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Interactive comment on "Increased nitrate and decreased δ^{15}N–NO$_3^-$ in the Greenland Arctic after 1940 attributed to North American oil burning" *by* Nathan J. Chellman et al.

Anonymous Referee #1

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Chellman et al report new measurements of ïĄď15N-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 ïĄď15N-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 ïĄď'15N-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 ïĄď'15N-NO3- values [Kendall et al., 2007].

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 ïĄď'15N-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‰À 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‰Ẇithout this dominant and isotopically heavy source in the preindustrial, the authors would not be able to reproduce the observed trends in ïĄď15N-NO3- using the NOx emissions inventories.

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.

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 ïĄď15N-NO3-, and this is not the time period when the trends in ïĄď15N-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 ïĄď15N-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 ïĄď15N-NO3- in Table 1? The lack of such a comparison is suspect.

Other issues:

The introduction states 6 NOx sources: vehicles, coal, lightning, stratospheric, soil and biomass burning, providing a range of ïĄď15N-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 ïĄď15N-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 ïĄď15N-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.

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-emissions-inventories/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 ïĄď'15N of vehicle emitted NOx should decrease significantly due to the mandatory installation of catalytic converters. The converter effectively reduces NOx emissions but increases its ïĄď'15N value. This regime shift should be considered in the four-source model instead of assuming a constant ïĄď'15N signature from the oil source. They further suggest that "if the ïĄď'15N of atmospheric NO3− is controlled by the source ïĄď'15N-NOx ", "the ïĄď'15N 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.

The first time "ACT11d" and "D4" are mentioned, it should state what these are. I figured out later that they were other ice cores.

Page 7 line 10: Figure 1b does not provide a comparison with these other ice core records as this sentence suggests.

Page 7 line 18: State the resolution of Geng et al. [2014] so the reader can easily compare with this new data set.

Page 8 line 3: State how exPb is calculated.

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.

NH4+ should be shown in Figure 1. This is a biomass burning source signature on which the interpretation relies.

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.

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.

Page 8 lines 22-23: For reasons stated above, I totally disagree with this sentence.

Page 9 line 13: But earlier it is stated that exPb and nssS were coal tracers, now they are oil. Which one is it?

Page 10 line 1: r = -0.78. What is being compared to ïĄď15N-NO3- here? It is not explicitly stated.

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?

Page 11 lines18-20 and lines 23-25: but the decline in ïĄď15N-NO3- did not start until 1940, not 1900 or 1850 as the emissions would suggest.

Page 12 line 8: insert the word "modeled" before ïĄđ'15N-NO3-.

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

Table 1: State the time resolution of the measurements used for these calculations.

Figure 2: I thought these measurements were done at a time resolution of 3 per year. So how can monthly means be plotted here?

Figure 5c, f and i: Better to plot the ice-core NO3- and NOx emissions on separate y-axes.

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