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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Abstract. There are clear motivations for better understanding the atmospheric processes that transform nitrogen (N) oxides (NO$_x$) emitted from anthropogenic sources into nitrates (NO$_3^-$), two of them being that NO$_3^-$ contributes to acidification and eutrophication of terrestrial and aquatic ecosystems, and particulate nitrate may play a role in climate dynamics. For these reasons, oxygen isotope 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 (O$_3$). Recent laboratory experiments suggest that the isotopic equilibrium between NO$_2$ (the main precursor of NO$_3^-$) and O$_3$ may take long enough under certain field conditions that nitrates may be formed near emission sources with lower isotopic values than those formed further downwind. Indeed, previously published field measurements of oxygen isotopes in NO$_3^-$ in precipitation ($w$NO$_3^-$) and in particulate ($p$NO$_3^-$) samples suggest that abnormally low isotopic values might characterize polluted air masses. However, none of the air studies have deployed systems allowing collection of samples specific to anthropogenic sources in order to avoid shifts in isotopic signature due to changing wind directions, or separately characterized gaseous HNO$_3$ with $\Delta^{17}\text{O}$ values. Here we have used a wind-sector-based, multi-stage filter sampling system and precipitation collector to simultaneously sample HNO$_3$ and $p$NO$_3^-$, and co-collect $w$NO$_3^-$. The nitrates are from various distances ($<1$ to $>125$ km) downwind of different anthropogenic emitters, and consequently from varying time lapses after emission.

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

1 Introduction

Anthropogenic NO$_x$ (NO and NO$_2$) emissions are oxidized to nitrate in the atmosphere in the form of gaseous, wet or particulate forms. HNO$_3$ being one of the main precursors of $p$NO$_3^-$. All these species may have detrimental effects on atmospheric chemistry, climate and eutrophication of terrestrial and aquatic ecosystems.
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 nitrate to collectively refer to $p$NO$_3$, HNO$_3$ and wNO$_3$).

Triple oxygen isotopes ($\delta^{18}O$ and $\Delta^{17}O$) have been used to decipher atmospheric oxidation pathways of NO$_x$ leading to ambient nitrate. Michalski et al. (2003) performed the first measurement of $\Delta^{17}O$ values in atmospheric nitrate. The authors found nitrate highly enriched in $^{18}O$ and $^{17}O$, likely due to the transfer of anomalous oxygen atoms from ozone ($O_3$) via the NO$_x$–ozone photochemical cycle and oxidation to nitrate. During its formation, $O_3$ inherits abnormally high $\delta^{18}O$ and $\Delta^{17}O$ values through mass independent fractionation. The specific $\Delta^{17}O$ departure from the terrestrial mass-dependent fractionation line, named the $\Delta^{17}O$ anomaly, is often expressed as $\Delta^{17}O = \Delta^{17}O - 0.517 \times \delta^{18}O$ (Thiemens, 1999). Further investigations suggested that the $\delta^{18}O$ and $\Delta^{17}O$ values of wNO$_3^−$ and $p$NO$_3^−$ reflect several reactions taking place after the atmospheric emission of NO$_x$, i.e., atmospheric oxidation pathways transforming NO$_x$ into secondary products (Hastings et al., 2003; Michalski et al., 2003, 2004; Morin et al., 2007; Savarino et al., 2007; Alexander et al., 2009). Seasonal $\delta^{18}O$ differences in wNO$_3^−$ samples (less variable and lower values during summer) have been interpreted to be due to changes in these chemical pathways (Hastings et al., 2003). Modelling and validation based on sparse existing data provide hope regarding a global understanding of atmospheric nitrate (Alexander et al., 2009); however, further measurements need to be done on the ground, particularly at mid-latitudes.

Additional studies dealing with triple oxygen isotope characterizations have addressed questions of methodology (Kaiser et al., 2007; Smirnoff et al., 2012), transfer of the ozone $^{17}O$ anomaly to atmospheric nitrate (Liang and Yung, 2007; Savarino et al., 2008; Michalski et al., 2014) or sources and chemical pathways of high (Arctic) and low (Taiwan) latitude nitrate (Morin et al., 2008; Guha et al., 2017, respectively). Triple oxygen isotope characterizations of field NO$_3^−$ samples are not yet widespread. Also rare are the nitrate $\delta^{18}O$ and $\Delta^{17}O$ values of field samples downwind from NO$_x$-emitting sources at mid-latitudes (Kendall et al., 2007; Proemse et al., 2013). The few existing studies have chiefly characterized wNO$_3^−$ or the sum of $p$NO$_3^−$ and HNO$_3$ (Michalski et al., 2004; Morin et al., 2007, 2008, 2009; Alexander 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 ap-

portion the contribution of anthropogenic emissions to regional atmospheric nitrate loads (Proemse et al., 2013).

In the past, due to sampling challenges, HNO$_3$ and $p$NO$_3^−$ were generally collected together (without differentiation). Therefore, no studies have separately and simultaneously collected and analyzed the HNO$_3$ and $p$NO$_3^−$ $\delta^{18}O$ and $\Delta^{17}O$ values, and discussed these isotopic characteristics of nitrate collected downwind of anthropogenic emitters. While HNO$_3$ and $p$NO$_3^−$ can be in equilibrium (e.g., if $p$NO$_3^−$ is in the form of solid NH$_4$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 Sect. 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 mass-dependent oxygen fractionations in nitrates collected separately may help to identify 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 (CFPPs), (2) city traffic, (3) chemical industries and metal refining, (4) fertilizer plant and oil refinery and (5) gas compressors plus cattle and swine feedlots. To this end, we employed wind-sector-based active samplers to collect HNO$_3$ and $p$NO$_3^−$ as well as wNO$_3^−$ downwind of the source types. The objective of this work was to assess the atmospheric NO$_x$ reaction pathways and determine processes responsible for the distribution of HNO$_3$, w- and $p$NO$_3^−$ in a mid-latitudinal region.

2 Methodology

2.1 Regional context

While national reported NO$_x$ emissions in Canada declined steadily from 2000 to 2015, emissions in the province of Alberta have remained relatively constant since 2004 (Environment and Climate Change Canada, 2016). Pioneering work was accomplished , measuring nitrate on emitted PM$_{2.5}$ (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, 2013). However, the Edmonton area in central Alberta, known to generate the highest NO$_x$ emissions in Canada, and the area of southern Alberta, characterized by dense gas compressor station and agricultural emissions, have never been investigated.

This research project investigated nitrates ($p$NO$_3^−$, HNO$_3$ and wNO$_3^−$) from two main emission source areas: the Gene-

see and Edmonton areas of central Alberta, and the Vaux-
hall area of southern Alberta (Fig. 1a). These areas experience a continental climate, but the mean annual temperature
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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): CFPs 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$_x$ emissions reported in 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$^{-1}$ (2 km h$^{-1}$) 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. S2).

Ambient air was pulled through a three-stage filter pack system to collect, sequentially, particulate matter on a Teflon filter, gaseous nitric acid (HNO$_3$) on a Nylasorb nylon filter and gaseous ammonia on a citric acid-coated Whatman 41 filter (all 47 mm). The Teflon–nylon filter method for $p$NO$_3^-$ and HNO$_3$ has been extensively compared and evaluated, and is currently used by national monitoring networks targeting regional background sites, CAPMoN in Canada and CASTNet (Clean Air Status and Trends Network) in the

Figure 1. Aerial images showing sampling sites (green triangles) in central and southern Alberta (a), and in the greater Edmonton area (b), along with emissions of NO$_x$ as tonnes of NO$_2$ reported in the National Pollutant Release Inventory for 2013 (Environment and Climate Change Canada, 2018b).
United States. Previous testing showed negligible collection of HNO$_3$ on the Teflon filter, < 3 % breakthrough of HNO$_3$ from the nylon filter with loadings more than 3 times higher than reported here and blanks for pNO$_3^-$ and HNO$_3$ of approximately 0.2 µg N per filter (Anlauf et al., 1985, 1986). Intercomparisons with more labour-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 pNO$_3$ and positive bias in HNO$_3$ under hot (> 25 °C) and dry conditions, particularly in high ambient concentrations (e.g., Appel et al., 1981). However, other field studies have shown no significant differences in HNO$_3$ between filter packs and denuder and/or TD-LAS 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$_2$ (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$_4$NO$_3$ for samples with mean temperatures below 5 °C, but there is a possibility for nitrate loss of up to 30 % in the warmest sampling periods.

After the first five sample periods, an experimental active sampling system for NO$_2$ and NO$_x$ was added downstream of the three-stage filter pack. This system consisted of one or two custom cartridges packed with Maxxam Analytics’ resin to selectively collect NO$_2$, and one- or two-stage filter packs containing two identical Maxxam Analytics’ impregnated filters designed to collect NO$_x$ (mostly NO due to upstream collection of NO$_2$). Oxygen isotopes in NO$_2$ and NO$_x$ were not measured since we could not rule out oxygen isotope exchange during the extraction process; however, concentrations meeting the quality control (QC) criteria (Savard et al., 2017) are presented for reference in Table S1.

Here we report on oxygen isotopes in the simultaneously sampled HNO$_3$ and pNO$_3^-$, along with co-sampled w/NO$_3$ in rain and snow samples. Note that precipitation events did not occur regularly (see Fig. S1), 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$^{-1}$ (2 km h$^{-1}$). 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–particle sam-

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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$_x$ sources; fertilizer plant largest NH$_3$ source |
| Fort Saskatchewan (113.14° W, 53.72° N) | Fertilizer plant and oil refinery | 9–14 (11) | N, 27° | 20/09/2013–20/01/2014; 1 | –8.1 | Fertilizer plant largest NH$_3$ and NO$_x$ source; oil refinery major NO$_x$ source |

$n$: number of sampling sessions. Avg T: average temperature during each of the consecutive sampling sessions.
Savard et al., 2017). The present article deals solely with the thermal decomposition of $N_2O$ and the detection limit (1.1 µmol L$^{-1}$) was also measured in the extracts. Nitrite concentrations above the detection limit for the method with sulfanilamide (31-107-04-1-A) was 0.01 M solution of NaCl. Particulate NO$_3$ from Teflon filters was extracted using 10 mL of ultrapure water (ELGA). To reduce possible evaporation, filters were placed in an ultrasonic bath with ice. The extractions were performed during 1 h and samples were left for 48 h 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$^{-1}$ of NO$_3^-$–N. Nitrite concentrations were also measured in the extracts. Nitrite concentrations above the detection limit (1.1 µmol L$^{-1}$ of NO$_3^-$–N) were found in a handful of samples at Terrace Heights. These samples were excluded from the reported data.

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

### Table 2. Isotopic reproducibility (modified median absolute deviation) established using two to four parallel active CAPMoN sampling set-ups in seven separate sampling periods, resulting in ($n$) total samples.

| N compound (n) | $\delta^{18}O/‰$ | $\Delta^{17}O/‰$ |
|---------------|-----------------|-----------------|
| Teflon filters |                 |                 |
| $\rho$NO$_3$  | 2               | 1               |
| Nylon filters |                 |                 |
| HNO$_3$       | 1               | 0.7             |

2.3 Analytical procedures

Nitric acid from nylon filters was extracted using 10 mL of 0.01 M solution of NaCl. Particulate NO$_3$ from Teflon filters was 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 1 h and samples were left for 48 h 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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3 Results and interpretation

3.1 Isotopic reproducibility when using the CAPMoN filter pack 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 2 to 4 absolute deviations from this median were calculated (Tables 2, S1). Although there were 4 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 for each compound (Table 3). The median absolute deviation was Gaussian (Randles and Wolfe, 1979; Sirois and Vet, 1999). This suite of parallel tests indicates that all measured species show coherent and reproducible values in NH$_3$ and NH$_4^+$, with subsequent collection of the same samples (Savard et al., 2017). As expected, there were no systematic differences in the absolute isotopic values (δ$^{17}$O and δ$^{18}$O) between the samples, which were thought to be artifically high and low, respectively, with more fractionation at higher temperatures (winter) relative to lower temperatures (summer) when volatilization is minimal (Keck and Wittmaack, 2005). We find the $\rho$NO$_3^-$ isotopic values ($\Delta^{17}$O and $\Delta^{18}$O) to be generally higher during winter than during summer (see Sect. 3.4). Moreover, the $\rho$NO$_3^-$ δ$^{18}$O minus HNO$_3$ δ$^{18}$O differences are negative during summer (see Sect. 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 $\delta^{15}$N values in NH$_3$ and NH$_4^+$; Savard et al., 2017). We therefore conclude that, while volatilization may occur in the summer samples, other isotope effects must be larger in order to lead to the observed differences. In addition, volatilization would cause mass-dependent fractionation and would not affect the $^{17}$O anomaly; therefore, $\Delta^{17}$O values remain robust indicators of chemical pathways in this situation. Finding that the sampling protocols are adequate for isotopic work is in agreement with a previous study using a comparable method that found minimal fractionation for $\rho$NO$_3^-$ and HNO$_3$ (Elliott et al., 2009).

3.2 Concentrations and isotopic ratios of nitrates in Alberta samples

The range of HNO$_3$–N concentrations measured by the filters (from 0.01 to 0.15 µg m$^{-3}$; average of 0.06) is slightly lower than that of $\rho$NO$_3^–$N (from 0.20 to 0.36 µg m$^{-3}$; average of 0.12). For context, the median concentrations at all CAPMoN sites, which represent non-urban areas across Canada, range from 0.02 to 0.25 µg m$^{-3}$ for HNO$_3$–N and from 0.007 to 0.45 µg m$^{-3}$ for $\rho$NO$_3^–$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 0.01–0.02 µg m$^{-3}$ of NO$_3^–$–N for both HNO$_3$ and $\rho$NO$_3^–$N (preliminary internal data). Therefore, the lowest concentrations in our samples approached average background concentrations, while the highest were 20 or more times higher than the regional background. The range of NO$_3^–$–N concentrations of wNO$_3^–$ samples was 10.71–34.29 µmol L$^{-1}$. 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$^{-1}$ of NO$_3^–$–N, while at the most polluted site in southern Ontario (Longwoods) the volume-weighted mean concentration was approximately 21.43 µmol L$^{-1}$ (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 δ$^{18}$O and $\Delta^{17}$O values of HNO$_3$ (gas), w- and $\rho$NO$_3^–$N show no apparent systematic ordering (Tables 3, S1 and S2), in contrast to what was found for $\delta^{15}$N values in the same samples (Savard et al., 2017). As expected, there is no systematic tendency when looking at the samples collected from the anthropogenic sources: CFPPs HNO$_3$ and $\rho$NO$_3^–$N have the highest δ$^{18}$O and $\Delta^{17}$O averages, but not the highest delta values for wNO$_3^–$N values; chemical industries show the lowest $\delta^{18}$O and $\Delta^{17}$O averages for w- and $\rho$NO$_3^–$N, but not for HNO$_3$. Though the number of samples was limited, wNO$_3^–$N $\Delta^{17}$O values were roughly correlated with the weighted average $\Delta^{17}$O values of $\rho$NO$_3$ and HNO$_3$ in samples covering the same time periods, consistent with scavenging of both HNO$_3$ and $\rho$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. S3), as previously suggested in the literature (Michalski et al., 2003).
Table 3. Average oxygen isotopic ratios for NO$_3^-$ sampled as gas (HNO$_3$), $w$ (precipitation) and $p$ (particulate matter) relative to VSMOW.

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

($)$ shows number of sampling periods characterized.

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

| $\delta^{18}$O/‰ | $\Delta^{17}$O/‰ | Regional context | Location | Authors |
|------------------|------------------|------------------|----------|---------|
| HNO$_3$          |                 |                  |          |         |
| 62.4–81.7        | 19.3–29.0        | Various contaminated sites | Alberta, Canada | This study |
| $p$NO$_3^-$      |                 |                  |          |         |
| 43–62            | 20–27            | Coast, Trinidad Head | California, USA | Patris et al. (2007) |
| 78–92            | 29.8–35.0        | High Arctic (Alert, Ellesmere Is.) | Nunavut, Canada | Morin et al. (2007) |
| 62–112           | 19–43            | Coast | Antarctica | Savarino et al. (2007) |
| 15.6–36.0        | $-0.2$ to $1.8$  | Oil sands mining stacks, PM$_{2.5}$ | Alberta, Canada | Proemse et al. (2012) |
| 49–86            | 19–27            | Coast (onboard sampling) | California, USA | Vicars et al. (2013) |
| 10.8–92.4        | 2.7–31.4         | Mt. Lulin, partly polluted air masses | Central Taiwan | Guha et al. (2017) |
| 48.4–83.2        | 13.8–30.5        | Various contaminated sites | Alberta, Canada | This study |
| $w$NO$_3^-$      |                 |                  |          |         |
| 66.3–84.0        | 20.2–36.0        | Shenandoah National Park | Virginia, USA | Coplen et al. (2004) |
| 70–90            | 20–30            | Bimonthly sampling across state | New England, USA | Kendall et al. (2007) |
| 68–101           | 20.8–34.5        | Rishiri Island, polluted air masses | Northern Japan | Tsunogai et al. (2010) |
| 51.7–72.8        | 18.9–28.1        | Highway traffic emissions | Ontario, Canada | Smirnoff et al. (2012) |
| 35.0–80.7        | 15.7–32.0        | Oil sands mining (with some dry dep.) | Alberta, Canada | Proemse et al. (2013) |
| 57.4–74.4        | 19.2–30.1        | Various contaminated sites | Alberta, Canada | This study |

Undifferentiated and bulk NO$_3^-$

| $\delta^{18}$O/‰ | $\Delta^{17}$O/‰ | Regional context | Location | Authors |
|------------------|------------------|------------------|----------|---------|
| 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 | 65° S to 79° N Atlantic | Morin et al. (2009) |
| 56.6–82.3*       | 16.7–30.2*       | Various contaminated sites | Alberta, Canada | This study |

Note: isotopic values rounded to the whole number are from published graphs (except for precise O values in Morin et al., 2007). * Calculated using weighted averages of HNO$_3$ and $p$NO$_3^-$ isotopic results.

Considering all nitrate species, the Alberta $\delta^{18}$O and $\Delta^{17}$O values range between $+48.4$ and $+83.2\%e$, and between $13.8\%e$ and $30.5\%e$, respectively (Tables 4, S1, Fig. S4). These ranges indicate that ozone partly transferred its isotopic anomaly to nitrates during NO$_x$ cycling and oxidation (nitrate derived through combustion in O$_2$ would show $\delta^{18}$O and $\Delta^{17}$O values of $23.5\%e$ and $0\%e$, respectively). When examining the existing $\delta^{18}$O and $\Delta^{17}$O data for $w$- and $p$NO$_3^-$ in the literature, the ranges for our mid-latitude samples are within those previously reported (Table 4).
The $\delta^{18}O$ and $\Delta^{17}O$ trends in nitrates from cold and warm sampling periods

The $\delta^{18}O$ and $\Delta^{17}O$ ranges for HNO$_3$ identified by sampling period are narrower than those of the simultaneously collected $p$NO$_3^-$ (Fig. 2; Table S1), suggesting that there are additional mechanisms affecting HNO$_3$, or that $p$NO$_3$ is derived from different pathways with more variation in isotopic signatures. Overall, the $\Delta^{17}O$ and $\delta^{18}O$ results for HNO$_3$, $w$NO$_3^-$ and $p$NO$_3$ clearly show higher $\delta^{18}O$ and $\Delta^{17}O$ values during cold periods relative to warm periods (Fig. 2), with the exception of HNO$_3$ $\delta^{18}O$ values, which were similar in cold and warm periods. The collection of several samples lasted over periods overlapping fall and winter and, in such cases, the results are labelled as covering the two seasons; note that for many fall cases, the average sampling temperatures were below 0°C (Table S3). Nevertheless, plotting by sampling period can be regarded as a general repartition of results between warm and cold months, which show lower and higher isotopic values, respectively, in both the $w$- and $p$NO$_3^-$.

A series of reactions listed in Table 5 summarizes the main atmospheric processes taking place during the production of nitrates in contaminated air masses. First, during anthropogenic combustion of fossil fuels, NO$_x$ (NO and NO$_2$) is produced through reactions of air N$_2$ with atmospheric O$_2$ at high temperatures (Reaction R1; Table 5). Then, NO$_x$ cycles between NO and NO$_2$ through a series of reactions involving sunlight (Reaction R5), O$_3$ (Reactions R2, R4) and peroxy (HO$_2$) or alkyl peroxy (RO$_2$) radicals (Reaction R3; Morin et al., 2007; Fang et al., 2011; Michalski et al., 2014; here we use RO$_2$ to refer collectively to HO$_2$ and RO$_2$).

The oxidation of NO$_x$ (specifically NO$_2$) to HNO$_3$ further incorporates additional O atoms from different oxidants (Reactions R6–R8; Table 5). Production of nitrate via Reaction (R6) is restricted to daytime (since OH is generated through photochemistry), whereas production through Reactions (R4), (R7) and (R8) dominates at night. In addition, N$_2$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 N$_2$O$_5$ (Reaction R8), HNO$_3$ is likely to be retained on the reaction particle as $p$NO$_3^-$ due to its hygroscopicity (Seinfeld and Pandis, 2006). We have neglected contributions from BrO cycling due to the location far from the coast, and from reactions of NO$_3$ with hydrocarbons (Reaction R12) since they are predicted to have a minimal contribution to nitrate formation in this region (Alexander et al., 2009). Finally, HNO$_3$ in the gas phase can be irreversibly scavenged by wet surfaces or precipitation (Reaction R9) and calcium carbonate on particles (Reaction R11), and can equilibrate with solid ammonium nitrate where there is excess ammonia available (Reaction R10).

It has been previously suggested that the $\delta^{18}O$ and $\Delta^{17}O$ values of $w$- and $p$NO$_3^-$ formed during summer are lower

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**Figure 2.** Triple O isotopic results obtained for simultaneously collected atmospheric HNO$_3$ (a), $w$NO$_3^-$ (b) and $p$NO$_3^-$ (c), in Alberta, identified by sampling periods (cold months – blue; warm months – red).
than those during winter due to a higher contribution from the N₂O₅ path (Reactions 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 pNO₅ 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-contaminants

The distribution and proportion of HNO₃ and pNO₅ 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 pNO₅ samples (n of w/NO₃ too low) with meteorological and air quality parameters measured routinely at nearby monitoring stations where available (Table S3). We found that the pNO₅ and HNO₃ δ¹⁸O and Δ¹⁷O values correlate with RH, with pNO₅ values showing stronger statistical links than HNO₃ (Table 6). The N₂O₅ hydrolysis reaction (Reaction R8) rate increases with humidity (Kane et al., 2001), which may explain this positive correlation. Significant inverse relationships exist between temperature and pNO₅ δ¹⁸O, pNO₅ Δ¹⁷O and HNO₃Δ¹⁷O. These negative links likely arise since N₂O₅ is more stable under cold conditions, leading to a higher contribution of R8. The stronger links with pNO₅ may be due to Reaction (R8) taking place on surfaces (such as particles) with liquid water, which is likely to retain the HNO₃ as pNO₅ rather than release it to the gas phase. Therefore, in winter, R8 may contribute more to pNO₅ than to HNO₃(g). Moreover, the highest δ¹⁸O and Δ¹⁷O values for both pNO₅ and HNO₃ were found for fall–winter samples collected at high RH (76 %) and low temperature (−10 °C). In contrast, the lowest pNO₅ isotopic values were found for samples with similar proportions of HNO₃ and pNO₅, and sampled during moderately humid (60–63 %) and warm (8–20 °C) periods. The accompanying shift in δ¹⁸O and Δ¹⁷O differences between pNO₅ and HNO₃ will help infer the mechanisms that dominate during the cold and warm periods (Sect. 4.2).

Concentrations of oxidants, co-contaminants (e.g., SO₄ aerosols) and NO₃ influence the dominance and rates of the discussed reactions (Brown et al., 2006; Michalski et al., 2014). However, while temperature, RH and O₃ are well captured within a 5 km radius, other pollutant measurements like continuous SO₂, PM2.5 and NOₓ can have large gradients near sources; therefore it is not surprising that no correlations were found with SO₂ or PM2.5 measured at sites 4–5 km away (Table 6). Surprisingly, only the pNO₅ Δ¹⁷O and δ¹⁸O 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 HNO₃ as well due to the daytime-only OH pathway. However, daylight hours do not take into account light intensity, which can significantly influence the oxidation rate through this pathway and consequently both the δ¹⁸O and Δ¹⁷O values.

### 3.5 Comparison with high-latitude pNO₅

An interesting aspect of the Alberta pNO₅ cold-period Δ¹⁷O ranges is that they compare relatively well with the range obtained for the Canadian Arctic (Fig. 4), during winter, when night-time conditions and the N₂O₅ pathway prevail without interruption (Morin et al., 2008; for comparison with HNO₃ values see Fig. S4). This observation supports the suggestion that the N₂O₅ pathway produces around 90 % of nitrates during mid-latitudinal cold months (Michalski et al., 2003; Sect. 4.1). The δ¹⁸O ranges of cold months are similar...
in Alberta and in the Arctic. This similarity goes against previous suggestions that at higher latitudes, nitrate $\delta^{18}O$ annual means should be higher than at mid-latitudes due to local ambient conditions and atmospheric chemistry affecting the proportions of species involved in producing nitrate (Morin et al., 2009), namely, the sole influence of the $N_2O_5$ pathway during the Arctic winter (Fang et al., 2011).

The $\Delta^{17}O$ departure between the Alberta and Arctic winter parallel lines is about 3%. Such a 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 (Sect. 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$_3^-$ in the sampled anthropogenic plumes in Alberta (see Sect. 4.3 for details), whereas the seasonal departure in Arctic samples comes from the oxidation to nitrate through the dominant OH and $N_2O_5$ pathways during summer and winter, respectively. Finally, the $\Delta^{17}O$ averages for the Alberta summer and winter results approximately fit within ranges predicted for the studied area by global modelling (Alexander et al., 2009), suggesting that global modelling of nitrate distribution worldwide is promising.

### 3.6 Isotopic differences between HNO$_3$ and pNO$_3^-$

As far as the isotopic characteristics are concerned, an important feature to keep in mind is that the HNO$_3$ of central and southern Alberta has distinct properties relative to simultaneously sampled pNO$_3^-$ . In practical terms, the relationships between the simultaneously sampled HNO$_3$ and pNO$_3^-$ are of four types (Fig. 3): (i) HNO$_3$ $\delta^{18}O$ and $\Delta^{17}O$ are both lower than pNO$_3^-$; (ii) HNO$_3$ has lower $\Delta^{17}O$ but higher $\delta^{18}O$ values than pNO$_3^-$; (iii) HNO$_3$ has higher $\delta^{18}O$ values and similar $\Delta^{17}O$ ones relative to pNO$_3^-$; and (iv) HNO$_3$ has higher $\delta^{18}O$ and $\Delta^{17}O$ values than pNO$_3^-$ (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 pNO$_3^-$ and HNO$_3$ in the northeastern United States with similar seasonal changes of $\delta^{18}O$ differences (no $\Delta^{17}O$ measurement). The HNO$_3$ $\delta^{18}O$ values were generally similar or lower than the pNO$_3^-$ values during winter and fall, and slightly to much higher during spring and summer, with the spring and fall pNO$_3^-$–HNO$_3$ relationships being roughly intermediate between the winter and summer ones. The average $\delta^{18}O$ difference of pNO$_3^-$ minus HNO$_3$ reported between winter and summer (15%$\epsilon$) by Elliott et al. (2009) agrees with the difference for fall–winter and summer obtained here (12%$\epsilon$).

The marked shifts in isotopic differences between the separately analyzed HNO$_3$ and pNO$_3^-$ reported here likely reflect changes in the dominant reactions and processes leading to the production of the two nitrates (see Sect. 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$_3$ source.

### Table 6. Correlation coefficients ($r$) of NO$_3^-$ isotopic deltas with meteorological parameters and concentration (or ratio) of co-contaminants. In bold are the significant correlation coefficients, equal or above the 95% significance value.

|          | Relative humidity | Temperature | Daylight (fraction) | PM | SO$_2$ | O$_3$ |
|----------|-------------------|-------------|---------------------|----|--------|-------|
|          | $r$    | $R^2$  | $r$    | $R^2$  | $r$  | $r$  | $R^2$ |
| HNO$_3$  |        |        |        |        |      |      |       |
| $\delta^{18}O$ | 0.8 | 0.59  | -0.4  | -0.3  | 0.1  | 0.0  | -0.29 |
| $n$    | 8    | 15    | 15    | 13    | 13   | 13   |       |
| $\Delta^{17}O$ | 0.6 | -0.5  | 0.24  | -0.4  | 0.4  | 0.3  | -0.03 |
| $n$    | 8    | 15    | 15    | 13    | 13   | 13   |       |
| pNO$_3^-$ |        |        |        |        |      |      |       |
| $\delta^{18}O$ | 0.9 | 0.79  | -0.6  | 0.34  | -0.6 | 0.35 | 0.1   |
| $n$    | 7    | 15    | 15    | 12    | 12   | 12   |       |
| $\Delta^{17}O$ | 0.9 | 0.73  | -0.6  | 0.34  | -0.7 | 0.44 | 0.0   |
| $n$    | 7    | 15    | 15    | 12    | 12   | 12   |       |
In the present subsection, we estimate the $\Delta^{17}$O values of NO$_2$ involved during the production of the Alberta nitrates based on the observed nitrate values and discuss the implications of these estimations. Generally, winter to summer isotopic differences are thought to be due to the high oxygen isotopic values of N$_2$O$_5$ due to interaction with O$_3$ (Johnston and Thiemens, 1997; Michalski et al., 2003; Morin et al., 2008; Vicars et al., 2012) and low values of OH in isotopic equilibrium with atmospheric H$_2$O (Dubey et al., 1997). According to Table 5, the first reaction pathway produces nitrates via R4-R7-R8 with two-thirds of the O atoms coming from NO$_2$, one-sixth from O$_3$ and one-sixth from H$_2$O, while the second produces nitrates via Reaction (R6) with two out of three O atoms coming from NO$_2$ and one-third 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 $\sim$39‰ as was recently measured (Vicars and Savarino, 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 night-time) 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 mixture of O from the pathways operating during daytime (Reaction R6) and nighttime (Reactions R4-R7-R8) a priori. 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 Reaction (R3) with Reaction (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 Reactions (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$_3^-$ that did not reach an isotopic steady state with O$_3$, retaining some of its original signature (assumed to be $\Delta^{17}$O = 0‰). Most studies have assumed that an isotopic steady state is established between O$_3$ and NO$_3^-$ within a few minutes after emission of NO$_3^-$ from a combustion source – or at least, that nitrate formation is negligible before NO$_3^-$ isotopic equilibrium is reached. However, recent modelling by Michalski et al. (2014) suggests that isotopic equilibration of NO$_3^-$ 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 min. While the fraction of NO$_3^-$ converted to nitrate in this transit time may be small, these are large...
sources of NOx in an area with very low background nitrates. For example, a plume containing 10 mmol mol$^{-1}$ of NO2 mixing with background air with 0.1 pmol mol$^{-1}$ of OH (Howell et al., 2014) would produce HNO3 via Reaction (R6) at a rate of 0.011 μg m$^{-3}$ min$^{-1}$ of NO$_3$ – N at $T = 7^\circ$C (Burkholder et al., 2015), or an equivalent amount of a typical nitrate sample in 10 min (Table S1). Even if equilibration with O3 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 NOx that had not yet reached an isotopic steady state with O3. These two mechanisms are not exclusive and could both contribute to lower NOx, and therefore nitrate, $\Delta^{17}$O values.

An additional piece of evidence suggests that the NOx 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 NO2 concentration divided by the sum of HNO3 and pNO3 concentrations (Fig. 5). This observation is consistent with the unequilibrated NO2 hypothesis. However, it does not rule out the possible contribution of RO2, since VOC releases from the NOx sources could lead to elevated RO2 concentrations in the plume.

4.2 Causes of shifts in HNO3 to pNO3 isotopic differences

A challenging question is as follows: why do the HNO3 to pNO3 isotopic differences shift seasonally (Fig. 3)? One factor that may influence the relationship between HNO3 and pNO3 is the mass-dependent isotopic equilibrium between NH4NO3 and HNO3 (Reaction R10); however, this mechanism would result in higher $\delta^{18}$O in pNO3 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 N2O3 pathway is likely to produce more pNO3$^-$ than HNO3(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 pNO3$^-$.

For some of the spring and summer samples, both $\delta^{18}$O and $\Delta^{17}$O values were lower in pNO3$^-$ than in HNO3 (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 HNO3 dry-deposits to surfaces more rapidly than pNO3$^-$ (Zhang et al., 2009; Benedict et al., 2013), which would create the discussed isotopic shifts in the situation where NO2 has low $\Delta^{17}$O values in a fresh plume. The first nitrates formed in the plume shortly after emission from the NOx source have low $\delta^{18}$O and $\Delta^{17}$O values, either because NOx has not yet reached an isotopic steady state with O3 or because it reacted with $^{17}$O-poor RO2 present in the plume due to VOC emissions. Those nitrates that form as pNO3$^-$ or that partition to pNO3$^-$ remain in the plume for longer than HNO3, which is removed from the plume rapidly upon contact with vegetation or other surfaces. As the plume travels, the NOx becomes more enriched, and the newly formed nitrates take on higher $\delta^{18}$O and $\Delta^{17}$O values. However, pNO3$^-$ collected further downwind will derive from a mixture of low-$\delta^{18}$O and -$\Delta^{17}$O pNO3$^-$ formed earlier, plus high-$\delta^{18}$O and -$\Delta^{17}$O pNO3$^-$ formed more recently, while HNO3 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 pNO3$^-$ 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 HNO3 to pNO3 isotopic differences between cold and warm sampling periods – a differential N2O5 contribution resulting in higher $\Delta^{17}$O values in pNO3$^-$ than in HNO3, and a differential deposition resulting in lower $\Delta^{17}$O values in pNO3$^-$ – would essentially compete against each other, with local conditions and chemistry influencing the results. In winter, when the N2O5 pathway is most important, the first mechanism predominates, as supported by the observation that pNO3$^-$ concentrations are higher during that season (trend i). Conversely, in summer, when the N2O5 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 an 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 dif-
In summary, examining the isotopic relationship of HNO3 to pNO3 (Fig. 3) reveals the complexity of anthropogenic NOx oxidation mechanisms. The lower pNO3 isotopic values relative to the HNO3 values during warm months may reflect differential removal rates from plumes containing NO2 temporarily low in 17O.

4.3 Low 18O and 17O trends in global w- and pNO3 – 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 NOx 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 O3 and oxidation through the well-known OH and N2O5 oxidation paths. However, NO2 not in isotopic equilibrium with O3, and/or NO reacted with RO2, 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 RO2 and/or HO2 would help distinguish between the two mechanisms. Meanwhile, our results raise the following question: are these overall effects observable in triple oxygen isotopes of nitrates from other polluted sites?

The full 17O and 18O ranges for pNO3, wNO3 and HNO3 (between 13.8‰ and 20.5‰ and 48.4‰ and 83.2‰; Table 4) compare well with the isotopic ranges obtained for bulk deposition NO3 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. S1) 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 18O and 17O values.

Previous work in the Athabasca region reported very low 18O and near-zero 17O values for pNO3 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 O2. Similar isotopic signatures are very likely produced in source emissions of NOx in the studied Edmonton and Vauxhall areas (e.g., CFPPs, gas compressors, industries). This source signature may persist into pNO3 collected close to the sources. Within the first few hours in the atmosphere (less, in polluted areas), the NOx 18O and 17O values rapidly increase due to isotope exchange with O3 (Reactions R2, R3, R5 and O3 formation, Table 5; Michalski et al., 2014) and reach isotopic equilibrium. Though the e-folding lifetime for NOx oxidation to nitrites may be longer than these few hours, depending on the NOx/VOC ratio, only a fraction of the oxidized source NOx 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 17O values within 12 km of the emission sites, and where direct stack emissions of pNO3 were ~ 5000 times lower than NOx emissions (Wang et al., 2012).

In a methodological test study, we obtained low values for wNO3 sampled near a high traffic volume highway in Ontario, Canada (Smirnov et al., 2012). Low 18O and 17O 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 18O values in wNO3 from a polluted city (Fang et al., 2011), in pNO3 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, 2009) and of coastal California (Patris et al., 2007), the information from the literature integrated with the interpretation proposed for the Alberta low 18O and 17O values in summer nitrates may reflect
the involvement of air masses that include nitrates from oxidation of NO₂ with light isotopes in plumes. In such cases, while not ruling out a higher contribution from RO₂ oxidation of NO, it is also possible that significant portions of the collected nitrate were formed before the NO₃−O₃ isotopic equilibrium was reached (see Sect. 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 δ¹⁸O and Δ¹⁷O may reflect relative proximity to anthropogenic N emitters in general. Further research work on plume NO₃ to nitrates chemical mechanisms may help to validate this suggestion. In the future, the assumption of an NO₃ isotopic steady state with O₃ should be explored, given recent findings (Michalski et al., 2014), the critical importance of NO₃ isotope characteristics on resulting nitrate isotopic values (Alexander et al., 2009) and the suggestion regarding the evolution of NO₃−NO₃⁻ signals in fresh anthropogenic plumes (present study).

5 Conclusion

The HNO₃, wNO₃ and pNO₃ from anthropogenic sources in central and southern Alberta, simultaneously collected with wind-sector-based conditional sampling systems, produced δ¹⁸O and Δ¹⁷O 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 (HNO₃), having distinct isotopic characteristics relative to the wet and particulate forms, implies that understanding nitrate formation and loss requires the nitrate species to be characterized individually. Particularly NO₃⁻ in these samples generally shows higher δ¹⁸O and Δ¹⁷O values than HNO₃ in the fall–winter period as the heterogeneous N₂O₅ pathway favours the production of pNO₃⁻. In contrast, HNO₃ has higher δ¹⁸O and Δ¹⁷O values during warm periods, which we propose is due to faster dry deposition rates relative to pNO₃⁻ in the event that low-Δ¹⁷O NO₂ is oxidized in the plume. The mechanisms conferring nitrate with relatively low isotopic values, whether oxidation before the NO₃−O₃ 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.

Data availability. All data interpreted and discussed in the article are presented in the Supplement (Tables S1, S2 and S3).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-18-10373-2018-supplement.

Author contributions. MMS contributed scientific leadership and expertise in isotope geochemistry, integrated and interpreted all data, and wrote most of the article. ASC contributed expertise in atmospheric chemistry and isotope geochemistry, participated in all aspects of the interpretation, and greatly helped in the writing of the article. RV was responsible for designing and supervising the air sampling missions. AS was responsible for conducting the air sample preparation and their isotopic analyses and insuring the QA and QC of the produced results.

Competing interests. The authors declare that they have no conflict of interest.

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