of these estimations. Generally, winter to summer isotopic differences are thought to be due to the high oxygen isotopic values of N\textsubscript{2}O\textsubscript{5} due to interaction with O\textsubscript{3} (Johnston and Thiemens, 1997; Michalski et al., 2003; Morin et al., 2008; Vicars et al., 2012) and low values of OH in isotopic equilibrium with atmospheric H\textsubscript{2}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\textsubscript{2}, 1/6 from O\textsubscript{3} and 1/6 from H\textsubscript{2}O, while the second produces nitrates via R6 with 2 out of 3 O atoms
coming from NO$_2$ and 1/3 from OH (e.g., Michalski et al., 2003). Using these proportions with the Alberta $\Delta^{17}$O values of p-NO$_3^-$ and HNO$_3$ in weighted averages allows us to make a rough estimation of the maximum and minimum $\Delta^{17}$O values of NO$_2$ oxidized to nitrates in the air masses sampled. The calculations assume the O from O$_3$ contributes a signal of ~39 ‰ as was recently measured (Vicars et al., 2014) and that $\Delta^{17}$O of OH and H$_2$O are zero. The estimated NO$_2$ $\Delta^{17}$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 N$_2$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 N$_2$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 NO$_2$ $\Delta^{17}$O ranges indicate that the potential parent NO$_2$ had a smaller $^{17}$O anomaly than O$_3$ (39 ‰; Vicars and Savarino, 2014) or NO$_2$ in isotopic equilibrium with O$_3$ alone (45 ‰; Michalski et al., 2014) in all possible scenarios.

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

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

4.2 Causes of shifts in HNO$_3$ to p-NO$_3^-$ isotopic differences

A challenging question is why do the HNO$_3$ to p-NO$_3^-$ isotopic differences shift seasonally (Fig. 3)? One factor that may influence the relationship between HNO$_3$ and p-NO$_3^-$ is mass-dependent isotopic equilibrium between NH$_4$NO$_3$ and HNO$_3$ (R10); however, this mechanism would result in higher $\delta^{18}O$ in p-NO$_3^-$ and unchanged $\Delta^{17}O$ values and, therefore, cannot be solely responsible for any of the observed patterns (Fig. 3). Alternately, the trend for cold months (trend i) could be due to the fact that the heterogeneous N$_2$O$_5$ pathway is likely to produce more p-NO$_3^-$ than HNO$_3$(g), which would result in a higher contribution from ozone and explain why $\delta^{18}O$ and $\Delta^{17}O$ values are both higher in p-NO$_3^-$. A previous study addressing why p-NO$_3^-$ on coarse particles is more enriched than on fine particles invoked a similar explanation (Patris et al., 2007).

For some of the spring and summer samples, both $\delta^{18}O$ and $\Delta^{17}O$ values were lower in p-NO$_3^-$ than in HNO$_3$ (trend iv), therefore the mechanism above cannot dominate the fractionation; nor can a mass-dependent process be responsible. We suggest a different fractionation process because HNO$_3$ dry deposits to surfaces more rapidly than p-NO$_3^-$ (Zhang et al., 2009; Benedict et al., 2013), which would create the discussed isotopic shifts in the situation where NO$_2$ has low $\Delta^{17}O$ values in a fresh plume. The first nitrates formed in the plume shortly after emission from the NO$_x$ source have low $\delta^{18}O$ and $\Delta^{17}O$ values, either because NO$_x$ has not yet reached isotopic steady state with O$_3$ or because it reacted with $^{17}O$-poor RO$_2$ present in the plume due to VOC emissions. Those nitrates that form as p-NO$_3^-$ or that partition to p-NO$_3^-$ remain in the plume for longer than HNO$_3$, which is removed from the plume rapidly upon contact with vegetation or other surfaces. As the plume travels, the NO$_x$ becomes more enriched, and the newly formed nitrates take on higher $\delta^{18}O$ and $\Delta^{17}O$ values. However, p-NO$_3^-$ collected further downwind will derive from a mixture of low-$\delta^{18}O$ and -$\Delta^{17}O$ p-NO$_3^-$ formed earlier, plus high-$\delta^{18}O$ and -$\Delta^{17}O$ p-NO$_3^-$ formed more recently, while HNO$_3$ will have a larger proportion formed more recently and will therefore have higher $\delta^{18}O$ and $\Delta^{17}O$ values.

The fact that we find the lowest isotopic values in summer p-NO$_3^-$ samples collected from various anthropogenic sources at distances less than 16 km supports this suggestion (Table 1).

The above two mechanisms that we propose to explain the shifts in HNO$_3$ to p-NO$_3^-$ isotopic differences between cold and warm sampling periods – differential N$_2$O$_5$ contribution resulting in higher $\Delta^{17}O$ values in p-NO$_3^-$ than in HNO$_3$, and differential deposition resulting in lower $\Delta^{17}O$ values in p-NO$_3^-$ – would essentially compete against each other, with local conditions and chemistry influencing the results. In winter, when the N$_2$O$_5$ pathway is most important, the first mechanism dominates, as supported by the observation that p-NO$_3^-$ concentrations are higher during that season (trend i). Conversely, in summer, when the N$_2$O$_5$ pathway is less important and dry deposition is likely faster due to absence of snow cover, higher surface wetness and high leaf areas, the second mechanism is more important (trend iv). The local reactant concentrations, wind speeds and radiative fluxes (which control the time to reach isotopic equilibrium) would also be factors in the second mechanism. We find intermediate trends (ii, iii) in the transitional seasons, as expected. In addition to these non-mass-dependent fractionation
processes, mass-dependent fractionation in formation and loss of nitrate likely contributes to the observed $\delta^{18}O$ differences. For instance, kinetic fractionation may be involved in the production of trend $iii$.

In summary, examining the isotopic relationship of $\text{HNO}_3$ to $\text{p-NO}_3^-$ (Fig. 3), reveals the complexity of anthropogenic NOx oxidation mechanisms. The lower $\text{p-NO}_3^-$ isotopic values relative to the $\text{HNO}_3$ values during warm months may reflect differential removal rates from plumes containing NO$_2$ temporarily low in $^{17}O$.

4.3 - Low $\delta^{18}O$ and $\Delta^{17}O$ trends in global w- and p-$\text{NO}_3^-$ - Implications for polluted air masses

Atmospheric nitrates measured in central and southern Alberta were sampled downwind of well-identified anthropogenic sources to verify the potential role of emitted NO$_x$ isotopic signals through to final nitrate isotopic ratios (primarily N isotopes; see Savard et al., 2017). As expected, the measured oxygen isotopes of the various nitrate groups are consistent with exchange with O$_3$ and oxidation through the well-known OH and N$_2$O$_5$ oxidation paths. However, NO$_2$ not in isotopic equilibrium with O$_3$, and/or NO reacted with RO$_2$ may have significantly influenced the overall results. Co-contaminants in the emissions and sampling plumes at short distances from the sources may have favoured these two mechanisms, and quantifying RO$_2$ and/or HO$_2$ would help distinguish between the two mechanisms. Meanwhile, our results raise the question: are these overall effects observable in triple oxygen isotopes of nitrates from other polluted sites?

The full $\Delta^{17}O$ and $\delta^{18}O$ ranges for p-$\text{NO}_3^-$, w-$\text{NO}_3^-$ and $\text{HNO}_3$ (between 13.8 and 20.5 ‰, 48.4 and 83.2 ‰; Table 4) compare well with the isotopic ranges obtained for bulk deposition NO$_3^-$ samples collected downwind from oil sands mining operations in the lower Athabasca region farther north in Alberta (Proemse et al., 2013). Moreover, the isotopic values in cold and warm months delineated here essentially overlap with the data sets of winter and summer from the lower Athabasca region (Fig. 6). This correspondence exists despite the slightly different climatic conditions (Fig. SM-1), and very different sampling methods (bulk/throughfall deposition samples using open ion exchange resin collectors, vs. wind sector-specific active sampling on filters and precipitation-only collectors). Notably, many points carry relatively low $\delta^{18}O$ and $\Delta^{17}O$ values.

Previous work in the Athabasca region reported very low $\delta^{18}O$ and near-zero $\Delta^{17}O$ values for p-$\text{NO}_3^-$ sampled directly within oil-sands industrial stacks, i.e., in the emissions measured in-stack and diluted with ambient air (Proemse et al., 2012). These values are very close to those of O$_2$. Similar isotopic signatures are very likely produced in source emissions of NO$_x$ in the studied Edmonton and Vauxhall areas (e.g., CFPP, gas compressors, industries). This source signature may persist into p-$\text{NO}_3^-$ collected close to the sources. Within the first few hours in the atmosphere (less, in polluted areas), the NO$_x$ $\delta^{18}O$ and $\Delta^{17}O$ values rapidly increase due to isotope exchange with O$_3$ (R2, R3, R5 and O$_3$ formation, Table 5; Michalski et al., 2014) and reach isotopic equilibrium. Though the e-folding lifetime for NO$_x$ oxidation to nitrates may be longer than these few hours, depending on the NO$_x$/VOC ratio, only a fraction of the oxidized source NO$_x$ will create a measurable contribution to the ambient nitrate where the background air is very low in nitrate. This is likely the case in the oil sands region, where Proemse et al. (2013) reported the lowest $\Delta^{17}O$ values within 12 km of the emission sites, and where direct stack emissions of p-$\text{NO}_3^-$ were ~5000 times lower than NO$_x$ emissions (Wang et al., 2012).
In a methodological test study, we obtained low values for w-NO$_3^-$ sampled near a high traffic volume highway in Ontario, Canada (Smirnoff et al., 2012). Low $\delta^{18}$O and $\Delta^{17}$O values in atmospheric nitrates during warm months (65 and 20 % or less, 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 $\delta^{18}$O values in w-NO$_3^-$ from a polluted city (Fang et al., 2011), in p-NO$_3^-$ from Taiwan collected partly from air masses influenced by pollutants (Guha et al., 2017) and from a polluted coastal site in California (Michalski et al., 2004; Patris et al., 2007; Table 4). However, sampling in these three other regions did not use collection restricted to air masses transported from targeted anthropogenic sources. So uncertainties persist regarding the ultimate sources of nitrates with low isotopic values.

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

5 Conclusion

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

The gaseous form of nitrate (HNO$_3$) having distinct isotopic characteristics relative to the wet and particulate forms implies that understanding nitrate formation and loss requires characterizing the nitrate species individually. Particulate-NO$_3^-$ in these samples generally shows higher $\delta^{18}$O and $\Delta^{17}$O values than HNO$_3$ in the fall-winter period as the heterogeneous N$_2$O$_5$ pathway favours the production of p-NO$_3^-$. In contrast, HNO$_3$ has higher $\delta^{15}$O and $\Delta^{17}$O values during warm periods, which we propose is due to faster dry deposition rates relative to p-NO$_3^-$ in the event that low-$\Delta^{17}$O NO$_2$ is oxidized in the plume. The mechanisms conferring nitrate with relatively low isotopic values, whether oxidation before NO$_x$-O$_3$ equilibrium is reached or higher
contributions from RO₂, 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 δ¹⁸O and Δ¹⁷O values may reflect nitrates produced from undifferentiated anthropogenic NOₓ emissions.

Future research should explore the assumption of NOₓ isotopic equilibration with O₃, given the critical importance of NOₓ 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 NOₓ 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.

<table>
<thead>
<tr>
<th>Site (coordinates)</th>
<th>Sources</th>
<th>Distance Km (mean)</th>
<th>Sector direction; opening</th>
<th>Sampling period;</th>
<th>n</th>
<th>Avg T (°C)</th>
<th>Context</th>
</tr>
</thead>
<tbody>
<tr>
<td>Genesee (114.14° W, 53.31° N)</td>
<td>Coal-fired power plants</td>
<td>7–35</td>
<td>NW, 35°</td>
<td>30/09/2010 – 21/06/2011</td>
<td>6</td>
<td>11.7, 12.2, 5.5, -9.8, -0.9, 12.2</td>
<td>3 plants</td>
</tr>
<tr>
<td>Vauxhall (112.11° W, 50.06° N)</td>
<td>Gas compressors and cattle and swine feedlots</td>
<td>12-125+; 7.5-45+</td>
<td>W, 65°</td>
<td>25/10/2011 – 13/12/2011</td>
<td>3</td>
<td>2.6, 0.7, -3.5</td>
<td>65+ compressors; 200+ feedlots</td>
</tr>
<tr>
<td>Terrace Heights (113.44° W, 53.54° N)</td>
<td>Urban traffic</td>
<td>&lt;1-15 (4)</td>
<td>W, 150°</td>
<td>24/07/2012 – 25/10/2012</td>
<td>4</td>
<td>20.3, 15.6, 7.9, -1.8</td>
<td>Park in residential area, 3.5 km east of downtown core</td>
</tr>
<tr>
<td>Fort Saskatchewan (113.14° W, 53.72° N)</td>
<td>Chemical industries and metal refining</td>
<td>3-7 (4)</td>
<td>NW, 88°</td>
<td>12/04/2013 – 06/09/2013</td>
<td>4</td>
<td>4.3, 15.7, 16.3, 17.7</td>
<td>Chemical plant and metal refinery largest NOx sources; fertilizer plant largest NH3 source</td>
</tr>
<tr>
<td>Fort Saskatchewan (113.14° W, 53.72° N)</td>
<td>Fertilizers plant and oil refinery</td>
<td>9-14 (11)</td>
<td>N, 27°</td>
<td>20/09/2013 – 20/01/2014</td>
<td>1</td>
<td>-8.1</td>
<td>Fertilizer plant largest NH3 and NOx source, oil refinery major NOx source</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>N compound (n)</th>
<th>δ¹⁸O/‰</th>
<th>δ¹⁷O/‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon filters</td>
<td>p-NO₃⁻ (19)</td>
<td>2</td>
</tr>
<tr>
<td>Nylon filters</td>
<td>HNO₃ (18)</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3. Average oxygen isotopic ratios for NO₃⁻ sampled as gas (HNO₃), w (precipitation) and p (particulate matter) relative to VSMOW.

<table>
<thead>
<tr>
<th>Matrix Source</th>
<th>Gas</th>
<th>w</th>
<th>p</th>
<th>Gas</th>
<th>w</th>
<th>p</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>δ¹⁸O/‰</td>
<td>Δ¹⁷O/‰</td>
<td>δ¹⁸O/‰</td>
<td>Δ¹⁷O/‰</td>
<td>δ¹⁸O/‰</td>
<td>Δ¹⁷O/‰</td>
</tr>
<tr>
<td>Coal-fired power plants</td>
<td>69.7 (5)</td>
<td>66.1 (4)</td>
<td>70.7 (4)</td>
<td>25.1 (5)</td>
<td>25.4 (4)</td>
<td>26.6 (4)</td>
</tr>
<tr>
<td>Fertilizers plant &amp; oil refinery</td>
<td>63.2 (1)</td>
<td>71.4 (1)</td>
<td>69.5 (1)</td>
<td>19.3 (1)</td>
<td>26.0 (1)</td>
<td>23.8 (1)</td>
</tr>
<tr>
<td>Chemical industries &amp; metal refining</td>
<td>65.7 (4)</td>
<td>61.9 (2)</td>
<td>54.6 (4)</td>
<td>21.8 (4)</td>
<td>21.4 (2)</td>
<td>18.5 (4)</td>
</tr>
<tr>
<td>Gas compressors</td>
<td>65.0 (2)</td>
<td>63.1 (3)</td>
<td>-63.1 (3)</td>
<td>24.5 (2)</td>
<td>-26.4 (3)</td>
<td>26.4 (3)</td>
</tr>
<tr>
<td>City traffic</td>
<td>65.7 (3)</td>
<td>67.2 (2)</td>
<td>59.6 (3)</td>
<td>21.2 (3)</td>
<td>24.4 (2)</td>
<td>22.5 (3)</td>
</tr>
<tr>
<td>Mean</td>
<td>66.8</td>
<td>66.0</td>
<td>62.6</td>
<td>23.0</td>
<td>24.3</td>
<td>23.4</td>
</tr>
</tbody>
</table>

(n): number of sampling periods characterized
Table 4. Compilation of triple oxygen isotopic ranges obtained for atmospheric and emitted nitrates.

<table>
<thead>
<tr>
<th>δ18O/‰</th>
<th>Δ17O/‰</th>
<th>Regional context</th>
<th>Location</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>62.4-81.7</td>
<td>19.3-29.0</td>
<td>Various contaminated sites</td>
<td>Alberta, Canada</td>
<td>This study</td>
</tr>
<tr>
<td>p-NO3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43-62</td>
<td>20-27</td>
<td>Coast, Trinidad Head</td>
<td>California, USA</td>
<td>Patris et al. (2007)</td>
</tr>
<tr>
<td>78-92</td>
<td>29.8-35.0</td>
<td>High Arctic (Alert, Ellesmere Is.)</td>
<td>Nunavut, Canada</td>
<td>Morin et al. (2007)</td>
</tr>
<tr>
<td>62-112</td>
<td>19-43</td>
<td>Coast</td>
<td>Antarctic</td>
<td>Savarino et al. (2007)</td>
</tr>
<tr>
<td>15.6-36.0</td>
<td>-0.2 to 1.8</td>
<td>Oil-sands mining stacks, PM 2.5</td>
<td>Alberta, Canada</td>
<td>Proemse et al. (2012)</td>
</tr>
<tr>
<td>49-86</td>
<td>19-27</td>
<td>Coast (onboard sampling)</td>
<td>California, USA</td>
<td>Vicars et al. (2013)</td>
</tr>
<tr>
<td>10.8-92.4</td>
<td>2.7-31.4</td>
<td>Mt. Lulin, partly polluted air masses</td>
<td>Central Taiwan</td>
<td>Guha et al. (2017)</td>
</tr>
<tr>
<td>48.4-83.2</td>
<td>13.8-30.5</td>
<td>Various contaminated sites</td>
<td>Alberta, Canada</td>
<td>This study</td>
</tr>
<tr>
<td>w-NO3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>66.3-84.0</td>
<td>20.2-36.0</td>
<td>Shenandoah National Park</td>
<td>Virginia, USA</td>
<td>Coplen et al. (2004)</td>
</tr>
<tr>
<td>70-90</td>
<td>20-30</td>
<td>Bi-monthly sampling across state</td>
<td>New England, USA</td>
<td>Kendall et al. (2007)</td>
</tr>
<tr>
<td>68-101</td>
<td>20.8-34.5</td>
<td>Rishiri Island, polluted air masses</td>
<td>Northern Japan</td>
<td>Tsunogai et al. (2010)</td>
</tr>
<tr>
<td>51.7-72.8</td>
<td>18.9-28.1</td>
<td>Highway traffic emissions</td>
<td>Ontario, Canada</td>
<td>Smirnoff et al. (2012)</td>
</tr>
<tr>
<td>35.0-80.7</td>
<td>15.7-32.0</td>
<td>Oil-sands mining (with some dry dep)</td>
<td>Alberta, Canada</td>
<td>Proemse et al. (2013)</td>
</tr>
<tr>
<td>57.4-74.4</td>
<td>19.2-30.1</td>
<td>Various contaminated sites</td>
<td>Alberta, Canada</td>
<td>This study</td>
</tr>
<tr>
<td>Undifferentiated and Bulk NO3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60-95</td>
<td>21-29</td>
<td>Polluted coastal area &amp; Remote land</td>
<td>California, USA</td>
<td>Michalski et al. (2004)</td>
</tr>
<tr>
<td>57-79</td>
<td>22-32</td>
<td>High Arctic</td>
<td>Nunavut, Canada</td>
<td>Morin et al. (2008)</td>
</tr>
<tr>
<td>36-105</td>
<td>13-37</td>
<td>Marine boundary layer</td>
<td>65S to 79N Atlantic</td>
<td>Morin et al. (2009)</td>
</tr>
<tr>
<td>56.6-82.3*</td>
<td>16.7-30.2*</td>
<td>Various contaminated sites</td>
<td>Alberta, Canada</td>
<td>This study</td>
</tr>
</tbody>
</table>

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 HNO3 and p-NO3 isotopic results.

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

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Reactions</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1) O2 + Q ⇒ O + O + Q ; N2 + O ⇒ NO + N ; N + O2 ⇒ NO + O</td>
<td>(R2) O + O3 + M ⇒ O3 ; NO + O3 ⇒ NO2 + O2</td>
<td>(R3) NO + RO2 ⇒ NO2 + RO</td>
</tr>
<tr>
<td>(R4) NO2 + O3 ⇒ NO3 + O2</td>
<td>(R5) NO2 + hv (sunlight) ⇒ NO + O</td>
<td>(R6) NO2 + OH + M ⇒ HNO3 + M</td>
</tr>
<tr>
<td>(R7) NO2 + NO3 ⇒ 2NO5</td>
<td>(R8) N2O5 + H2O(surface) ⇒ 2HNO3(aq)*</td>
<td>(R9) HNO3(g) + HNO3(aq)* ⇒ NO3(aq)* + H+ (aq)</td>
</tr>
<tr>
<td>(R10) HNO3(g) + NH3(g) ⇒ NHNO2(s)</td>
<td>(R11) HNO3(g) + CO2(g) ⇒ Ca(NO3)2(s) + HCO3</td>
<td>(R12) NO3 + HC(CH3)2S ⇒ HNO3 + products</td>
</tr>
</tbody>
</table>

Q is a stable molecule of high energy; M is either O2 or N2; RO2 stands for both HO2 and alkyl peroxy. HC stand for hydrocarbons. *This aqueous nitrate may be on a particle.
Table 6. Correlation coefficients (r) of NO3\textsuperscript{-} isotopic deltas with meteorological parameters and concentration (or ratio) of co-contaminants.

<table>
<thead>
<tr>
<th></th>
<th>Relative Humidity</th>
<th>Temperature</th>
<th>Daylight (fraction)</th>
<th>PM</th>
<th>SO\textsubscript{2}</th>
<th>O\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r</td>
<td>r\textsuperscript{2}</td>
<td>r</td>
<td>r\textsuperscript{2}</td>
<td>r</td>
<td>r</td>
</tr>
<tr>
<td>HNO\textsubscript{3}</td>
<td>(\delta^{18}\text{O})</td>
<td>0.8</td>
<td>0.59</td>
<td>-0.4</td>
<td>-0.3</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>8</td>
<td>15</td>
<td>15</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>(\Delta^{17}\text{O})</td>
<td>0.6</td>
<td>-0.5</td>
<td>0.24</td>
<td>-0.4</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>8</td>
<td>15</td>
<td>15</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>p-NO\textsubscript{3}\textsuperscript{-}</td>
<td>(\delta^{18}\text{O})</td>
<td>0.9</td>
<td>0.79</td>
<td>-0.6</td>
<td>0.34</td>
<td>-0.6</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>7</td>
<td>15</td>
<td>15</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>(\Delta^{17}\text{O})</td>
<td>0.9</td>
<td>0.73</td>
<td>-0.6</td>
<td>0.34</td>
<td>-0.7</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>7</td>
<td>15</td>
<td>15</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>

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

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 NOx as tonnes of NO2 reported to the National Pollutant Release Inventory for 2013 (Environment and Climate Change Canada, 2018b).

Figure 2: Triple O isotopic results obtained for simultaneously collected atmospheric HNO3 (A), w-NO3- (B) and p-NO3- (C), in Alberta, identified by sampling periods (cold months - blue; warm months - red).

Figure 3: Line-connected δ18O and Δ17O values for simultaneously collected HNO3 (empty symbols) and p-NO3- (solid symbols) from cold (blue) and warm (red) sampling periods.

Figure 4: Isotopic results for p-NO3- identified by sampling periods (solid lines), compared with summer and winter trends obtained for Arctic sites (dashed lines; derived from ln (1+ δ) in Morin et al., 2008).

Figure 5: Weighted Δ17O average for the sum of dry nitrates as a function of NO2 concentration divided by p-NO3 plus HNO3 concentrations, a ratio indicative of the maturity of a plume.

Figure 6: Isotopic ratios for atmospheric p-NO3-, w-NO3- and HNO3 samples in cold and warm periods from central and southern Alberta (this study), compared with previously published winter and summer bulk and throughfall deposition samples from the oil sands (OS) region from northern Alberta (Proemse et al., 2013), and p-NO3- in-stack emissions data for an OS upgrader located in the same region (Proemse et al., 2012). The grey dotted line connects NOx from theoretical combustion with O2 isotopic composition and at isotopic equilibrium with tropospheric O3 (Michalski et al., 2014).