



Increased nitrate and decreased δ^{15} N-NO₃⁻ in the Greenland Arctic after 1940 attributed to North American oil burning

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Abstract. Nitrogen oxides $(NO_x = NO + NO_2)$ have an important impact on the atmosphere and biosphere through controls on oxidant concentrations and the formation of nitric acid (e.g. acid rain). Anthropogenic emissions from fossil fuel combustion, land use change, and agriculture have altered the global nitrogen cycle since the beginning of the Industrial Revolution but contributions from specific sources are difficult to quantify, hindering understanding of changes to the natural environment

- and design of effective mitigation strategies. Ice core records reveal changes in the nitrogen cycle over time in connection to climate, atmospheric chemistry, and the biosphere. Here we use a seasonally resolved ice core record of the nitrogen isotopic composition of nitrate (δ^{15} N-NO₃⁻), together with a broad suite of highly resolved (>22 samples y⁻¹) elemental and chemical tracers, to investigate sources of nitrate deposited in central Greenland from 1760 CE to present. A marked negative trend in δ^{15} N-NO₃⁻ since ~1940 CE paralleled a nearly three-fold increase in nitrate concentration. Based on correlated increases in
- 20 tracer concentrations, independent emission estimates of oil burning, and an isotope mixing model, North American oil combustion likely was the primary driver of recent changes in the nitrogen cycle recorded in Greenland.

1 Introduction

Anthropogenic emissions of nitrogen oxides (NO_x = NO + NO₂) have altered the global nitrogen cycle since the 25 Industrial Revolution. The primary sink for NO_x is the formation and deposition of nitrate (HNO₃ or NO₃⁻) via the interaction of NO_x with major oxidants in the troposphere. While the primary pre-industrial sources of NO_x are known, their relative contributions are highly uncertain: biomass burning (0.25–7 Tg N y⁻¹); microbial processes in soils (3.6–18.2 Tg N y⁻¹); and lightning (3–25 Tg N y⁻¹) (Holland et al., 1999). In modern times, models predict that fossil fuel combustion contributes more than 50% of total NO_x emissions globally (i.e., 22.4–26.1 Tg N yr⁻¹), with the rest of the budget including microbial processes

30 in soils (8.9±1.9 Tg N yr⁻¹), biomass burning (5.8±1.8 Tg N yr⁻¹), lightning (2–6 Tg N yr⁻¹), and stratospheric injection (0.1-0.6 Tg N yr⁻¹) (Jaeglé et al., 2005; Levy et al., 1999). Global chemical models often rely on comparison of simulated nitrate concentrations with observations, although these measurements are spatially limited with the largest data sets available in the



U.S. and Europe (Lamarque et al., 2005; Lamarque et al., 2013). However, nitrate concentration alone cannot provide individual constraints on either the variability and transport of NO_x source emissions or the chemistry of NO_x/NO_3^- in the atmosphere. Effective mitigation strategies require a direct way to attribute the impact of NO_x on air quality and acid deposition.

- 5 The nitrogen isotopic composition of nitrate (δ^{15} N-NO₃⁻ (‰) = (R_{sample}/R_{standard} 1) x 1000‰, where R = 15 N/¹⁴N and the standard is N₂ in air) is influenced directly by different NO_x sources and the chemical pathways that convert NO_x to NO₃⁻ (Fibiger et al., 2013; Fibiger et al., 2016; Morin et al., 2008). Concentration and isotopic studies combined may provide a way to quantify the contribution of specific sources of NO_x, though poorly constrained isotopic source signatures make such an approach difficult (Fibiger et al., 2014). For instance, three older studies report δ^{15} N-NO_x from vehicles: +3.4 to +3.9‰
- (Moore, 1977), -13 to -2‰ (Heaton, 1990), and -5 to +10‰ (Ammann et al., 1999); while a more recent study based upon tailpipe collections from 26 vehicles reported isotopic values spanning most of the previously reported ranges (~ -19 to +10‰ (Walters et al., 2015a)). The differences amongst these studies may be due to varying collection methods, varying types of collections (e.g., direct tailpipe vs. roadside emissions), and/or fuel and vehicle technologies (Fibiger et al., 2014; Walters et al., 2015a). For coal combustion, emissions collected in smokestacks show that δ¹⁵N-NO_x varies from 6 to 21‰ (Felix et al., 2015a).
- 15 2012; Heaton, 1990; Walters et al., 2015a), although methods of collection again vary and the most recent study finds that emission control technologies result in the higher end of the range. Lightning produced NO_x should have a δ^{15} N-NO_x near 0‰ and stratospheric NO a δ^{15} N-NO_x near 19‰. Fertilized, tropical soil emissions have very negative a δ^{15} N-NO_x, varying from -20 to -49‰ with degree of microbial processing and substrate- δ^{15} N. No direct measurements of the δ^{15} N-NO_x from biomass burning have been published (see Fibiger et al., 2014 and reference therein).
- 20 Despite the uncertainty in direct quantification of δ^{15} N-NO_x and attribution of NO_x sources, ice core studies might reveal trends or changes in δ^{15} N since different sources of NO_x (and therefore NO₃⁻) have varied significantly in time. Previous work shows a significant decline in δ^{15} N-NO₃⁻ in Summit, Greenland ice since the pre-industrial (Hastings et al., 2009). Additionally, records from lakes across the Northern Hemisphere suggest an isotopically distinct source of δ^{15} N that shifts sedimentary δ^{15} N records in the same direction starting in 1895 CE (Holtgrieve et al., 2011).





Hastings et al. (2009) interpreted the δ^{15} N decline observed in Greenland ice as reflecting a significant change in the sources of nitrate deposition, namely the introduction of anthropogenic emissions of NO_x from fossil fuel combustion. Felix and Elliott (2013) interpreted the Hastings et al. (2009) δ^{15} N-NO₃⁻ record as reflecting a significant increase in NO_x derived from soils amended with fertilizers, primarily since the advent of the Haber-Bosch nitrogen fixation method developed in the

5 early 20th century. Geng et al. (2014) hypothesized that the δ^{15} N-NO₃⁻ decline is instead explained by a change in the acidity of aerosols linked to anthropogenic emissions causing fractionation of δ^{15} N-NO₃⁻, dismissing earlier source-related hypotheses.

For ice core studies, the isotopic impact of post-depositional loss or recycling of nitrate in surface snow prior to burial also must be considered. Several isotopic studies at Summit, Greenland (72.6° N, 38.3° W), however, have shown that nitrate largely is preserved in the surface snow (Fibiger et al., 2013; Fibiger et al., 2016; Hastings et al., 2004; Jarvis et al., 2008), and

10 therefore reflects the original isotopic composition of atmospheric nitrate transported to and deposited at the site (Fibiger et al., 2016).

Here, we take an alternative approach to previous studies and attempt to resolve the conflicting hypotheses. We investigate links between a range of highly resolved elemental and chemical tracers, measured along with the δ^{15} N-NO₃⁻, from a core collected in 2010 at Summit, Greenland (hereafter, the Summit-2010 core). The tracers – representing a range of chemical, elemental, and isotopic sources of fallout – are used in conjunction with δ^{15} N-NO₃⁻ to investigate changes in NO_x sources and NO₃⁻ concentration in Greenland since 1760 CE. Based upon the δ^{15} N-NO₃⁻ measurements we focus on three specific periods: the pre-industrial (1760–1812 CE), the industrialization era (1860–1930 CE), and the modern era (1930–2002 CE). This approach provides constraints on major sources contributing to changes in NO_x and nitrate since 1760 CE and suggests the magnitude and sign of the isotopic signature of NO₃⁻ associated with these NO_x sources.

To further investigate source signatures, we used a mixing model between the four major sources of NO_x: oil burning, coal burning, biomass burning, and soil emissions. Despite large uncertainties in both emissions estimates and isotopic source signatures, this straightforward mixing model shows that large scale emissions trends could plausibly drive the δ^{15} N-NO₃⁻ decline observed in Greenland. Our findings disagree with the hypotheses that the changes in δ^{15} N-NO₃⁻ can be explained solely by (1) increased microbial activity in soils due to fertilizer use or (2) atmospheric processing on acidic aerosols.





2 Methods

2.1 Ice Core Analysis

An 87 m core was collected in 2010 in the dry snow zone of central Greenland near Summit station, using a 4" electromechanical drill and no drilling fluid. The core was measured and weighed onsite, packed in plastic tubing, and shipped

- 5 frozen in insulated boxes to the Desert Research Institute (DRI) in Reno, Nevada. The core was analyzed in July 2011 using a well-established continuous ice core analytical system (McConnell et al., 2007; McConnell and Edwards, 2008). Concentrations of a broad range of more than 30 elements and chemical species including nitrate were measured continuously with an effective sampling resolution of <0.01 m water equivalent. Average snowfall rate (1743 to 2010 CE), determined from the ice core, was ~221 kg m⁻² y⁻¹, resulting in temporal resolution of >22 samples per year. The chemical and
- 10 elemental records were dated using annual-layer counting of several seasonally varying elements and chemical species: water isotopes; hydrogen peroxide; sea salt tracers such as sodium; and continental dust tracers such as aluminum, calcium, and rare earth elements. Annual layer counting was confirmed using fallout from well-known volcanic events (Sigl et al., 2013). Annual cycles were calculated by binning and averaging values occurring within the same month for the time interval of interest. Analyses of ACT11d (66.5° N, 46.3° W; 294.4 m) collected in 2011, and D4 (71.4° N, 44.0° W; 145.5 m) collected in 2003,
- 15 were conducted on the same analytical system and also dated with annual layer counting and volcanic synchronization (Sigl et al., 2013).

2.2 Isotope Analysis

During continuous analysis a fraction collector was used to capture aliquots of the meltwater into pre-cleaned polystyrene vials for subsequent offline measurements of the isotopes of nitrate with depth resolution 0.07 m water equivalent or ~3 samples per year. Vials were kept frozen or refrigerated at all times prior to measurement of δ¹⁵N-NO₃⁻. Isotopic analysis was conducted at Brown University using the denitrifier method (Casciotti et al., 2002; Hastings et al., 2005; Kaiser et al., 2007; Sigman et al., 2001). The denitrifier method uses denitrifying bacteria that lack nitrous oxide reductase to convert dissolved NO₃⁻ to N₂O gas, which is then analyzed on a continuous flow isotope ratio mass spectrometer (ThermoFinnigan 25 Delta V) to determine the isotopic composition. The bacteria used in this study was *Pseudomonas aureofaciens*. The analyte





 N_2O is passed, with a helium carrier gas, through a series of purification (removal of water, CO_2 , and VOCs) and sample collection steps to a mass spectrometer which then measures the ${}^{15}N/{}^{14}N$ and ${}^{18}O/{}^{16}O$ ratios of the sample (based on m/z 44, 45, and 46).

- All samples contained at least 3.1x10⁻⁴ g (5 nmol) of nitrate with the majority containing at least 6.2x10⁻⁴ g (10 nmol).
 On average, there were three replicates measured out of each run of 15 samples. The sample measurements were referenced against internationally recognized standards with assigned δ¹⁵N and δ¹⁸O values as follows: IAEA-N3 (4.7‰) and USGS34 (-1.8‰) for δ¹⁵N (‰ vs. air N₂); IAEA-N3 (25.6‰), USGS34 (-27.9‰), and USGS35 (57.5‰) for δ¹⁸O (‰ vs. VSMOW) (Böhlke et al., 2003). Multiple nitrate standards, with similar concentrations to samples, are run with each set of samples. The sample δ¹⁵N and δ¹⁸O data are both corrected for the blank size (below detection for all runs included in this study) and the
- 10 δ^{18} O data are additionally corrected for exchange with water during the denitrification process (assuming an average sample δ^{18} O of water value of -30‰ vs. VSMOW) (see correction scheme outlined in Kaiser et al., 2007).

We analyzed 504 samples from two subsets of aliquots of the Summit-2010 core for δ^{15} N-NO₃⁻: those corresponding to 1760–1812 CE to characterize the pre-industrial period, and those from 1860–2002 CE to characterize changes from the beginning of the Industrial Revolution to the present. Samples from 1812-1860 CE were not analyzed because of instrument

- 15 time limitations. Replicate measurements demonstrated reproducibility of the record; the pooled standard deviation for 91 replicate δ^{15} N-NO₃⁻ measurements was 0.8‰. In addition, a total of 378 nitrate reference materials were analyzed: 126 each of USGS35, USGS34, and IAEA-N3 with δ^{15} N-NO₃⁻ pooled standard deviations of 0.36‰, 0.42‰, and 0.41‰, respectively. Several samples from the Summit-2010 core were combined to make additional measurements at 25 nmol nitrate for
- Δ^{17} O-NO₃⁻ for 18 sections distributed throughout the core to correct for the contribution of ¹⁴N¹⁴N¹⁷O to the mass 45 signal 20 measured on the mass spectrometer with the denitrifier method (Hastings et al., 2005). Typically, it is assumed that the δ^{17} O and δ^{18} O of a compound will behave mass dependently, such that the δ^{17} O could be assumed from the δ^{18} O signal that is determined from the ratio of masses 46 and 44 (i.e. ¹⁴N¹⁴N¹⁸O/¹⁴N¹⁴N¹⁶O). However, atmospheric nitrate contains an anomalous signature of δ^{17} O and δ^{18} O, quantified as Δ^{17} O = δ^{17} O – 0.52 x δ^{18} O (e.g., Michalski et al., 2003). For these measurements, N₂O generated from the denitrifiers is further reduced to N₂ and O₂ in a gold tube heated to 780 C, with the O₂ subsequently measured at masses 32, 33, and 34 to determine ¹⁷O/¹⁶O and ¹⁸O/¹⁶O for the original sample nitrate (Kaiser et al.,





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2007). Reference materials USGS34 and USGS35 with assigned Δ^{17} O-NO₃⁻ values of -0.292‰ and 21.6‰ (Böhlke et al., 2003), respectively, were used to correct sample data with each run. The average Δ^{17} O (±1 σ) for the 18 samples was 26.2(±2.6)‰, which compares well with the average value of 27.9(±0.9)‰ measured at lower resolution over the time period 1692-1976 CE by Alexander et al. (2004). The average value of 26.2‰ was used to correct the δ^{15} N data (see also Hastings et al., 2005). The average value is appropriate to use as the difference in δ^{15} N between using the lowest measured Δ^{17} O (21‰) and highest (31‰) is smaller than the typical reproducibility for replicate measurements (i.e., <0.5 ‰).

2.3 Isotope Mixing Model

An isotope mixing model was developed using emissions estimates of NO_x and fossil fuels since 1800 CE as well as published estimates of δ^{15} N-NO₃⁻ source signatures. We developed separate emissions scenarios for Canada, the United States (U.S.), and Western Europe using regional NO_x emission datasets. National NO_x emission data for fossil fuel emissions in 1990 CE from the Edgar-Hyde 1.3 model (van Aardenne et al., 2001) were subdivided by the relative proportions of estimated CO₂ emissions from solid (coal) and liquid (oil) fuels (Boden et al., 2016) to get simulated separate NO_x emissions for both coal and oil. We assumed that NO_x emissions scale directly with CO₂ emissions for both types of fuel.

- Agricultural NO_x emissions estimates from the Edgar-Hyde 1.3 model (van Aardenne et al., 2001) were used to scale U.S. fertilizer use (US Department of Commerce, 1975; US Department of Commerce Census 1970-2010, 2010) to get a highresolution estimate of fertilizer-driven soil NO_x emissions. Because no detailed fertilizer consumption records are available for Canada and Western Europe, we substituted the Edgar-Hyde 1.3 agricultural emissions directly between 1990 and 1940 CE without scaling. However, we force the soil emissions to approach zero between 1940 and 1900 CE to have a similar trend
- 20 as the U.S. fertilizer curve, as the strong negative δ^{15} N-NO₃⁻ observed from biogenic soil emissions has only been documented for fertilized soils.

Biomass burning NO_x emissions estimates for North America in 2000 CE (Hoelzemann et al., 2004) were used to scale the high-resolution ammonium (NH₄⁺) record from the Summit-2010 core. NH₄⁺ has been used in previous studies as a forest fire tracer (Fuhrer et al., 1996; Zennaro et al., 2014). We assumed an equal split in North American burning, as the U.S.

25 and Canada have similar landmass area, and identical temporal variability.





Source signatures for δ^{15} N-NO₃⁻ were chosen based on previously reported values. We assigned δ^{15} N-NO_x signatures as follows: -5‰ for oil, +12‰ for coal, -27‰ for soil emissions, and +12‰ for biomass burning (Felix and Elliott, 2013; Hastings et al., 2009; Walters et al., 2015a; Walters et al., 2015b). We assume δ^{15} N-NO₃⁻ recorded in the ice is equivalent to δ^{15} N-NO_x emitted from sources and post-depositional processing is negligible at Summit, Greenland.

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3 Results and Discussion

3.1 Nitrate, δ^{15} N-NO₃⁻, and source tracer variability since 1750

The Summit-2010 record of nitrate concentration (Figure 1a) is similar to previously reported records from Greenland ice cores (Burkhart et al., 2006; Fischer et al., 1998; Mayewski et al., 1990) as well as measurements from two other Greenland cores (Figure 1b) so we interpret it as representative of changes in nitrate concentration and deposition throughout the Greenland Arctic. The mean nitrate concentration in the Summit 2010 core was near 1 micromolar (μM) during the preindustrial, followed by a small increase to approximately 1.5 μM around 1910 CE, a decline to near pre-industrial levels by 1930 CE, and then a pronounced, nearly three-fold increase to more than 2.8 μM between 1940 to 1990CE (i.e., modern era), followed by some decline to present.

- Variations in δ^{15} N-NO₃⁻ (Figure 1c) were substantially different than those in nitrate concentration. The δ^{15} N-NO₃⁻ record is compatible with a previously published, lower resolution (~0.33 samples per year) ice core record also from Summit (Hastings et al., 2009) and a recently published somewhat higher resolution record (Geng et al., 2014) (Figure 5). Overall, δ^{15} N-NO₃⁻ declined from a pre-industrial (1760 to 1812 CE) average of 12.0 (±3.9)‰ (±1 \Box , n=113; Figure 1c dashed line) to a modern average (1930 to 2002 CE) of 3.6 (±5.7)‰ (±1 \Box , n=235). Despite changes in nitrate concentration, there was no
- significant change in δ¹⁵N-NO₃⁻ between the pre-industrial and industrialization era (industrialization era δ¹⁵N-NO₃⁻ average 10.8 [±3.8]‰ [±1□, n=155]). Modern-era δ¹⁵N-NO₃⁻ decreased from about 1940 to 1980 CE and remained below 0‰ from ~1980 through 2002 CE, except for a short-lived anomaly of +18‰ in 1987 CE. The seasonal cycle of δ¹⁵N-NO₃⁻ changed dramatically between the pre-industrial and modern eras (Figure 2a). During the pre-industrial and industrialization eras, δ¹⁵N-NO₃⁻ had a late summer and fall maximum whereas the cycle inverted to a late winter and spring maximum in the modern era, consistent with snowpit measurements at Summit, Greenland (Figure 2a; Hastings et al., 2004).





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The dominant source region for air masses arriving at Summit is North America with smaller, seasonally dependent contributions from Europe and Asia (Kahl et al., 1999). The primary elemental and chemical source tracers presented here are black carbon (BC), excess lead (exPb), and non-sea-salt sulfur (nssS) (Figure 1d-f; Table 1). Secondary tracers include ammonium (NH₄⁺), cerium (Ce), and thallium (Tl). Based upon previous studies the rock-forming element Ce was used as an indicator of continental dust (McConnell and Edwards, 2008), sea-salt sodium (ssNa) of sea spray (DeAngelis et al., 1997), NH₄⁺ as a biomass burning indicator (Fuhrer et al., 1996; Zennaro et al., 2014), and Tl for continental dust and coal (McConnell and Edwards, 2008). Previous work shows that during the pre-industrial era, BC at Summit derived almost entirely from biomass burning emissions, exPb from dust and forest fires, and nssS from marine biogenic emissions and volcanism

(McConnell et al., 2007). In the industrialization era, emissions of BC, lead, and sulfur from inefficient fossil fuel (primarily

- 10 coal) combustion overwhelmed background emissions (McConnell et al., 2007; McConnell and Edwards, 2008). During the modern era, industrial BC emissions were much lower as a result of more efficient coal combustion (Bond et al., 2004), but lead and sulfur emissions significantly increased from combustion of liquid fossil fuels (gasoline and bunker fuels). The Greenland ice core records reflect these emissions changes as well as implementation of the U.S. Clean Air Act and similar legislation in other countries that greatly reduced industrial lead and nssS emissions starting in the early 1970s (McConnell et
- 15 al., 2002; McConnell and Edwards, 2008).

We compared the δ^{15} N-NO₃⁻ and nitrate records with long-term and seasonal changes in tracer concentrations to further investigate likely sources of nitrogen emissions impacting the Greenland Arctic since 1760 CE (Table 1, Figures 1-2). During the pre-industrial, seasonal cycles in nitrate and δ^{15} N-NO₃⁻ were highest in late summer into fall, coincident with an increase in BC (Figure 2). Correlations were highly significant only for nitrate and the biomass burning tracers BC and NH₄⁺

20 (Table 1), suggesting biomass burning as the primary source of nitrate during this period. δ^{15} N-NO₃⁻ was positively correlated with BC and NH₄⁺, and negatively correlated with continental dust tracers (exPb, Ce, Tl), which peaked in spring (Figure 2, Table 1). The positive and significant correlation with biomass burning tracers and a mean δ^{15} N-NO₃⁻ of 12‰ during this time, indicate that biomass burning emissions must contribute to a significantly positive signature for δ^{15} N-NO₃⁻.

Seasonal patterns began to evolve during the industrialization era (Figure 2), indicating substantially different sources of nitrate and industrial pollutants compared with the pre-industrial. Late spring and late summer nitrate concentrations were





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higher (Figure 2b), paralleling increases in BC and nssS linked to coal burning (Figure 2c,e) (McConnell et al., 2007; McConnell and Edwards, 2008); this finding is confirmed in the Summit-2010 record by large increases in BC during the industrialization era (Figure 1d, 2c) and high correlations (Table 1) between BC and industrial pollutant tracers (nssS, exPb, TI). The highly significant and positive correlations between nitrate and biomass burning (BC, NH₄⁺) and industrial pollutant tracers suggest a mixture of the two sources for nitrate, but the lack of correlation between δ^{15} N-NO₃⁻ and source tracers or nitrate concentration indicates that no single source of nitrate dominated during the industrialization period. Moreover, the absence of any significant trends in δ^{15} N-NO₃⁻ despite large increases in coal-burning tracers during this era indicates that the δ^{15} N-NO₃⁻ signatures of coal burning and biomass burning were similar. The estimated δ^{15} N-NO_x of coal burning, prior to the implementation of scrubbing technologies is ~12‰ (Felix et al., 2012), consistent with the 12‰ measured in the ice core

10 during the pre-industrial when nitrogen emissions were dominated by biomass burning.

During the modern era, relationships between δ^{15} N-NO₃⁻, nitrate concentration, and source tracers indicate different sources of nitrate compared to earlier eras. The seasonal cycle of δ^{15} N-NO₃⁻ closely paralleled seasonal cycles in the industrial, oil-combustion-dominated tracers (exPb, nssS) and was the inverse of seasonality observed during the pre-industrial. The modern seasonal cycle observed in the Summit-2010 core is consistent with modern snowpit observations of δ^{15} N-NO₃⁻ at

- Summit (Figure 2a, black dots; Hastings et al., 2004). In the modern, the lowest values occurred in fall and early winter and the highest values in late winter and spring (Figure 2a). Variations in nitrate concentration were significantly and positively correlated (Table 1) with the oil combustion tracers, and significantly and negatively correlated with δ^{15} N-NO₃⁻. These patterns support the hypothesis that the dominant source of nitrate during the modern era had a negative isotope signature very different from the positive δ^{15} N-NO₃⁻ signatures of earlier eras dominated by coal and biomass burning emissions. This interpretation
- 20 requires a negative δ^{15} N-NO₃⁻ for modern era emissions on the order of -10‰, a value consistent with the range of estimates for NO_x produced from oil burning (Heaton, 1990; Walters et al., 2015a; Walters et al., 2015b).

Estimates of historical emissions from U.S. fossil fuel combustion (Boden et al., 2016) are consistent with our ice core measurements (Figure 3). The rapid increase in estimated coal-combustion emissions that began in 1860 CE and initially peaked in ~1920 CE closely paralleled substantial increases in coal-combustion tracers and small increases in nitrate, although no identifiable changes in δ^{15} N-NO₃⁻ resulted. After 1930 CE, increases in estimated oil-burning emissions in North America





in the modern era closely paralleled increases in the oil-burning tracers and rapid declines in δ^{15} N-NO₃⁻ (r=-0.78, p<0.01; Figure 3).

3.2 Previous research

- 5 It has been proposed that soil emissions associated with fertilizer use were the primary driver of the negative trend in δ¹⁵N-NO₃⁻ (Felix and Elliott, 2013), largely because this source has an apparent δ¹⁵N-NO_x signature of -20‰ to -49‰ (Li and Wang, 2008) and U.S. fertilizer consumption has a strong negative correlation to ice core δ¹⁵N-NO₃⁻ from 1930 to 2001 (r=-0.78, p<0.05; Figure 3). Soil emissions, however, cannot explain the much larger decline in wintertime δ¹⁵N-NO₃⁻ compared to late spring and summer (Figure 2a) since the pre-industrial. Additionally, North American NO_x emissions from agricultural soil emissions are estimated to be on average less than 10% of those from fossil fuel combustion during the 20th century (van
- Aardenne et al., 2001) making it highly unlikely that soil emissions were the primary driver of δ^{15} N-NO₃⁻ change in Greenland as suggested by Felix and Elliot (2013).

Another study concluded that atmospheric chemical processes, not source signatures, were responsible for the observed decrease in δ^{15} N-NO₃⁻. Geng et al. (2014) suggested that the ice core record of δ^{15} N-NO₃⁻ was a result of fractionation

- 15 related to the partitioning between gas-phase (HNO_{3(g)}) and particulate nitrate (p-NO₃⁻), modulated over time by changes in atmospheric acidity. The proposed mechanism was that acidity drove NO₃⁻ away from the particulate phase, resulting in isotopically depleted ¹⁵N in HNO_{3(g)} and preferential transport of this HNO_{3(g)} to Greenland. To demonstrate this mechanism, Geng et al. (2014) determined the portion of HNO_{3(g)} using acidity concentrations estimated by charge balance from ice core measurements of nssS and NH₄⁺ and found that HNO_{3(g)} began to increase in 1850 CE, 50 years earlier than increases in NO₃⁻
- concentrations observed in Greenland ice cores. Our Summit-2010 ice core records included direct measurements of acidity (Pasteris et al., 2012) which we used to calculate HNO_{3(g)} via the Geng et al. formulation ([HNO₃] = [H⁺] (nss[SO4²⁻] [NH4⁺])). Using these direct acidity measurements resulted in nearly identical total NO3⁻ and HNO3(g) values for the entire 250 year period. In other words, using direct measurements rather than estimates of acidity in the calculations showed no clear change in the partitioning of NO3⁻ during the past 250 years, thereby casting doubt on the acidity-driven fractionation
 mechanism proposed by Geng et al. (2014) to explain the observed changes in δ¹⁵N-NO3⁻. We note that estimating acidity





charge balance necessarily includes cumulative error associated with the separate measurements of the individual ions as well as ignores the contributions of organic acids. Furthermore, Geng et al. (2014) assumed an annual average temperature in the northern mid-latitudes of 289 K (25 C), which, if decreased to a more realistic temperature, would further contribute to a significantly different predicted change in δ^{15} N-NO₃⁻ than observed. Finally, Geng et al. dismissed a relationship between δ^{15} N-NO₃⁻ and NO_x sources based upon the incorrect assumption that anthropogenic sources of NO_x carry only positive source signatures (see Fibiger et al. (2014) introduction and recent better characterized combustion-engine emissions by (Walters et al., 2015a; Walters et al., 2015b)). Given the wide variation of more than 40‰ in measured δ^{15} N-NO₃⁻ source signatures and significant increase in overall NO_x emissions over the past 100 years, it is unrealistic to dismiss all source contributions to the δ^{15} N-NO₃⁻ signal.

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3.3 Isotope mixing model using NO_x emissions estimates

The observed δ¹⁵N-NO₃⁻ ice core record can be simulated using NO_x emissions based on historical estimates of fossil fuel combustion, fertilizer use, and biomass burning tracers in combination with plausible δ¹⁵N-NO₃⁻ signatures for NO_x from oil burning (-5‰), coal burning (+12‰), biomass burning (+12‰), and soil emissions (-27‰). Using a four-component isotope mixing model (Figure 5) and assuming no source-dependent preferential transport from the source regions to Summit, we simulated δ¹⁵N-NO₃⁻ from Canadian, U.S., and European-based NO_x emissions which are the primary air mass source regions for Summit (Kahl et al., 1999). Results show that as coal-emitted NO_x increased between 1850 and 1900 CE, the δ¹⁵N-NO₃⁻ remained close to pre-industrial levels of ~12‰. After 1900 CE, the dominant source of NO_x transitioned to oil in all regions, coincident with a rapid decrease in δ¹⁵N-NO₃⁻. Soil emissions from fertilized agriculture also increased during this

20 time.

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The observed overall decrease of δ^{15} N-NO₃⁻ measured in the Summit-2010 ice core was ~12‰. The Canadian, U.S., and western Europe emissions scenarios resulted in isotopic decreases between 1850 and 1975 CE of 11‰, 12‰, and 10‰, respectively. With soil emissions excluded from the model, decreases in δ^{15} N-NO₃⁻ only declined to 9‰ in the Canada and Western Europe simulations and 11‰ in the U.S. simulations, indicating that oil emissions alone likely are driving most of the observed change.





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Without source-dependent preferential transport, overall changes in NO_x emissions must be reflected proportionally in nitrate concentrations changes in the ice core record. Although nitrate deposited at Summit during the past 250 years likely came from a number of source regions (Kahl et al., 1999), the relative increase of NO_x emissions in the Canada simulation was a factor of 4 to 5 (Figure 5c) which is comparable to the relative increase of 2 to 3 in the ice core record. This is in marked contrast to the relative increases in NO_x emissions in the U.S. and Western Europe simulations which were ~40 and ~50,

respectively (Figure 5f,i).

Over the past 70 years, the four-component model is surprisingly effective at capturing the magnitude and overall variability in the ice core record, including some rapid variability over the past 30 years. However, the δ^{15} N-NO₃⁻ decline led the observed decrease in ice by 20 and 10 years in the U.S. and Canada simulations, and lagged by 5 years in Western Europe

10 simulation. These discrepancies could be the result of inaccuracies in estimated NO_x emissions, changing δ^{15} N-NO₃⁻ source signatures through time, or sources not considered in this study (e.g. lightning, natural gas).

The large error inherent to the NO_x emissions estimates and δ^{15} N-NO₃⁻ source signatures precludes the use of nitrogen isotopes to directly constrain or quantify source emissions at this time. It is likely that some fractionation during transport, such as that described by Geng et al. (2014), plays some role in determining δ^{15} N-NO₃⁻ relative to δ^{15} N-NO_x. However, results

of the four-component mixing model demonstrate that changes in source emissions alone can account for the observed changes in ice core δ^{15} N-NO₃⁻ during the past 250 years, suggesting that fractionations associated with atmospheric chemistry were relatively small.

4 Conclusions

20 The δ^{15} N-NO₃⁻ deposited to Greenland is consistent with changes in the sources of atmospheric nitrate during the last 250 years. Detailed records of a suite of source tracers along with the concentration and δ^{15} N of nitrate indicate substantial changes in anthropogenic NO_x sources and imply different δ^{15} N-NO₃⁻ signatures for those sources. The evolving seasonal variability in δ^{15} N-NO₃⁻ along with concentrations of nitrate and source tracers, as well as isotopic mixing model simulations, suggest a negative δ^{15} N-NO₃⁻ deposition signal associated with NO_x from oil combustion compared to positive signatures 25 associated with biomass and coal burning. These findings which are based on more comprehensive and detailed ice core





measurements cast doubt on two recently proposed hypotheses to explain the significant and rapid changes found in the ice core δ^{15} N-NO₃⁻; specifically (1) fertilized soil emissions, and (2) acidity-driven production of HNO_{3(g)} during atmospheric transport. The rapid decrease in δ^{15} N-NO₃⁻ concurrent with increasing nitrate and oil-burning tracer concentrations, along with oil combustion emission estimates and tracer correlation results, suggest that oil burning was the primary source of the

5 widespread, 2.8-fold increases in nitrate in Greenland during the 20th century and likely explains similar declines in δ^{15} N observed in lake sediments across the Northern Hemisphere during the modern era (Holtgrieve et al., 2011).

5 Author contribution

NC and JM were responsible for measurements at DRI and isotopic sample collection. NC and MH were responsible for isotopic measurements at Brown University. NC, JM, and MH all contributed to interpretation and writing.

6 Data Availability

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Data from this paper is available at The Advanced Cooperative Arctic Data and Information Service (ACADIS, www.aoncadis.org) at https://www.aoncadis.org/project/collaborative_research_the_impact

15 _of_bromine_chemistry_on_the_isotopic_composition_of_nitrate_at_summit_greenland.html, Dataset: Subannual isotopic composition of nitrate at Summit, Greenland 1760-2002.

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Figure 1: Nitrate and source tracer measurements in the Summit-2010 ice core. (a) Nitrate concentration, (b) nitrate anomaly from average of three Greenland cores (Summit-2010, ACT11d, and D4) compare to pre-industrial, (c) δ^{15} N-NO₃⁻ with dashed line indicating pre-industrial average (isotope data missing from 1812-1860 CE, see Sect. 2.2), (d) black carbon, (e) non-sea salt sulfur, and (f) excess lead.







Figure 2: Seasonality of tracers in the Summit-2010 core. (a) δ^{15} N-NO₃⁻, black dots are snowpit measurements in 2001 and 2002 CE at Summit, Greenland from Hastings et al. (2004), (b) nitrate, and (c-e) source tracers since 1760 CE.







Figure 3: δ^{15} N-NO₃⁻ (21 point running average in black; note reversed y-axis) compared to estimated CO₂ emissions from liquid (oil) and solid (coal) fossil fuels (Boden et al., 2016) as well as U.S. fertilizer consumption since 1890 (U.S. Department of Commerce (1975); U.S. Department of Commerce Census (2010)).



Figure 4: Comparison of NO_3^- and calculated $HNO_{3(g)}$ from (a) Summit-2010 and (b) Geng et al. (2014). Summit-2010 record does not indicate any difference from 1810 to 1860 CE (shaded in gray) as reported by Geng et al. (2014).

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Figure 5: Mixing model results for separate emissions scenarios for Canada (top) and U.S. (bottom). (a,d,g) Model results in red plotted with three existing δ^{15} N-NO₃⁻ records from Summit. (b,e,h) Simulated national NO_x emissions by source. (c,f,i) Comparison of increases in simulated NO_x emissions and measured NO₃⁻ concentrations relative to pre-industrial values (note difference in y-axes).

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	NO ₃ -	BC	NH_4^+	nssS	exPb	Tl	Ce
$\delta^{15}N\text{-}NO_3\text{-}$	0.25	0.18	0.20	-0.08	-0.27	-0.28	-0.32
NO ₃ -		0.68	0.57	0.12	0.04	0.13	0.06
BC			0.74	0.05	0.02	0.18	0.04
$\mathrm{NH_4^+}$				-0.05	-0.05	-0.01	-0.02
nssS					0.15	0.50	0.21
exPb						0.43	0.48
Tl							0.60
Industrialization: 1860-1930 (n=175)							
	NO3 ⁻	BC	$\mathrm{NH_4^+}$	nssS	exPb	Tl	Ce
$\delta^{15}N\text{-}NO_3\text{-}$	-0.01	-0.08	0.04	-0.03	-0.05	-0.07	-0.07
NO ₃ -		0.59	0.36	0.53	0.39	0.61	0.39
BC			0.29	0.60	0.59	0.76	0.34
$\mathrm{NH_4^+}$				-0.03	0.01	0.21	-0.03
nssS					0.57	0.67	0.52
exPb						0.77	0.47
Tl							0.54
Modern: 1930-2002 (n=235)							
	NO3 ⁻	BC	$\mathrm{NH_4^+}$	$nssS^*$	exPb [†]	Tl	Ce
$\delta^{15}N\text{-}NO_3\text{-}$	-0.39	0.30	-0.19	-0.29	-0.27	0.25	0.18
NO ₃ -		-0.25	0.47	0.52	0.57	-0.13	0.00
BC			0.05	0.17	-0.03	0.64	0.40
$\mathrm{NH_{4}^{+}}$				0.07	-0.04	-0.05	-0.02
nssS*					0.81	0.52	0.41
$exPb^{\dagger}$						0.53	0.40
Tl							0.72

 $\label{eq:correlations to rssS span from 1930-1985 as environmental legislation caused nesS to return to near pre-industrial levels by 1985 \\ 'Correlations to exPb span from 1930-1975 as environmental legislation caused exPb to return to near pre-industrial levels by 1975 \\ Bold indicates p < 0.05, bold italic indicates p < 0.01$

Table 1: Correlations between source tracers and $\delta^{15}\text{N-NO}_3^-$