Anonymous Referee #2

We thank the reviewer for the thorough comments and review of our manuscript. These comments have helped us develop a more robust approach to our mixing model and significantly improve our paper.

This paper relates the changes in NOx emissions to the observed deposition of nitrate (and isotopes) and additional tracer. This paper is interesting and well written, and brings new information to the understanding of the ice core records in the Northern hemisphere. I have however one major comment that the authors should address before publication. Namely, while they acknowledge that there is significant range/uncertainty in the isotopic composition of the various NOx emissions, by the time they perform the analysis using the isotopic mixing model, a single value is used. It seems that it would be quite critical to explore the range of uncertainty to bring this information into the possible mix of emissions. I would therefore recommend that the authors take a more probabilistic approach to their mixing model and perform, for example, a certain number of simulations to span the range of uncertainties.

Thank you for this suggestion- our mixing 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 signatures. The 1000 model runs are averaged and plotted with ±1 standard deviation to show the spread of possible outcomes. Please also see our response to Reviewer #1, as our method for reconstructing NO_x emissions has also been significantly modified. Below is an updated Figure 5 using this new method with our updated NO_x emissions.

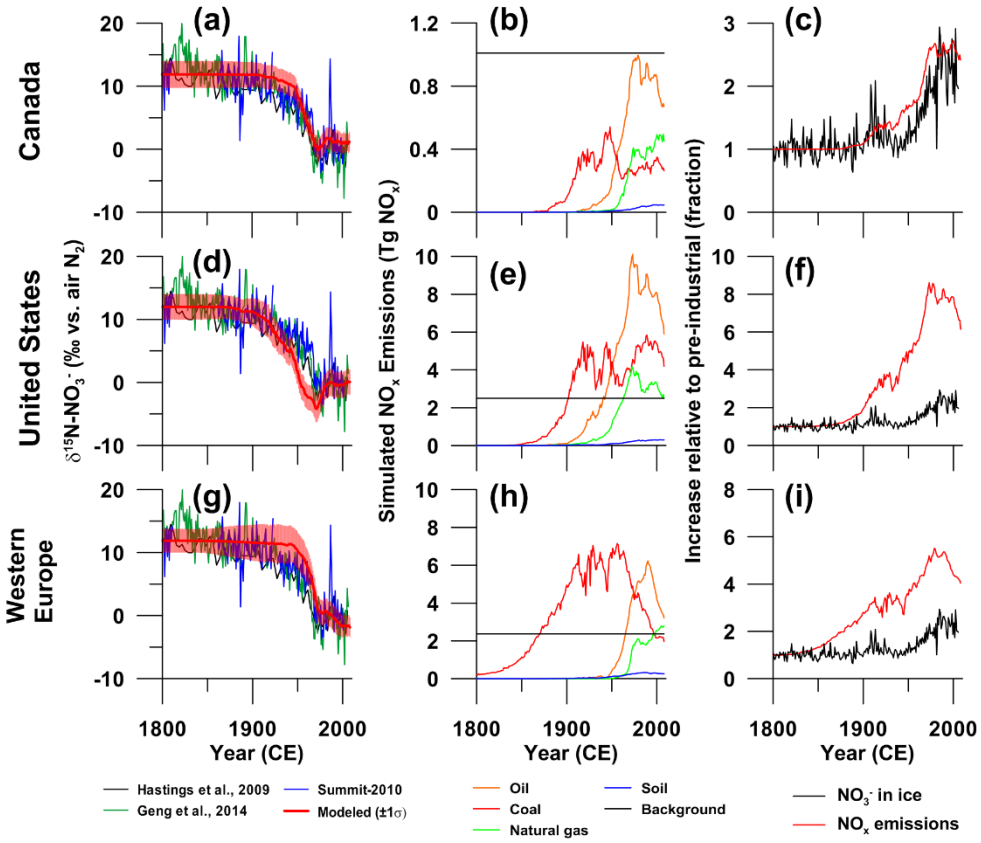
Chosen source signature distributions (mean±1σ):
Oil (pre-1970, pre-catalytic converters): -10±4‰
Oil (1970-1980): Linear increase, 0.5‰/yr from -10±4 in 1970 to -5±4‰ in 1980 to simulate increased $\delta^{15}N$ from introduction of catalytic converters
Oil (post-1980, w/ catalytic converters): -5±4‰
(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‰



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).

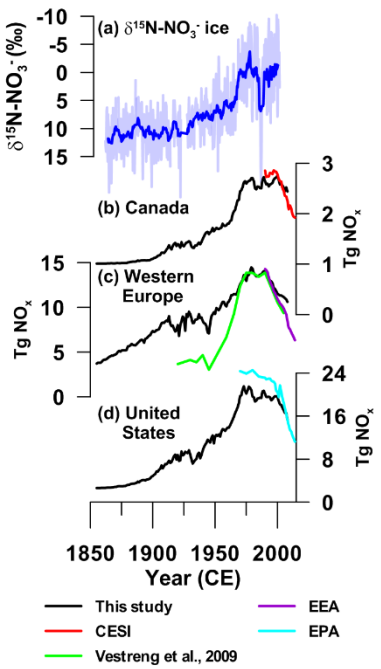
Minor comments

Page 1, line 29: I would change "budget" to "fluxes into the troposphere"

This will be changed.

Page 6, line 14: the assumption of NOx emission scaling with CO2 seems to be inappropriate for the conditions after the existence of catalytic converters. A clear case is the drastic recent reduction in NOx emissions from the US power plants while the CO2 emissions are obviously unchanged.

Thank you for noting this – we have updated our simulated NO_x emissions after 1970 to be consistent with EDGAR4.2 NO_x emissions instead of CO_2 emissions. We still use CO_2 emissions pre-1970, however, as the NO_x emissions estimates prior to 1970 are poorly constrained. See above for source signatures. Comparisons to other inventories are shown in our updated Figure 3 (below). (Please also see our response to Reviewer #1 regarding a similar point.)

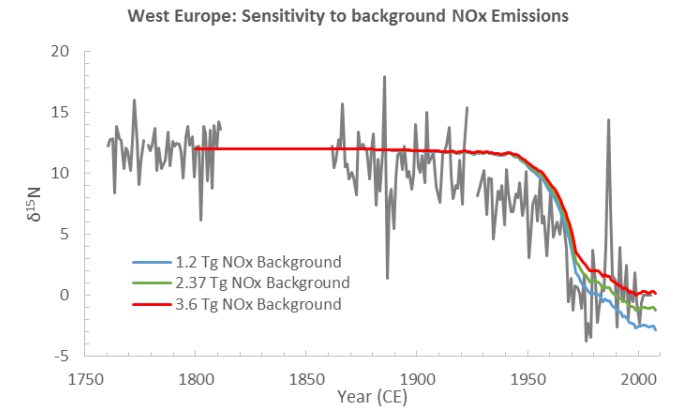


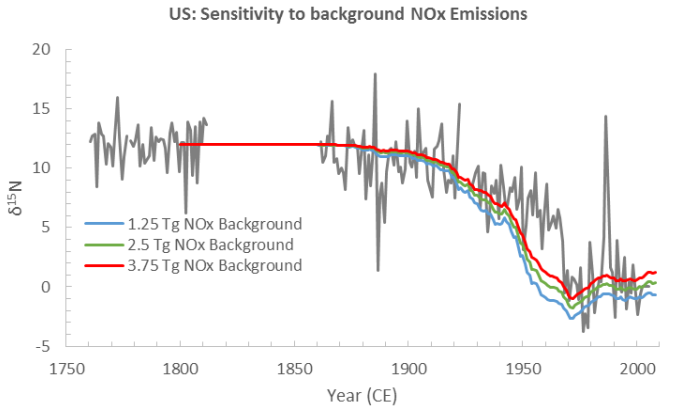
Updated Figure 3: $\delta^{15}N\text{-}NO_3^-$ in the Summit-2010 core (a) compared to total simulated NO_x emission from this study for each region (b,c,d). NO_x emissions estimates from other sources compare well to our total reconstructed NO_x emissions, which are based primarily on the EDGAR4.2 model.

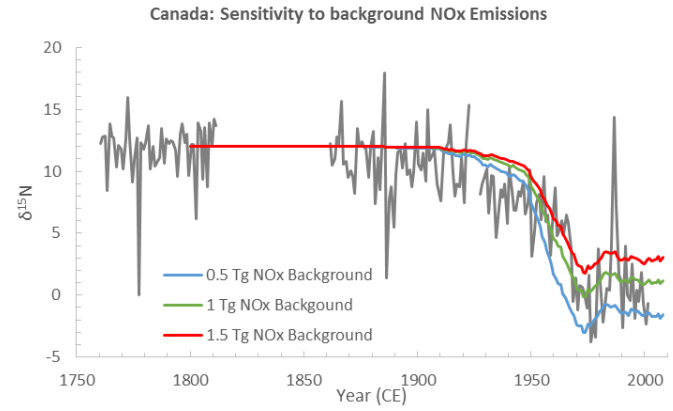
Page 7, line 25: there is a wide variety of emission databases (especially for the last few decades), especially for biomass burning. What is the sensitivity of the results to the choice of the database?

We recognize that non-fossil fuel NO_x emissions are very poorly constrained. We have chosen our new background NO_x emissions as described below by averaging a number of current estimates. For biomass burning, we assume that burning over the past 200 years has been similar to modern times, thus we can use values from databases that only predict modern biomass burning emissions. For soils, it is important to note that the $\delta^{15}N$ has only been quantified for fertilized soils and that we incorporate a separate estimate of fertilized-soil NO_x emissions from the EDGAR4.2 model. For lightning, we use a recent study (Miyazaki et al., 2014) that estimates annual and seasonal lightning NO_x emissions. The contribution of stratospheric NO_x to the troposphere is very uncertain, with one of the only global estimates from Jaeglé et al. (2005). We assume a nominal amount of 0.01 Tg NO_x/yr.

For the US and Western Europe, the background NO_x has very little effect on the overall $\delta^{15}N$ predicted by our mixing model, since the amount of background NO_x is small relative to the contribution from fossil fuels. However, for Canada, the background NO_x represents ~30% of NO_x emissions since 1970 and therefore has a larger role in driving the mixing model. The figures below demonstrate how varying the background NO_x emissions by ±50% affects the mixing model using fixed $\delta^{15}N$ signatures. The timing of the large drop in $\delta^{15}N$ is largely preserved, but the magnitude of the decrease is affected by the amount of background NO_x.







Details on determining pre-Industrial background NO_x emissions below. Estimates in Tg N were converted to Tg NO_x by multiplying by ratio of molecular weight NO_2 (46 g/mol) to N (14 g/mol)

US

US Total for background NO_x: 0.3+1.65+0.57+0.01 = 2.5 Tg NO_x/yr

Biomass burning

EPA, 1990-2014 average	0.2 Tg NO_x/yr
EDGAR 4.2, 1970-2000 average	0.06 Tg NO_x/yr

GFED4.1, 1997-2014 average 0.1 Tg NO_x
Jaeglé 2005 0.12 Tg N/yr (0.4 Tg NO_x/yr)
Hoelzemann 2004, all of N America 1-1.2 Tg NO/yr (use half for US)

Average estimate: 0.3 Tg NOx/yr

Natural Soil
Jaeglé 2005 0.86 Tg N/yr (2.8 Tg NO_x/yr)
Edgar Hyde 1.3, for agriculture in 1890 0.161 Tg N/yr (0.53 Tg NO_x/yr)

Average estimate: 1.65 Tg NO_x/yr

Lightning
Miyazaki 2014, all of N America 0.3-0.4 Tg N/yr (1.15 Tg NO_x/yr; use half for US)

Average estimate: 0.57 Tg NO_x/yr

Stratosphere
Jaeglé 2005, global 0.1 Tg N/yr (0.3 Tg NO_x/yr)

Average estimate- negligible: 0.01 Tg NO_x/yr

CANADA
Canada total for background NO_x: 0.31+0.12+0.57+0.01 = 1.01 Tg NO_x/yr

Biomass burning
EDGAR 4.2, 1970-2000 average 0.2 Tg NO_x/yr
GFED4.1, 1997-2014 average 0.12 Tg NO_x/yr
Hoelzemann 2004, all of N America 1-1.2 Tg NO/yr (use half for Canada)

Average estimate: 0.31 Tg NO_x/yr

Natural Soil
Edgar Hyde 1.3, for agriculture in 1890 0.038 Tg N/yr (0.12 Tg NO_x/yr)

Average estimate: 0.12 Tg NO_x/yr

Lightning
Miyazaki 2014, all of N America 0.3-0.4 Tg N/yr (1.15 Tg NO_x/yr; use half for Canada)

Average Estimate: 0.57 Tg NO_x/yr

Stratosphere
Jaeglé 2005, global 0.1 Tg N/yr (0.3 Tg NO_x/yr)

Average estimate- negligible: 0.01 Tg NO_x/yr

WESTERN EUROPE
Western Europe total for background NO_x: 0.23+2+0.13+0.01 = 2.37 Tg NO_x/yr

Biomass burning

Hoelzemann 2004	0.017-0.024 Tg NO_x/yr
Jaeglé 2005, all of Europe	0.19 Tg N/yr (0.62 Tg NO_x/yr)
GFED4.1, 1997-2014 average	0.05 Tg NO_x/yr

Average estimate: 0.23 Tg NO_x/yr

Natural Soil

Jaeglé 2005, all of Europe	1.1 Tg N/yr (3.6 Tg NO_x/yr)
Edgar Hyde 1.3, for agriculture in 1890	0.15 Tg N/yr (0.5 Tg NO_x/yr)

Average estimate: 2 Tg NO_x/yr

Lightning

Miyazaki 2014, all of Europe	0.07-0.11 Tg N/yr (0.26 Tg NO_x/yr; use half for West Europe)

Average estimate: 0.13 Tg NO_x/yr

Stratosphere

Jaeglé 2005, global	0.1 Tg N/yr (0.3 Tg NO_x/yr)

Average estimate- negligible: 0.01 Tg NO_x/yr

Page 7, lines 17,18,21: the sigma symbol did not print correctly
Noted, thank you.

Page 7, line 22: any idea on what happened in 1987?
It's not clear. We controlled for any potential contamination and re-measured this sample several times with the same results each time (seemingly anomalously high $\delta^{15}N$ and low $\delta^{18}O$ (not shown)). Given the recently published findings of Fibiger et al. (2016) our best guess is that this represents some type of local contamination since this value is not seen in the other ice core records (Hastings et al., 2009; Geng et al., 2014), although we note that these other records are at different time resolution. The text has been updated to reflect this point.

Page 8, line 2: a more recent and widely used reference is Stohl et, 2008 (http://onlinelibrary.wiley.com/doi/10.1029/2005JD006888/abstract) It would be good to check the findings of the studies.
Thank you, this reference will be included.

Page 9, line 22: there should be a more quantitative statement then "consistent".
We will update this sentence.

Page 12, line 6: this seems to assume that the same fraction NOx makes it to be nitrate deposition. It seems that it would be worth discussing whether this should be the case (changes in transport, chemical background, ...)

This is an interesting point. From the standpoint of the mixing model, the proportional increase in NO_x emissions since pre-industrial does not matter- only the relative mix of NO_x from each source affects the $\delta^{15}N$ recorded in the ice regardless of how much nitrate is deposited. However, from a mass balance standpoint, the proportional increase in NO_x emissions is important. Should the change in nitrate concentration we observe in the ice be directly proportional to the amount of NO_x emitted? If so, then a plausible answer to achieve mass balance is that NO_x from Canada is the only NO_x that is recorded in Greenland. This is likely not the case since the NO_x deposited from Greenland is most certainly sourced from a mix of geographic regions. But it is certainly clear that the dramatic increase in NO_x emissions in the US and Europe do not have a 1:1 effect on the NO_3^- concentration in the ice, otherwise the increase in NO_3^- concentration in the ice would be much larger. Since we are not modeling transport or deposition, we feel that further discussion of NO_x chemistry and transport is outside of the scope of this paper.

Figure 5: how do these emission estimates compare to standard emission databases (such as EDGAR)?
Thank you for this question. Please see response and updated figure above.

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.
Sources:

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

Miyazaki, K., Eskes, H. J., Sudo, K., and Zhang, C., Global lightning NO_x production estimated by an assimilation of multiple satellite data sets*, Atmos. Chem. Phys.*, 14, 3277-3305, doi:10.5194/acp-14-3277-2014, 2014.

Snape, C. E., C. Sun, A. E. Fallick, R. Irons and J. Haskell, 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.