Anonymous Referee #1

We thank the reviewer for his/her time and attention to detail regarding our manuscript. These suggestions have significantly improved our manuscript, especially with a more robust approach to whether the isotopic nitrate record can be matched with our current understanding of NO_x isotopic signatures.

Chellman et al report new measurements of d15N-NO3-, in addition to measurements of the concentrations of nitrate and other impurities, from a Greenland ice core over the periods 1760 – 1812 CE and 1860 – 2002 CE. This is the 4th paper interpreting the observed decrease in d15N-NO3- beginning around 1940, with each paper giving different reasons for the observed trend, usually benefitting from a higher temporal resolution and additional complementary measurements. Chellman et al interpret the observed trend as stemming from increases in oil burning sources of NOx relative to biomass burning sources of NOx, which they say is the dominant natural source of NOx in the preindustrial based on a similar seasonality. They discount a previous interpretation that the observed trends were due to increases in Agricultural soil NOx emissions [Felix and Elliott, 2013] (which were also discounted by Geng et al. [2014]), and the interpretation that the observed trends in d15N-NO3- are driven by changes in atmospheric acidity and its impacts on gas-particle partitioning of nitrate [Geng et al., 2014]. I am unconvinced by this new interpretation and also by their discounting of the explanation given in Geng et al. [2014]. The biggest reason I am unconvinced by their interpretation is that it relies on the assumption that the biomass burning signature of NOx is +12‰. To get this value, they must assume 1) that biomass burning is the only source of NOx in the preindustrial, and 2) that there is zero postdepositional loss. Most certainly neither of these assumptions are completely true.

1) Perhaps biomass burning is the dominant source, but lighting and soil microbes certainly contribute something, they are not zero. Since lightning and especially soil microbes supply a relatively light source of NOx and nitrate, biomass burning would have to be higher than 12‰ if postdepositional processing is negligible. However, even if the authors did assume a higher value than 12‰ for the biomass burning source, they could probably still get the same answer because there is enough wiggle room in their assumptions of the isotopic composition of other sources. I note that the biomass burning source of NOx is expected to be negative, as the nitrogen combusted and emitted to the atmosphere as NOx is thought to come from the biomass itself as the low combustion temperature is not able to convert atmospheric N2 to NOx (thermally formed NOx) [Salzmann and Nussbaumer, 2001], and N-nutrition from nitrification possesses negative d15N-NO3- values [Kendall et al., 2007].

We appreciate the reviewers concerns. We have modified the isotope mixing model exercise significantly (see below), including suggestions from both Reviewer #1 and #2. The purpose of the mixing model exercise is to test whether using isotopic source signatures, to the best of our current knowledge, fits with the observed record. Based on both reviewers' suggestions, we now account for uncertainty in the isotopic source signatures and have also tested the sensitivity of the predicted $\delta^{15}N$ to different emissions estimates (i.e. different emission inventories). We also now clearly state that the 12‰ pre-industrial value is assumed to represent the combination of pre-industrial sources (biomass burning, soil emissions, and lightning), not solely biomass burning emissions alone.

While we cannot provide an evidence-based argument for a very positive isotopic signature associated with biomass burning produced NO_x in the mid-latitudes during the pre-industrial, we certainly have enough anecdotal evidence to proceed with the mixing model approach. It is not clear from the reviewer's assertion why the biomass burning signature must be negative. As the reviewer correctly states, most biomass fires do not burn hot enough to produce thermal NOx, however the isotopic composition of thermally produced NOx has been shown to be negative [Snape et al., 2003; Walters et al., 2015, and reference therein]. As an additional note, Hastings' group has a paper recently revised (based on reviews) at Env. Sci. & Tech. (Fibiger and Hastings, in revision), data from which has been presented at several conferences (e.g. AGU, GRC, ACS), which directly captures and measures the δ^{15}N–NOx associated with laboratory burns of biomass and find a range from -7 to +12 ‰. This range represents a variety of biomasses from spruce and pine to grasses and hay. While based upon laboratory burns alone, this work shows that the strongest control on the δ^{15}N–NO_x is the δ^{15}N of the biomass itself. We will cite this work in our revised manuscript, if it is in press in time. However, given all of the above, there is no reason that an assumption of a positive signature associated with the combination of pre-industrial sources can be ruled out.

2) Of larger concern to me though is the assumption that there is zero postdepositional loss. The justification for this is given by referencing their own prior work on isotope measurements, but other work suggests otherwise. Their paper that specifically addressed this issue [Fibiger et al., 2013] relied on oxygen isotopes of nitrate which is sensitive to postdepositional recycling, but not sensitive to postdepositional loss. Ice-core d15N-NO3-is the opposite: it is very sensitive to postdepositional loss (fractionation factor on the order of -50‰ [Bernahu et al., 2014]), but not sensitive to postdepositional recycling. Observations of NOx fluxes from the snowpack in the summertime at Summit, Greenland are on the order of 2.5 x 108 mole cm-2 s-1 [Honrath et al., 2002]. Dibb et al. [2007] estimated a 5-25% loss of snow nitrate from photolysis. Geng et al. [2015] calculated that a 16% loss of snow nitrate from photolysis, which is in the middle of the range of estimates by Dibb et al. [2007], would lead to an enrichment of 12‰˙A value of 12‰ is heavy compared to observations of nitrate aerosol in the present day atmosphere (-6 to 6‰ with unpolluted regions lighter (-6 to -2‰ than polluted areas (0 to +6‰ [Morin et al., 2009]), again suggesting some postdepositional loss leading to this relatively heavy value of 12‰ and it doesn't take much postdepositional loss to lead to enriched values remaining in the snow because of the large fractionation factor.

In sum, I am definitely not convinced that the biomass burning signature of NOx is anywhere near 12‰ Without this dominant and isotopically heavy source in the preindustrial, the authors would not be able to reproduce the observed trends in d15N-NO3- using the NOx emissions inventories.

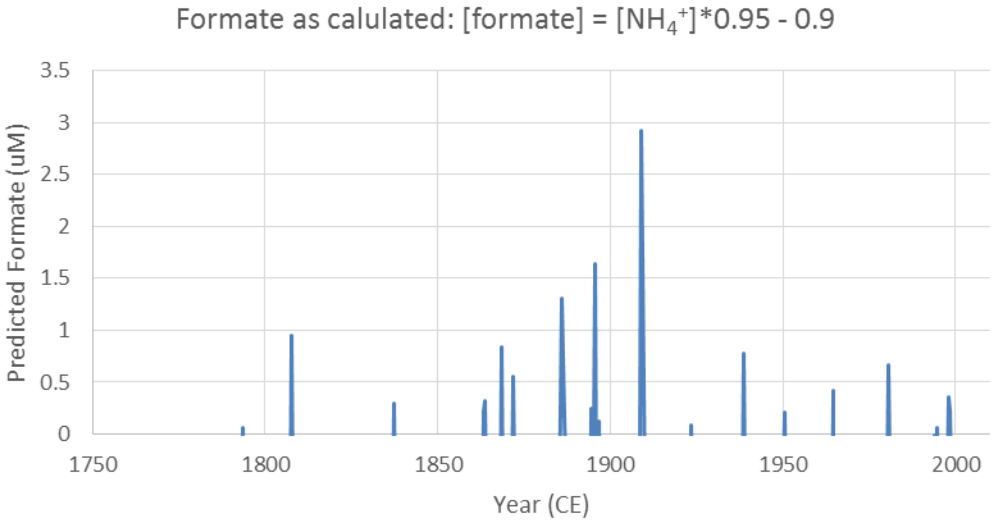
Fibiger et al. 2013 and 2016 address the issues raised here related to post-depositional processing. The flux of NO_x inferred by Honrath et al. (2002), and the fluxes determined by others in subsequent studies, can be explained in the context of very little loss of nitrate from the snow. From Fibiger et al. (J*GR-Atmospheres*, 2016):

> "Based on modeling of observed concentrations of a suite of gases at Summit, only a 2% loss of NO_3^- from the snow, prior to burial below the photic zone, is required to explain the NO_x concentrations above the snowpack in summertime [*Thomas et al.*, 2011]."

There is simply no good evidence to support that there is post-depositional processing that significantly modifies the isotopes of nitrate in surface snow at Summit, Greenland and therefore this assumption is incorrect and should not be encouraged in the literature. Early work by Hastings et al. (J*GR-Atmospheres*, 2003) showed no significant change in the δ^{15}N and δ^{18}O of nitrate in surface/near surface snow between March and August; Fibiger et al. (2013) focuses on Δ^{17}O and cannot explain the relationship between Δ^{17}O and δ^{18}O for nitrate in surface snow based upon post-depositional loss or recycling; Fibiger et al. (2016) find isotopic differences in snow nitrate and atmospheric (mist-chamber collected) nitrate that could be driven by nitrate formed from photolytically derived NO_x. However, no relation is found for surface snow nitrate (δ^{15}N, δ^{18}O, and Δ^{17}O) and local gas phase chemistry or atmospheric nitrate isotopic composition, suggesting that any photolytically derived NO_x that is recycled back to the surface must represent a very small pool of the total nitrate found in near-surface snow. There is clear evidence that the isotopic composition of nitrate at Summit represents an atmospheric signal and not significant post-depositional processing or recycling. It is a sound assumption to make here that post-depositional loss or recycling is not important in determining the isotopic composition of nitrate over the last ~300 years.

Secondly, I thought their discussion of the interpretation by Geng et al. [2014] was not very thorough. They discount the Geng et al. [2014] hypothesis because their same calculations of HNO3 using their measured acidity (which I agree is better than the calculated acidity in Geng et al. [2014]) show significant differences in the time period 1810 – 1860 CE, and it appears the fraction of HNO3 in total nitrate does not differ significantly between the preindustrial and modern periods. However, it has to be noted that the Geng et al. [2014] estimated the concentration of H+ without involving organic acids (e.g., MSA, formic acid), while the measured H+ takes into account the organic acids. So in the calculation of HNO3, the following equation should be used instead of the one currently in the manuscript: [HNO3] = [H+]m - ([nss-SO42-]-[NH4+]) - [Org.] Given the relatively small to no trend in organic acid concentrations in Greenland ice cores throughout the period of measurement (1776-1982) [Legrand and De Angelis, 1996], [Org.] should be relatively constant. If this constant term [Org.] is included, this will reduce the authors' calculated fraction of HNO3 in total nitrate in the preindustrial period more than in the modern period, because the absolute HNO3 concentrations are much higher in the modern period.

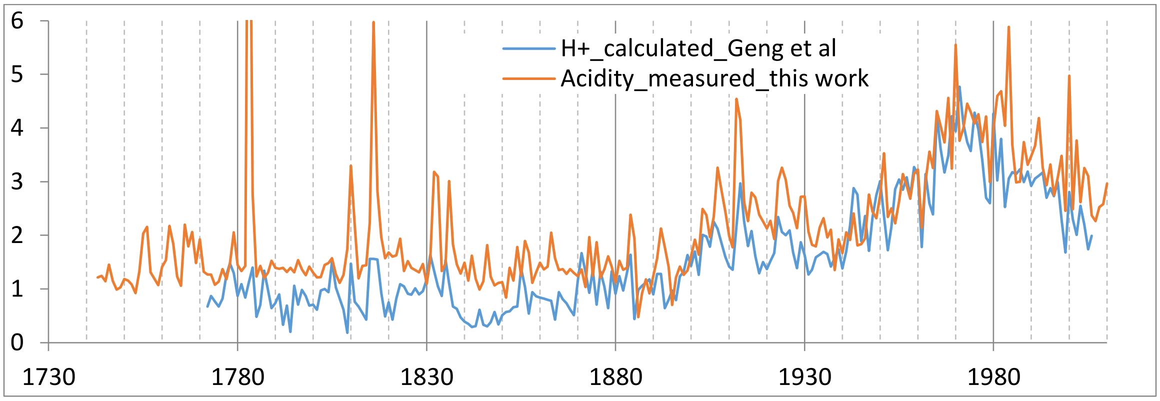
We appreciate the reviewer's comments and can certainly include more comparison with the Geng et al. work in the revised manuscript, as discussed below. Our primary discount of the Geng et al. work in our original manuscript was that it was not repeatable. We do note in the original manuscript that the calculated acidity by Geng et al. does not account for the presence of organic acids, but it could be more clear that our measured acidity does account for this. We note that the equation used in the manuscript was specifically to compare with Geng et al.'s calculation and that replacing the calculated acidity with measured acidity changes the computed fraction of HNO$_3$. Though we do not have complete organic acid data for the Summit-2010 core, the majority of organic acids occur during biomass burning events as formate (Pasteris et al., 2012), which can be estimated from the ammonium record by the equation [formate] = [NH$_4^+$]*0.95 – 0.9 (Legrand and De Angelis, 1996). When applying this approach to the Summit-2010 core, most of the record is below the threshold (i.e. negative; see figure below), with formate contributions only occurring at a few isolated events throughout the record. This supports that the organic acid contribution is minimal to the overall acidity of the core and would not significantly influence our calculations.



In addition, in this time-period of 1810-1860 where they show differences between the fraction of HNO3/NO3- between their calculations and that of Geng et al. [2014], the authors did not measure d15N-NO3-, and this is not the time period when the trends in d15N-NO3-are observed. The new results presented here and that from Geng et al. [2014] look quite similar in Figure 4 during the time period of the decreasing d15N-NO3- on which the manuscript focuses. If the authors measured acidity, they should be able to do a much more thorough analysis then what is shown here. Why isn't acidity shown in Figure 1? Why did they not examine the relationship between measured acidity and d15N-NO3- in Table 1? The lack of such a comparison is suspect.

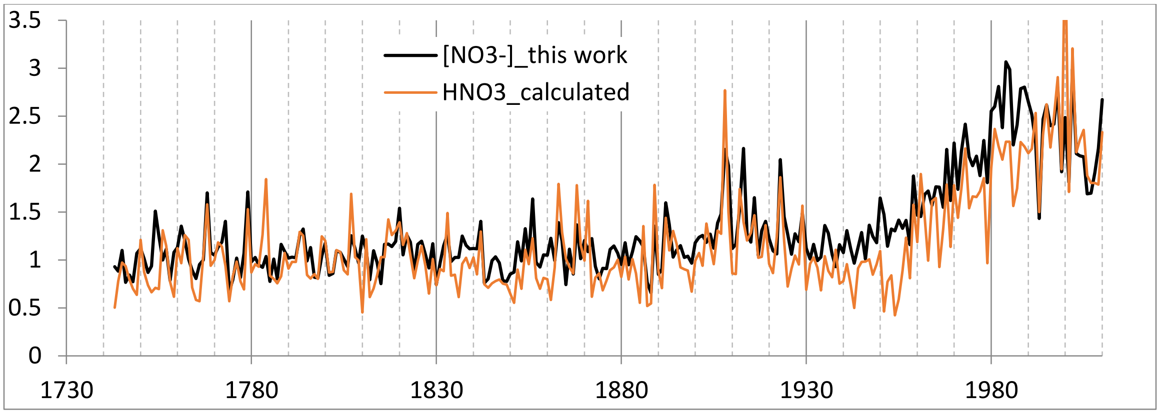
We did not all intend to make the reviewer suspicious and will include much of the following in the manuscript. The conclusions of the Geng et al. work are based on the following:
1) $\delta^{15}N$ of NO_x sources cannot explain the changes in the ice core record because anthropogenic sources are largely positive. This was not a fair assumption even with the variable literature values at the time, but is proven false with recent, better constrained, observations of fossil fuel combustion $\delta^{15}N$-NO_x.

2) The fraction of total nitrate present as HNO_3 (vs particulate NO_3^-) has significantly changed over time such that the HNO_3 is much lighter in the more recent past because the change in acidity of aerosols drives HNO_3 off of aerosols and this is associated with a fractionation that results in much lower $\delta^{15}N$-HNO_3. The calculation of the fraction of HNO_3 in Geng et al. is based upon calculated acidity. Measured acidity is higher through almost the entire record (see figure below), particularly before 1870.



Note that the very high values seen in ~1781 and 1815, are due to the Laki and Tambora volcanic eruptions which result in significant deposition of SO_4^{2-} (and therefore increased acidity following those events). The Geng et al. record deletes these events and instead interpolates between the years before and after the event.

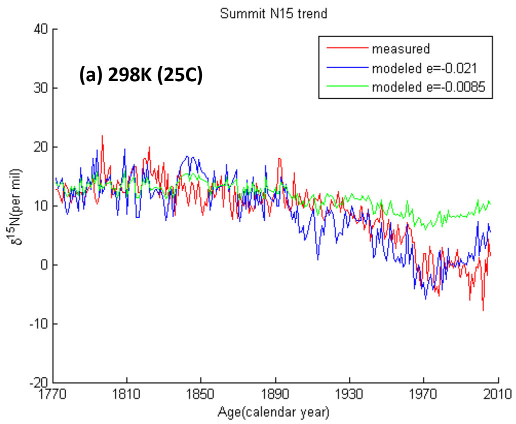
Thus, the change predicted by the Geng et al. calculated H^+ over the time period 1850-1970 is much greater than found in the directly measured acidity. To match the change in $\delta^{15}N$ over the period 1850-1970, Geng et al. need a significant change in the fraction of $HNO_3(g)$ over this period, which is not found if using the measured acidity. Our HNO_3 (calculated with measured acidity) record mirrors the measured core NO_3^- for most of the record (see figure below), meaning a significant switch or increase in deposition of $HNO_3(g)$ relative to $NO_3^-(p)$ based upon the acidity calculations is not observed in our core. The difference between measured NO_3^- and the calculated HNO_3 in Geng et al. (2014) is the basis of the acidity driven isotopic change hypothesis.

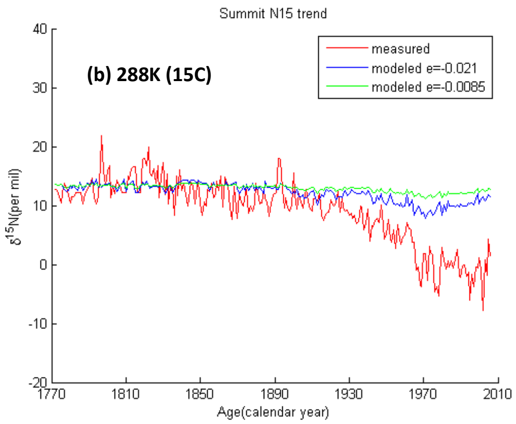


Nitrate concentrations measured in the Summit-2010 ice core and HNO_3 *calculated for the Summit-2010 via the Geng et al. formulation.*

3) The best-fit model for $\delta^{15}N$-NO_3^- presented in Geng et al. suggests a change in $\delta^{15}N$ of -15.6‰ since the pre-industrial compared to the observed change in $\delta^{15}N$ (in their record) of -14.4‰ (the $\delta^{15}N$ record found in our 2010 core is similar overall to the observed $\delta^{15}N$ in Geng et al). The model estimate for the change in $\delta^{15}N$ would be significantly lower if using measured acidity.

4) The Geng et al. modeled estimated change in $\delta^{15}N$ assumes an annual average temperature in the northern mid-latitudes (i.e. source region) of 298 K (25 C). If a more realistic temperature is used (e.g. 15 C) the simple Henry's law formulation leads to a significant under-prediction of the observed change in $\delta^{15}N$. When we ran the Matlab code for the Rayleigh model as published by Geng et al. at 288 K (15 C) (see figures below), there was barely any change in $\delta^{15}N$ from the pre-Industrial background. Also, we do not find correlations between $\delta^{15}N$ and measured acidity during the industrial era that are nearly as strong as the correlations published by Geng et al. (see table below).





	Time Period		Acidity (Geng et al.)		Time Period	Acidity (this study)	
			r	p		r	p
$\delta^{15}N$	1772-2006	Annual	-0.78	<0.01	1772-2002	-0.64	<0.01
		High Res				-0.55	<0.01
$\delta^{15}N$	1850-1970	Annual	-0.72	<0.01	1860-1970	-0.48	<0.01
		High Res				-0.29	<0.01
$\delta^{15}N$	1850-1950	Annual	-0.42	<0.01	1860-1950	-0.03	0.79
		High Res				-0.01	0.97

5) To explain the higher $\delta^{15}N$ values in the pre-industrial Geng et al. invoke "post-depositional processing" (though as pointed out by the reviewer, only post-depositional loss can lead to enrichment in ^{15}N in the snow). It is also suggested that increased acidity in the modern era should enhance the loss of NO_3^- from the snow leading to changes in $\delta^{15}N$ today, however, as discussed above there is sufficient evidence to conclude that post-depositional loss and post-depositional recycling of nitrate are not important processes in modern snow at Summit.

Therefore, based upon all of the above, we suggest that the change in $\delta^{15}N$ observed in Greenland ice cannot be explained by a significant change in acidity of aerosols.

Other issues:
The introduction states 6 NOx sources: vehicles, coal, lightning, stratospheric, soil and biomass burning, providing a range of d15N-NO3- signatures for all but the latter. Their mixing model contains 4 sources: oil, coal, biomass burning, and soil. Is oil the same as vehicle? If so the same terminology should be used throughout the paper, as I was never quite sure if it's the same thing. If not, then the range of d15N-NO3- for oil should be discussed along with the other sources, and vehicles should be considered in the analysis. Some justification should be given as to why they ignore the lightning and stratospheric source. I'm particularly perplexed as to why the ignore lightning, but perhaps it's because they assume no trends in this source. In any case, this should be discussed. Also, references are missing for the d15N-NO3- signatures of the stratospheric and soil signatures. These ranges for the source signatures are quite large, and the authors need to justify their choice of values used in their mixing model in section 2.3.

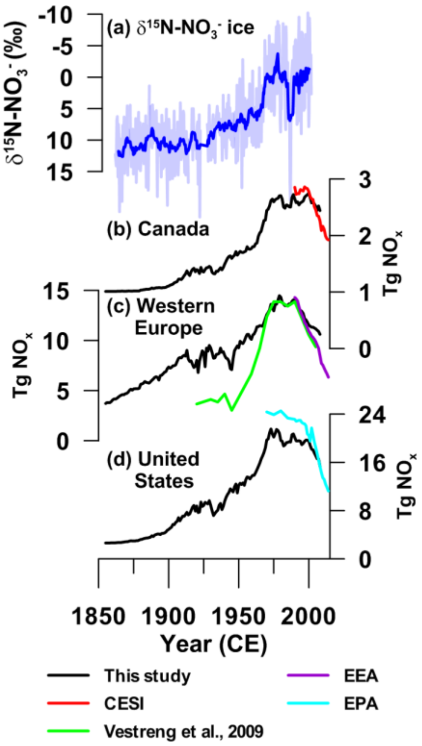
We have significantly changed the mixing model, per feedback from this review and Reviewer #2, who both noted our method of NO_x emissions reconstructions could be greatly improved. Instead of relying heavily on CO_2 emissions in modern times, which increase/stagnate despite decreasing NO_x emissions due to increased regulation, we will directly use NO_x emissions from EDGAR4.2 from 1970-2000 and only use CO_2 emissions prior to 1970 when there are not well-constrained NO_x reconstructions. Our new method is as follows:

NOx emissions from 1970-2000 from the EDGAR4.2 model were used to reconstruct NO_x emissions for Canada, the US, and Western Europe. We divided the EDGAR NO_x emissions into four categories (oil burning, coal burning, natural gas burning, and soil emissions) as described below. Since up to 75% of oil is used for transportation (US EIA), we assume that NO_x emissions from transportation are sourced completely from oil combustion. Thus, we combined the EDGAR NO_x emissions from all transportation-related sectors ("Road transportation", "Rail transportation", and "Domestic aviation") to estimate NO_x emissions from oil combustion. This approach allows us to capture the decline in NO_x emissions from emissions-control regulations beginning in the 1970s. To estimate NO_x emissions from coal and natural gas combustion, we combined the EDGAR NO_x emissions from major industrial/nontransportation sectors (“Public electricity generation”, “Other energy industries”, and “Manufacturing industries and construction”) and subdivided that total by the proportion of CO_2 emissions from each fuel. We directly use NO_x from soil emissions as modeled by EDGAR since 1970.

To extend our estimates for fossil fuel sources back to 1800, we scaled the CO_2 emissions from oil, natural gas, and coal to meet the EDGAR emissions in 1970. For fertilized soil emissions, we scaled fertilizer use to meet EDGAR soil NO_x emissions in 1970.

Additionally, instead of solely relying on biomass burning in the pre-industrial, we have replaced the original “biomass burning” source with a “natural background” source that assumes a combination of biomass burning, soil emissions, lightning, and the stratosphere without making assumptions about trends in the naturally-driven emissions from these sources. To avoid assuming the un-quantified source signatures of biomass burning and natural soil emissions, we instead fit the $\delta^{15}N\text{-}NO_3^-$ ice core record by assuming a combined pre-industrial mix that results in a 12‰ $\delta^{15}N\text{-}NO_3^-$. The missing references have been corrected.

The new simulated NO_x emissions compare well to other estimates from other databases and exhibit the decline in NO_x emissions observed over recent decades (see updated Figure 3 below). For the US, the simulated total NO_x is similar to EPA estimates, though EPA estimates are somewhat higher. For Canada, the simulated total NO_x compares well to estimates from Environment and Climate Change Canada/Canadian Environmental Sustainability Indicators (CESI). For Europe, the simulated NO_x agree with estimates from the European Environmental Agency (EEA) and Verstreng et al. (2009) back to 1970. However, the simulated emissions from this study remain higher than those predicted by Verstreng et al. (2009) from 1920 to 1970.



Updated Figure 3: $\delta^{15}N\text{-}NO_3^-$ in the Summit-2010 core (a) compared to total simulated NO_x emission from this study for each region (b,c,d). NO_x emissions estimates from other sources compare well to our total reconstructed NO_x emissions, which are based primarily on the EDGAR4.2 model.

We have also modified the mixing model to account for variation in source signature estimates. Instead of assuming a single $\delta^{15}N$ signature for each source, our model now randomly chooses a $\delta^{15}N$ signature from a predetermined normal distribution over 1000 model runs to test for sensitivity to the error in $\delta^{15}N$ source signature. The 1000 model runs are averaged and plotted with ±1 standard deviation to show the spread of possible outcomes. Chosen values, based on observations, for the source signatures are below (mean±1 standard deviation):

Oil (pre-1970, pre-catalytic converters): -10±4‰ (assuming a 5‰ lowering compared to using catalytic convertors based upon Walters et al., 2015a)
Oil (1970-1980): Linear increase, 0.5‰/yr from -10±4 in 1970 to -5±4‰ in 1980 to simulate increased $\delta^{15}N$ from introduction of catalytic converters
Oil (post-1980, w/ catalytic converters): -5±4‰
(Walters et al., 2015a; Walters et al., 2015b; Heaton, 1990; Fibiger et al., 2014)

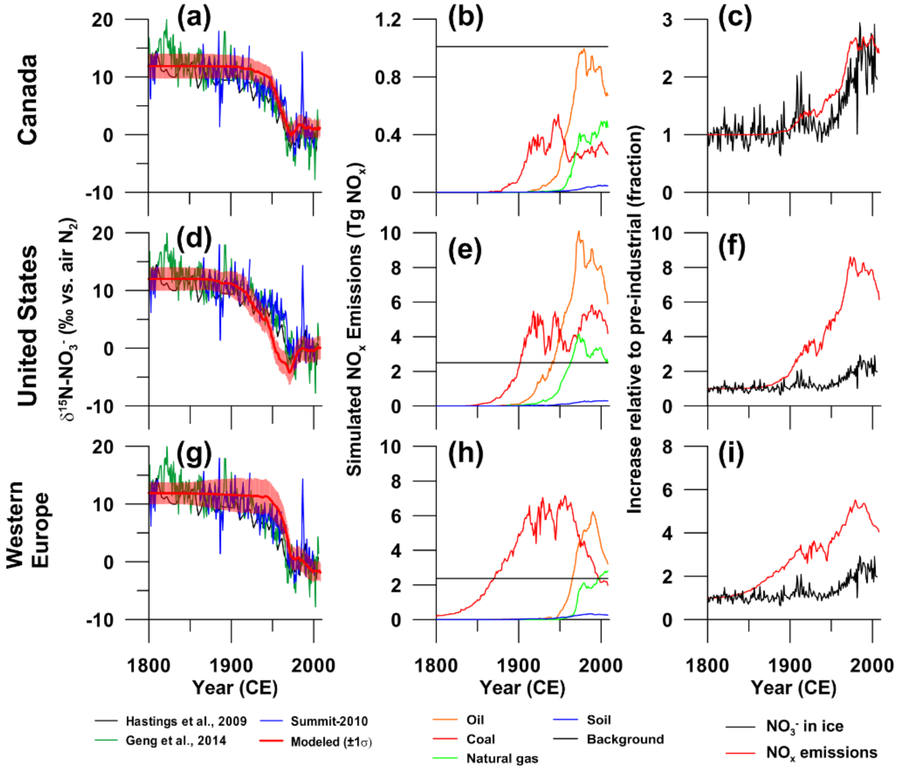
Coal: 12±4‰
(Felix et al., 2012; Heaton, 1990)

Natural Gas: -17±1‰
(Walters et al., 2015a)

Fertilized Soil: -27±4‰
(Felix and Elliot, 2013; Li and Wang, 2008)

"Background" (combination of biomass burning, natural soil emissions, lightning, stratosphere): 12±2‰

The model results are still consistent with oil burning as the primary driver of the observed $\delta^{15}N$ decline (see Updated Figure 5 below).



Updated Figure 5: Mixing model results for separate emissions scenarios for Canada (top), US (middle), and Western Europe (bottom). **(a,d,g)** Model results in red with ±1σ error for uncertainty in source signatures plotted with three existing $\delta^{15}N\text{-}NO_3^-$ records from Summit. **(b,e,h)** Simulated NO_x emissions by source. **(c,f,i)** Comparison of increases in simulated NO_x emissions and measure NO_3^- concentrations relative to pre-industrial values (note difference in y-axes).

The simulated NOx emission from oil and coal combustion is not consistent with expectations. For example, the EPA inventory data (https://www.epa.gov/air-emissionsinventories/air-pollutant-emissions-trends-data), and the Emission Database for Global Atmospheric Research (EDGAR) dataset V4.2 (http://edgar.jrc.ec.europe.eu) both describe emissions trends from the main NOx source categories. In particular, the EPA data indicate a continued decreasing trend in highway and off-highway vehicle NOx emissions from 1970 to 2000 in the US. This seems to be inconsistent with the simulated emissions in Figure 5e in this study, if the oil source is the same as vehicle emission. In addition, Walters et al. [2015] have suggested that after 1975, the d15N of vehicle emitted NOx should decrease significantly due to the mandatory installation of catalytic converters. The converter effectively reduces NOx emissions but increases its d15N value. This regime shift should be considered in the four-source model instead of assuming a constant d15N signature from the oil source. They further suggest that "if the d15N of atmospheric NO3− is controlled by the source d15N-NOx ", "the d15N of atmospheric NO3− produced between 1950 and 1975 should be significantly lower relative to NO3− produced after 1980 and this should be detectable in northern hemisphere ice cores." This appears to be at odds with the conclusion of this study.

Thank you for pointing out this inconsistency in the emissions estimates. See above for further discussion. Our updated calculations include a range associated with the isotopic source signatures and we change the isotopic signature associated with vehicle emissions after 1980. We also now include comparison of emissions estimates (see updated Figure 3 above). Our conclusions are consistent with Walters et al. (2015). In fact, the predicted $\delta^{15}N$ fits well with changes observed in the ice core, including recent changes associated with changes in vehicle emissions. This also fits well with the fact that the concentration of nitrate in ice is sensitive to total loading in the atmosphere while the isotopic composition is sensitive to the relative importance of different nitrate sources.

The first time “ACT11d” and “D4” are mentioned, it should state what these are. I figured out later that they were other ice cores.
Thank you, this will be clarified.

Page 7 line 10: Figure 1b does not provide a comparison with these other ice core records as this sentence suggests.
We will modify the sentence for clarity as follows and add a sentence later in the discussion comparing to the NO_3^- stack data:
“The Summit-2010 record of nitrate concentrations is similar to previously reported records from Greenland ice cores so we interpret it as representative of changes in nitrate concentration and deposition throughout the Greenland Arctic.”

Page 7 line 18: State the resolution of Geng et al. [2014] so the reader can easily compare with this new data set.
Geng et al. do not state their measurement resolution -- they measure at greater than annual resolution but plot their data and compare with other measurements at annual resolution. We will update our text to state their data is annual.

Page 8 line 3: State how exPb is calculated.
This parameter does need to be defined, we will add the following equation to methods:
$exPb = Pb_{total} – (Pb:Ce)*Ce$, where (Pb:Ce) is calculated using crustal abundances from Bowen (1979).

Page 8 line 5: ssNa+ is not shown or discussed anywhere in the paper. I assume that it is used to calculate nssSO42-, and how this is calculated should be explicitly stated.
Will add citation to Pasteris et al. (2012): “The sea salt components are determined using the various ion to sodium ratios in seawater and assuming that all of the sodium is sea salt derived.”

NH4+ should be shown in Figure 1. This is a biomass burning source signature on which the interpretation relies.
We have incorporated the biomass burning signature into a pre-industrial background for NO_x emissions, thus the NH_4^+ record is no longer pertinent.

The authors state that sulfate is mainly from combustion of liquid fossil fuels in the modern era (1930-2002). This goes against the observations of acidity and sulfate in rainwater, which are highest near coal-combustion sources in the U.S. even in the present day. It can be seen in the IMPROVE and CASTNET observations that there is very little sulfate in the west where coal combustion is low and liquid fuel burning is high. It wasn’t until the 1970 US CAA that sulfur emissions from coal decreased substantially as part of the US acid rain program that required sulfur scrubbers on coal-fired power plants, as evidenced in both the IMPROVE and the ice-core observations of sulfate and acidity.
We were incorrect in stating that nssS is primarily derived from liquid fuels. We will correct this in the manuscript.

Page 8 line 20: The correlation between biomass burning and nitrate suggests that the variability in nitrate is dominated by the variability in biomass burning, not that it is the sole source. If the other sources aren’t varying, they could still be significant.
The text has been modified to better reflect the relationship in variability and we have updated the text to be clear that the pre-industrial sources, combined, reflect a background that we are accounting for.

Page 8 lines 22-23: For reasons stated above, I totally disagree with this sentence.
Please refer to earlier discussion of the $\delta^{15}N$ signature of biomass burning. We will update this sentence to indicate that the combined pre-industrial emissions, not exclusively biomass burning, lead to a $\delta^{15}N\text{-}NO_3^-$ of 12‰.

Page 9 line 13: But earlier it is stated that exPb and nssS were coal tracers, now they are oil. Which one is it?
For coal, see above comment for correction. During the Industrialization era, exPb is clearly derived from coal, evidenced by the increase in exPb during this era of heavy coal burning and little oil consumption. During the modern era, exPb is sourced from a combination of coal combustion and leaded gasoline (see also more discussion in McConnell et al. (2008)). We will edit the manuscript text to clarify this.

Page 10 line 1: r = -0.78. What is being compared to d15N-NO3- here? It is not explicitly stated.
The sentence clearly states that this correlation is for U.S. fertilizer consumption and $\delta^{15}N\text{-}NO_3^-$ as found in Felix and Elliott (2013). (Note that Felix and Elliott compared to the Hastings et al., 2009 $\delta^{15}N$ record)

Figure 3: Why show CO2 and not NOx emissions? NOx emissions are in the mixing model so the authors obviously have this data. Why is CO2 shown here?
Thank you for pointing this out. Please see discussion above - updated NO_x emissions data is now shown in Figure 3.

Page 11 lines18-20 and lines 23-25: but the decline in d15N-NO3- did not start until 1940, not 1900 or 1850 as the emissions would suggest.
Emissions from oil burning outpaces coal in the mid-1900's, which is when the decline in $\delta^{15}N\text{-}NO_3^-$ begins. Prior to that coal is an important source and is positive in $\delta^{15}N$ so we do not expect a decline. We will edit these two sentences for clarity.

Page 12 line 8: insert the word "modeled" before d15N-NO3-.
This will be changed.

Page 12 line 20: change nitrate to NOx since this is what is actually emitted.
This will be changed.

Table 1: State the time resolution of the measurements used for these calculations.
We will add this information. These correlations are at our highest resolution isotopic measurement which is ~3 samples/yr.

Figure 2: I thought these measurements were done at a time resolution of 3 per year. So how can monthly means be plotted here?
We calculated the seasonal cycle by binning the data based on the midpoint of the measurement. For instance, if a data point spans from year 1862.426 to 1862.788, the midpoint of that sample is 1862.607. Thus, the midpoint of this data point corresponds to August of 1862. By binning all the data in this manner for each time period (Pre-industrial, Industrialization, Modern) we can get an average seasonal cycle. Even though we do not necessarily have a monthly data point for each year, by combining data for over >50 consecutive years we can see the seasonal cycle.

The limiting factor here is the isotope data. We have much higher resolution data for the other ice core parameters (NO_3^-, BC, exPb, nssS) that were measured continuously. The seasonal cycle calculated for these species using the high-resolution data is nearly identical to that of the seasonal cycle calculated using the lower resolution data, thus we are confident in this method. This will be explicitly added to the revised manuscript.

Figure 5c, f and i: Better to plot the ice-core NO3- and NOx emissions on separate y-axes.
We have plotted ice core NO_3^- and NO_x emission on the same axis in this figure to emphasize the difference between the relative increase of NO_3^- observed in the ice core and the relative increase in NO_x emissions from these regions. The relative increase of Canadian NO_x emissions is very similar to the ice core increase, while the increase of NO_x emissions from the US and Western Europe far exceeds the increase in the ice core.

References (to be included in revised manuscript):

Bowen, H.J.M. (1979). Environmental Chemistry of the Elements. *Academic Press, London*. 333.

CESI, https://www.ec.gc.ca/indicateurs-indicators/default.asp?lang=en&n=0870FFFC-1
Environment and Climate Change Canada, Canadian Environmental Sustainability Indicators: Data Sources and Methods for the Air Pollutant Emissions Indicators. Accessed 05 Sep 2016. https://www.ec.gc.ca/indicateurs-indicators/default.asp?lang=en&n=0870FFFC-1, 2016.

Edgar 4.2, http://edgar.jrc.ec.europa.eu/overview.php?v=42
European Commission, Joint Research Centre (JRC)/Netherlands Environmental Assessment Agency (PBL). Emission Database for Global Atmospheric Research (EDGAR), release version 4.2. http://edgar.jrc.ec.europa.eu, 2011

EEA, www.eea.europa.eu/data-and-maps/data/data-viewers/air-emissions-viewer-lrtap.
European Environmental Agency, Air Pollutant Emissions Data Viewer. Accessed 05 Sep 2016. www.eea.europa.eu/data-and-maps/data/data-viewers/air-emissions-viewer-lrtap.

Fibiger and Hastings, First measurements of the nitrogen isotopic composition of NO_x from biomass burning, Env. Sci. & Tech., in revision (to be cited if in press).

GFED4.1, https://daac.ornl.gov/VEGETATION/guides/global_fire_emissions_v3.1.html
Randerson, J.T., G.R. van der Werf, L. Giglio, G.J. Collatz, and P.S. Kasibhatla. 2015. Global Fire Emissions Database, Version 4, (GFEDv4). ORNL DAAC, Oak Ridge, Tennessee, USA. http://dx.doi.org/10.3334/ORNLDAAC/1293

Snape, C. E., C. Sun, A. E. Fallick, R. Irons and J. Haskell (2003), Potential of stable nitrogen isotope ratio measurements to resolve fuel and thermal NOx in coal combustion, *Fuel Chemistry Division Preprints, 48*(1), 1-3.

US EIA, http://www.eia.gov/totalenergy/data/monthly/.
US Energy Information Administration, Total Energy Monthly Energy Review- Petroleum Products Supplied by Type. Accessed 05 Sep 2016. http://www.eia.gov/totalenergy/data/monthly/#petroleum, 2016.

US EPA, https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data
US Environmental Protection Agency, National Emissions Inventory. Air Pollutant Emissions Trends Data. Accessed 05 Sep 2016. https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data, 2015.

Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I. S. A., and Tarrasón, L., Evolution of NO$_x$ emissions in Euroep with focus on road transport control measures, Atmos. Chem. Phys., 9, 1503-1520, 2009.

References:

Bernahu, T. A., C. Meusinger, J. Erbland, R. Jost, S. K. Bhattacharya, M. S. Johnson, and J. Savarino (2014), Laboratory sudy of nitrate photolysis in Antarctic snow. II. Isotopic effects and wavelength dependenced, J. Chem. Phys., 140(24), doi:10.1063/1.4882899.

Dibb, J. E., S. I. Whitlow, and M. Arsenault (2007), Seasonal variations in the soluble ion content of snow at Summit. Greenland: Constraints from three years of daily surface snow samples, Atmos. Env., 41, 5007-5019, doi:doi:10.1016/j.atmosenv.2006.12.010.

Felix, J. D., and E. M. Elliott (2013), The agricultural history of human-nitrogen interactions as recorded in ice core _15N-NO3−, Geophys. Res. Lett., 40(8), 1642-1646, doi:10.1002/grl.50209.

Fibiger, D. L., M.G. Hastings, J. E. Dibb, and L. G. Huey (2013), The preservations of atmospheric nitrate in snow at Summit, Greenland, Geophys. Res. Lett., 40(13), 3484-3489, doi:10.1002/grl.50659.

Geng, L., B. Alexander, J. Cole-Dai, E. J. Steig, J. Savarino, E. D. Sofen, and A. J. Schauer (2014), Nitrogen isotopes in ice core nitrate linked to anthropogenic atmospheric acidity change, Proc. Natl. Acad. Sci., 111(16), 5808-5812, doi:10.1073/pnas.1319441111.

Geng, L., M. C. Zatko, B. Alexander, T. J. Fudge, A. J. Schauer, L. T. Murray, and L. J. Mickley (2015), Effects of post-depositional processing on nitrogen isotopes of nitrate in the Greenland Ice Sheet Project 2 (GISP 2) ice core, Geophys. Res. Lett., 42, 5346-5354, doi:10.1002/2015GL064218

Honrath, R. E., Y. Lu, M. C. Peterson, J. E. Dibb, M. A. Arsenault, N. J. Cullen, and K. Steffen (2002), Vertical fluxes of NOx, HONO, and HNO3 above the snowpack at Summit, Greenland, Atmospheric Environment, 36(15-16), 2629-2640.

Kendall, C.,E. M. Elliott, and S. D. Wankel (2007), Tracing anthropogenic inputs of nitrogen to ecosystems, Blackwell Scientific Publications, Oxford.

Legrand, M., and M. De Angelis (1996), Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone, J. Geophys. Res., 101(D2), 4129-4145, doi:10.1029/95jd03296.

Morin, S., J. Savarino, M. M. Frey, F. Dominé, H.-W. Jacobi, L. Kaleschke, and J. M. F. Martins (2009), Comprehensive isotopic composition of atmospheric nitrate in the Atlantic Ocean boundary layer from 65S to 79N, J. Geophys. Res, 114, D05303, doi:doi:10.1029/2008JD010696.

Salzmann, R., and T. Nussbaumer (2001), Fuel staging for NOx reduction in biomass combustion: Experiments and modeling, Energ Fuel, 15(3), 575-582, doi:10.1021/Ef0001383.

Walters,W.W., S. R. Goodwin, and G. Michalski (2015), Nitrogen Stable Isotope Composition (_15N) of Vehicle-Emitted NOx, Environ. Sci. Technol., 49(4), 2278-2285, doi:10.1021/es505580v.