Evaluating Anthropogenic Impacts to the Nitrogen Cycle Based on the Isotopes of Nitrate

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Lots of folks to acknowledge!

- Eric Steig and Julia Jarvis (Univ of Washington)
- IsoLab at UW (Shelley Kunasek, Peter Neff, Andy Schauer)
- Jack Dibb (UNH)
- VECO Summit crew and Bella Bergeron (ICDS)
- Danny Sigman and the Sigman Lab (Princeton)

- JISAO and UW Atmospheric Sciences
- NSF Office of Polar Programs

And thank you for your attention!

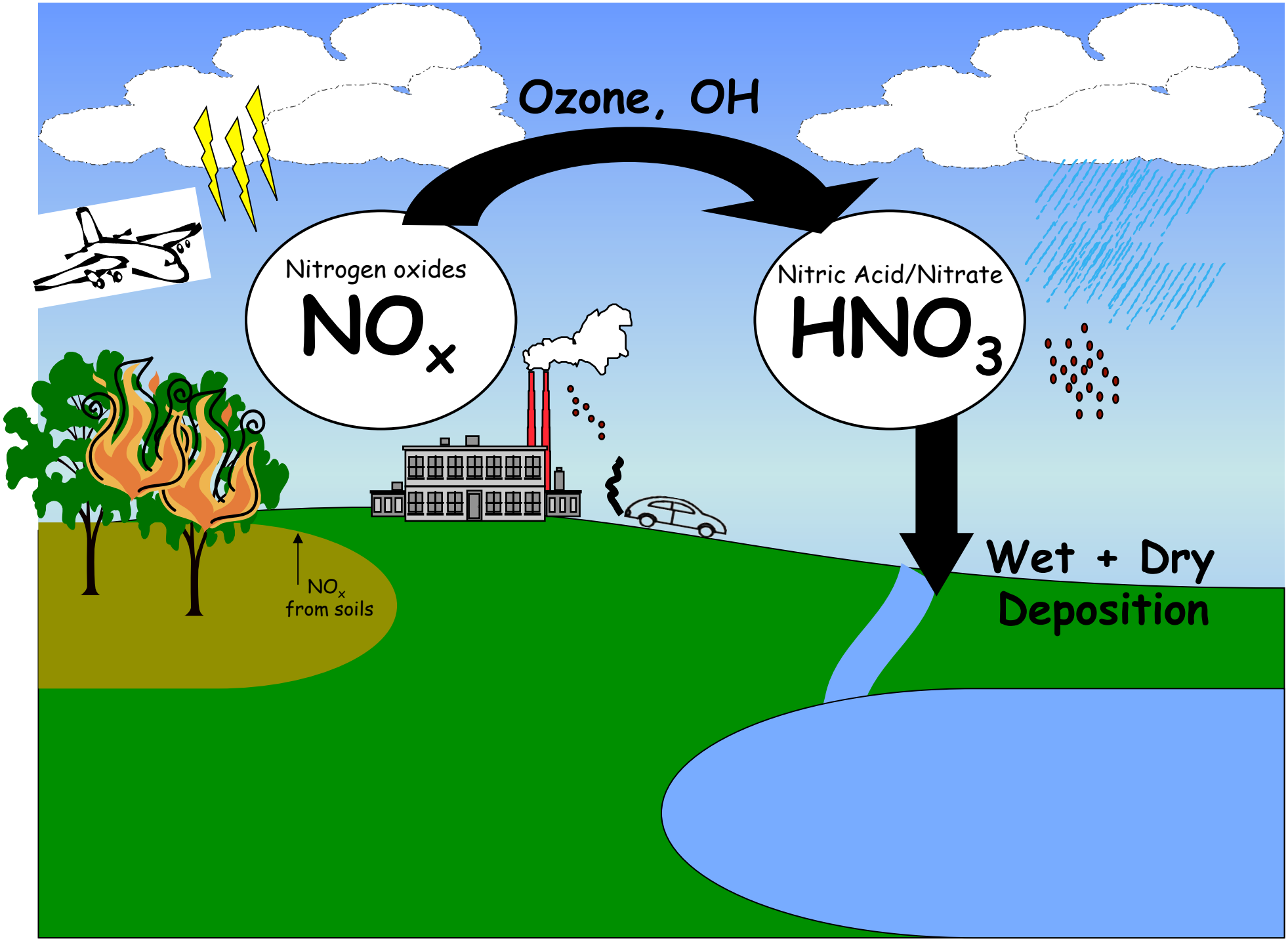
Talk Overview

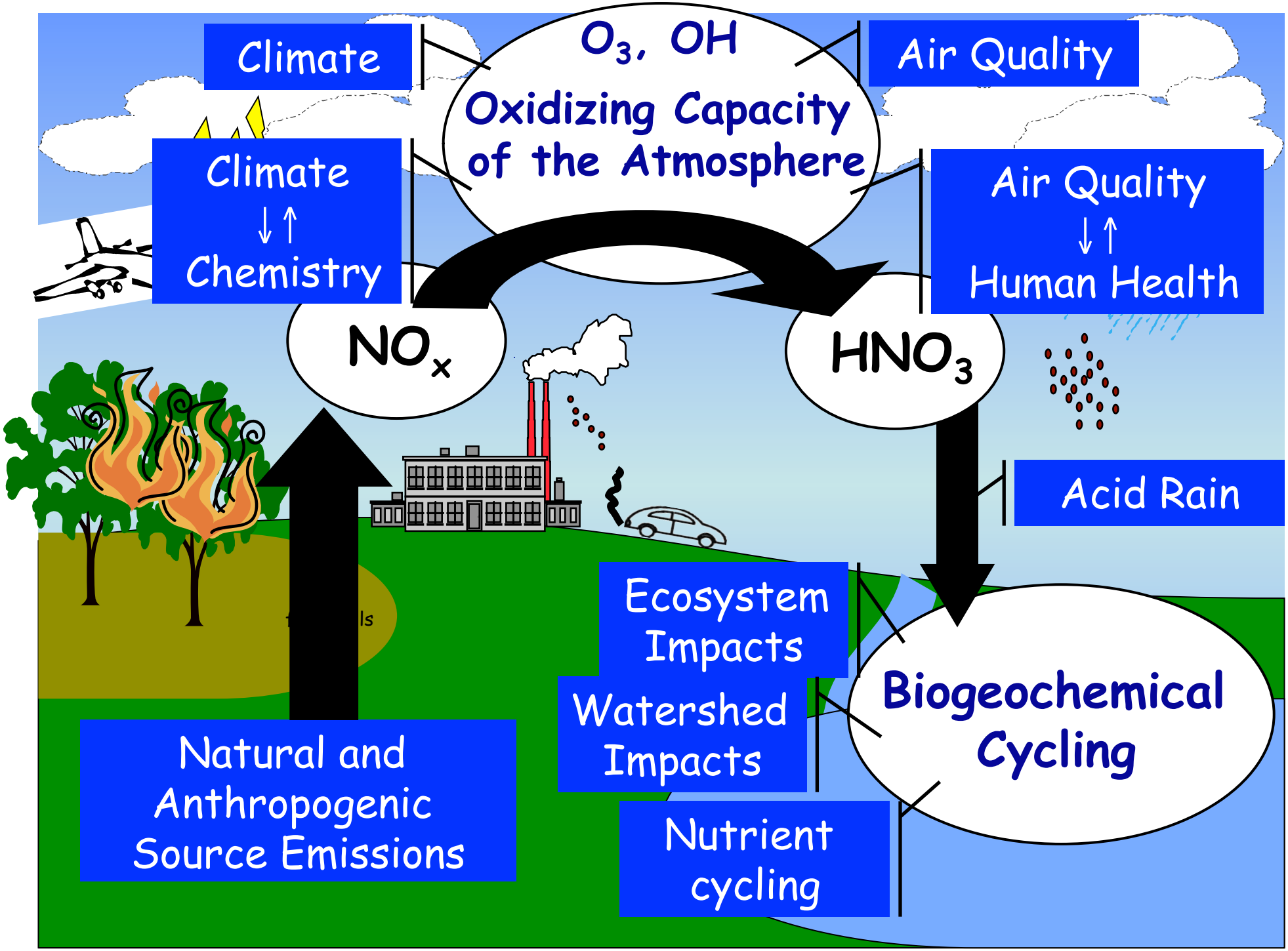
- Motivation and interest in studying atmospheric nitrate

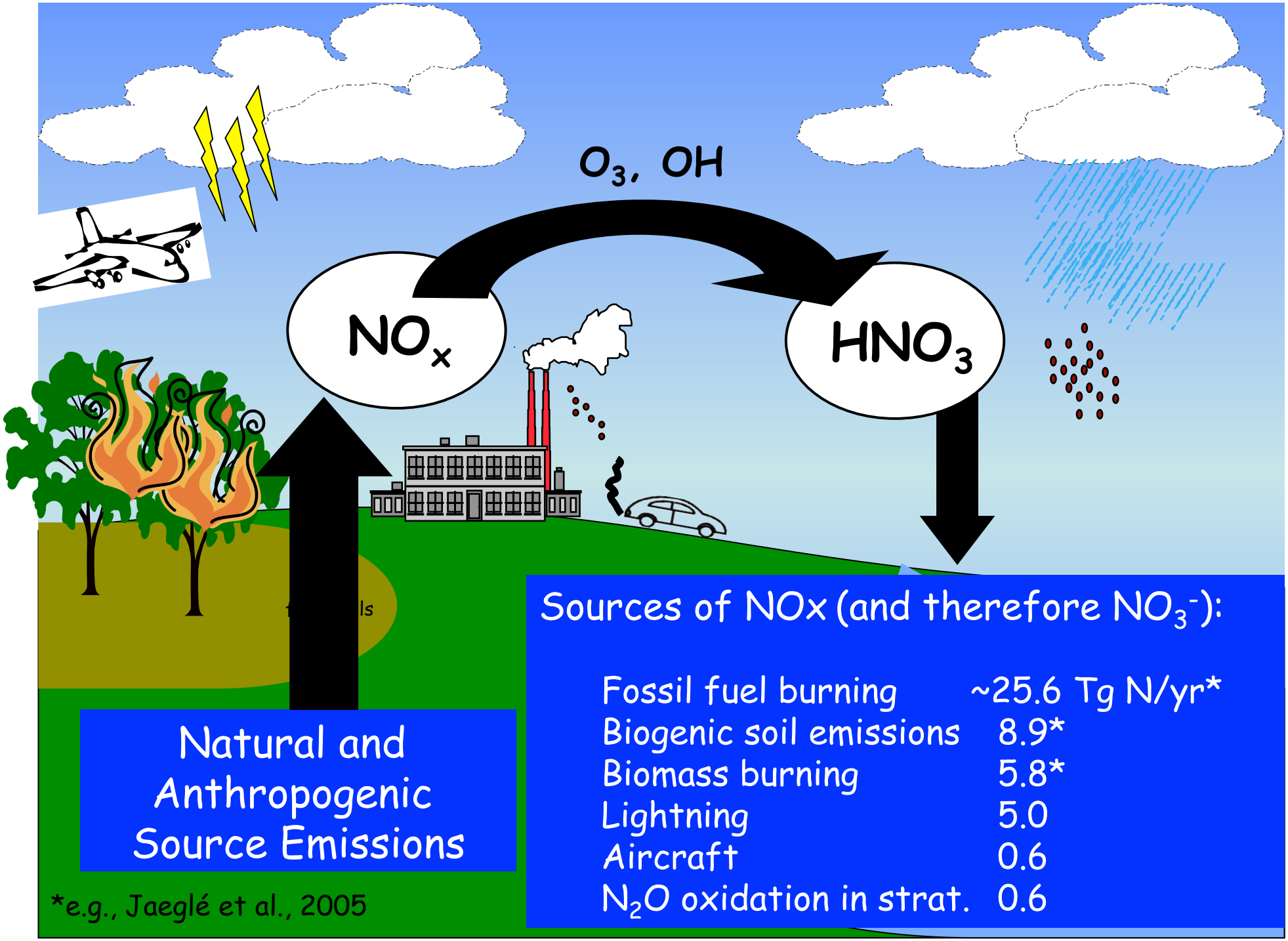
- Using isotopes of nitrate to elucidate sources and chemistry

- Variations in the isotopes of nitrate in a 100-meter ice core from Summit, Greenland
  ⇒evidence of fossil fuel emissions impact on nitrate record

- Conclusions/Implications


Ozone, OH
Nitrogen oxides
NO_x
Nitric Acid/Nitrate
HNO_3
Wet + Dry
Deposition
NO_x
from soils


Climate
O_3, OH
Oxidizing Capacity of the Atmosphere
Air Quality
Climate
↓↑
Chemistry
Air Quality
↓↑
Human Health
NO_x
HNO_3
Acid Rain
Ecosystem Impacts
Watershed Impacts
Nutrient cycling
Biogeochemical Cycling
Natural and Anthropogenic Source Emissions


O_3, OH
NO_x
HNO_3
Natural and Anthropogenic Source Emissions
Sources of NOx (and therefore NO_3^-):
Fossil fuel burning ~25.6 Tg N/yr*
Biogenic soil emissions 8.9*
Biomass burning 5.8*
Lightning 5.0
Aircraft 0.6
N_2O oxidation in strat. 0.6
*e.g., Jaeglé et al., 2005

NO_x (=NO+NO_2) Chemistry

(daytime or high-latitude summer)

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + h\nu \longrightarrow NO + O$$

$$NO_2 + OH \xrightarrow{M} \mathbf{HNO_3}$$

(nighttime or high-latitude winter)

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \xleftrightarrow{M} N_2O_5$$

$$N_2O_5 + H_2O \xrightarrow{aerosol} 2\mathbf{HNO_3}$$

Isotopes of NO_3^- reflect NO_x sources and chemistry

Overview on Isotopes

- denote isotopes in form ^{14}N where 14 is the mass number, or neutrons+protons

N : ^{14}N 99.64% ^{15}N 0.36%

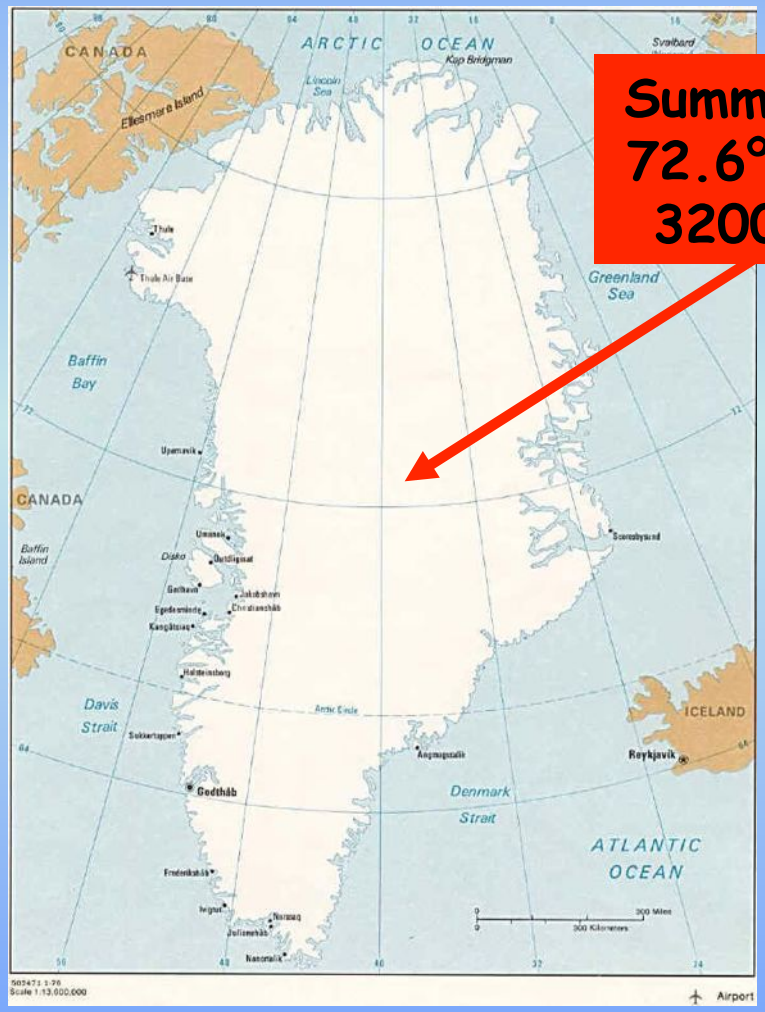
O : ^{16}O 99.763% ^{17}O 0.0375% ^{18}O 0.1995%

- definition of delta (δ) units:

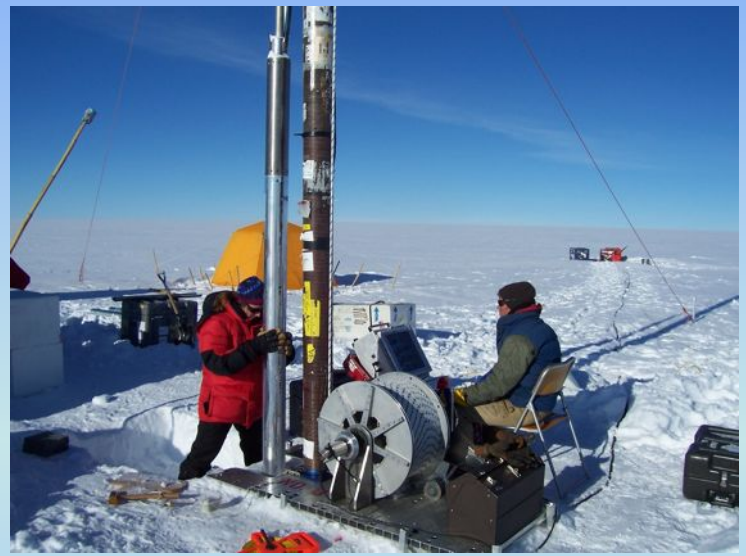
$$\delta^{15}N = \frac{[\ ^{15}N/^{14}N_{sample} - {}^{15}N/^{14}N_{std}\ ]}{^{15}N/^{14}N_{std}} * 1000 \quad \text{(per mil ‰ units)}$$

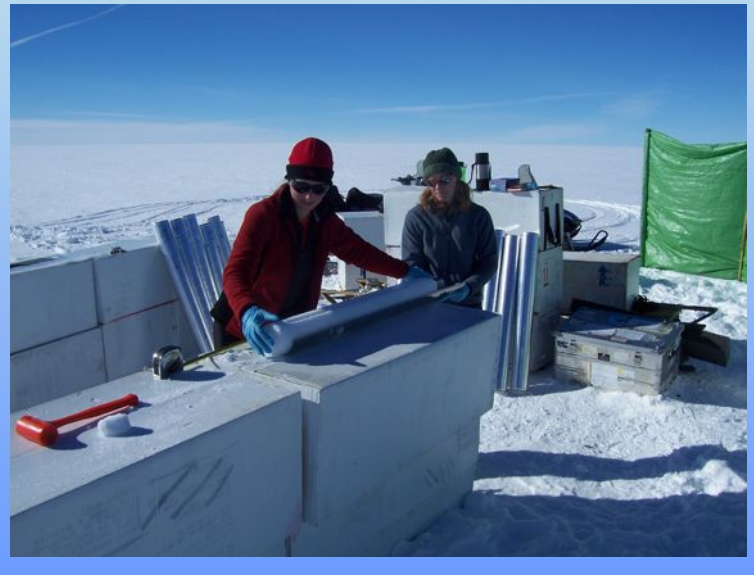
std for N is atmospheric N_2

Summit, Greenland



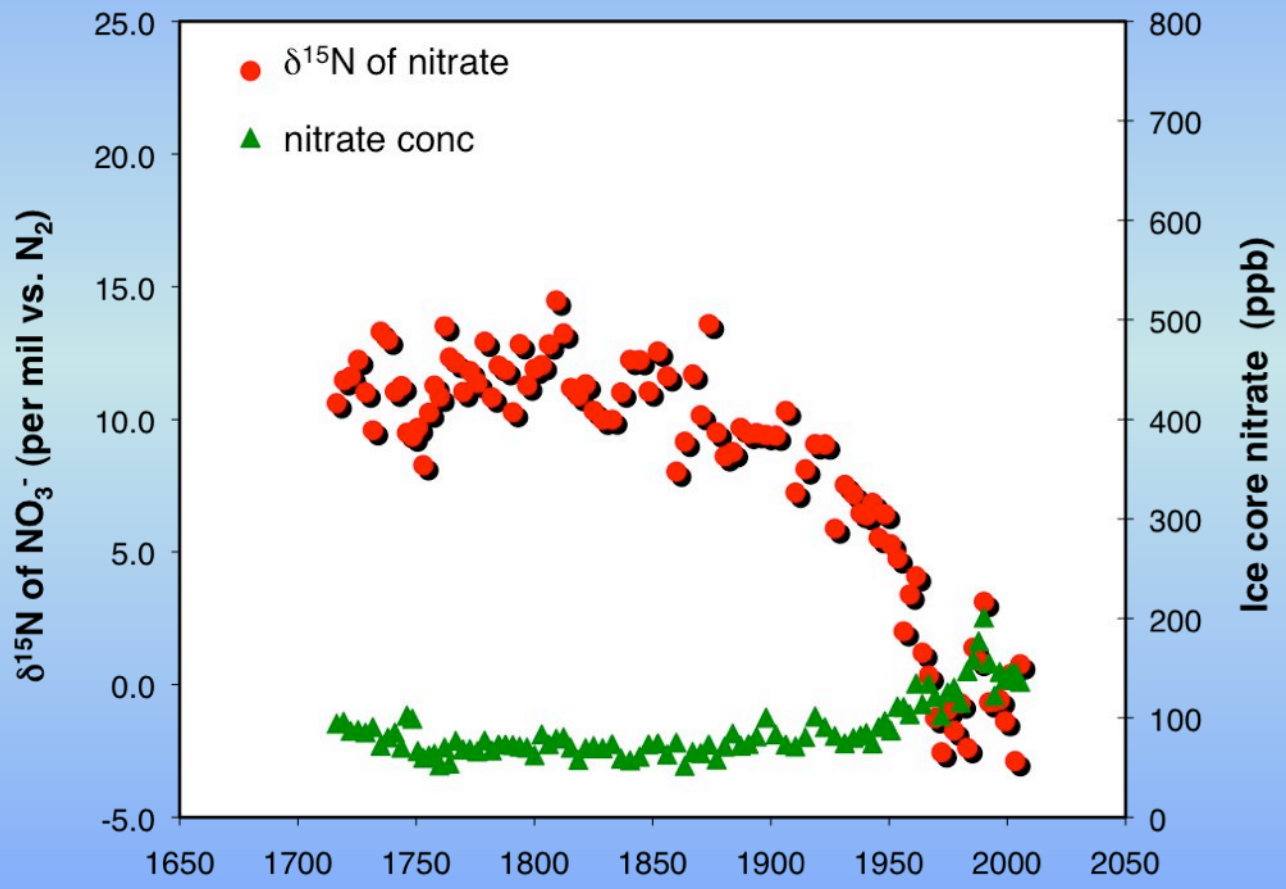
Summit (GISP2)
72.6°N 38.5°W
3200 m.a.s.l.





$\delta^{15}N$ of NO_3^- in recent Greenland ice

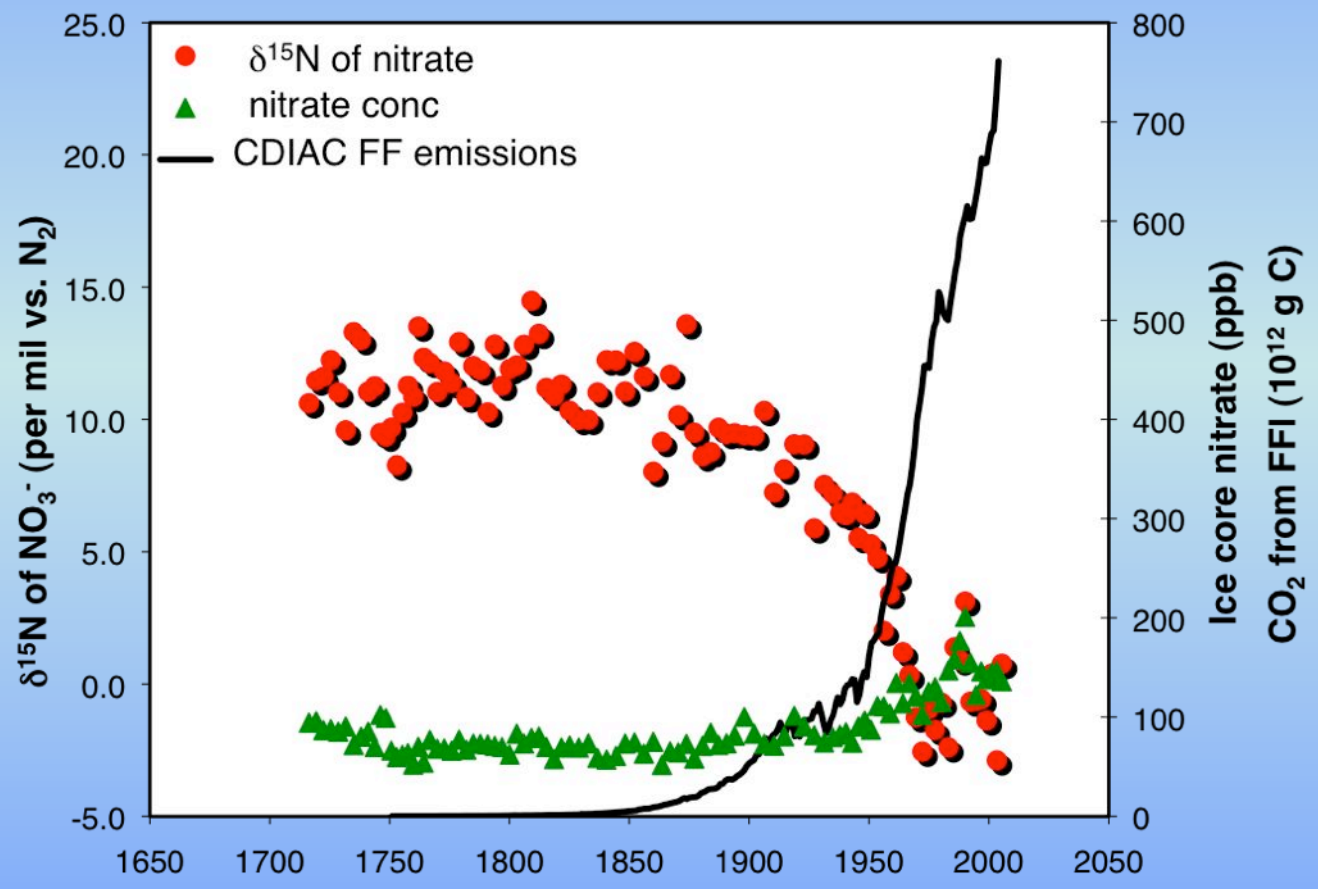
- A clear (negative) trend is found in $\delta^{15}N$ of NO_3^- in recent ice



Hastings et al., 2009

$\delta^{15}N$ of NO_3^- in recent Greenland ice

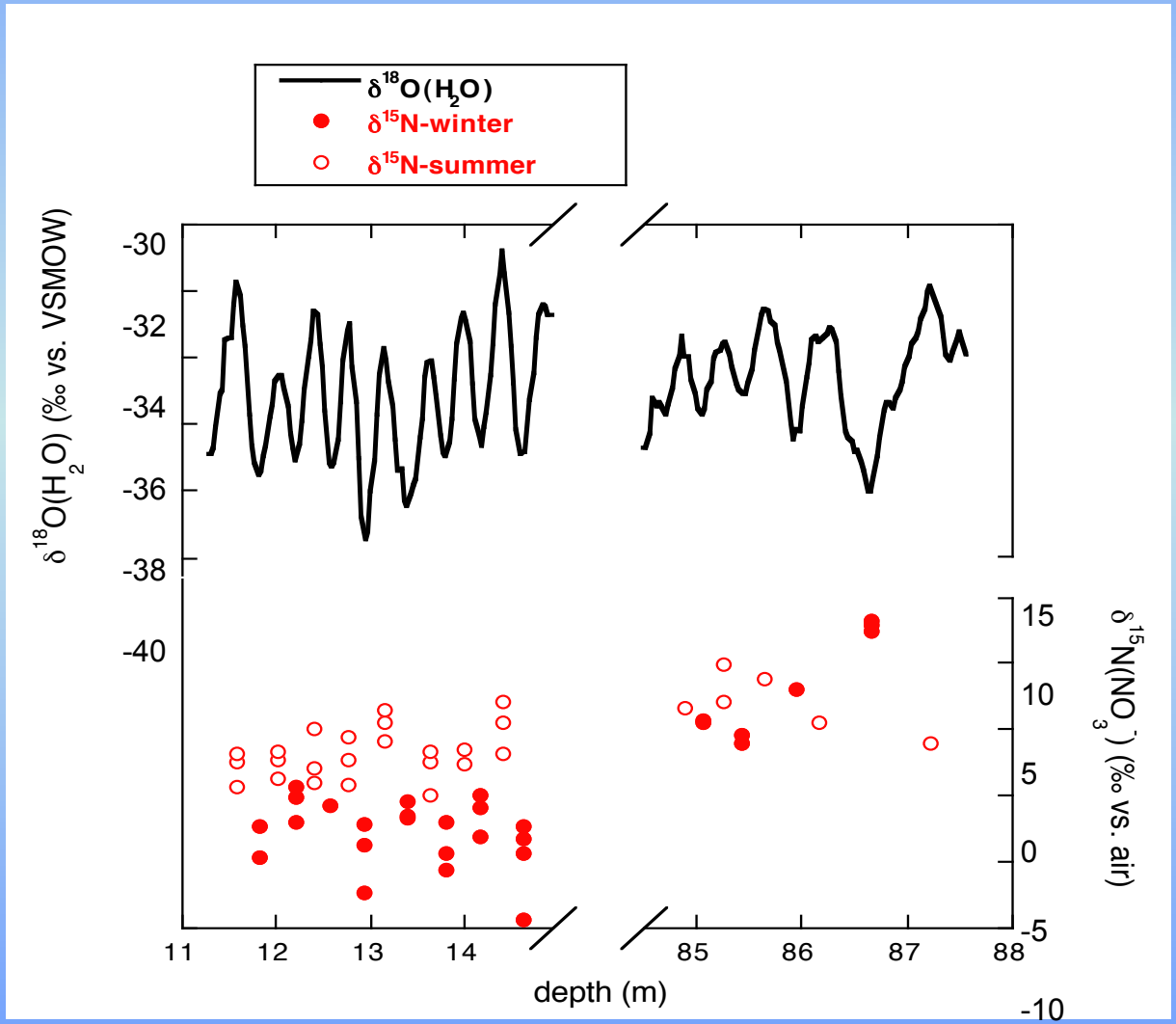
- A clear (negative) trend is found in $\delta^{15}N$ of NO_3^- in recent ice
- This trend closely follows estimates of fossil fuel burning over the last 250 years



Hastings et al., *Science*, 2009

Seasonal changes in $\delta^{15}N$ of NO_3^- in Greenland ice

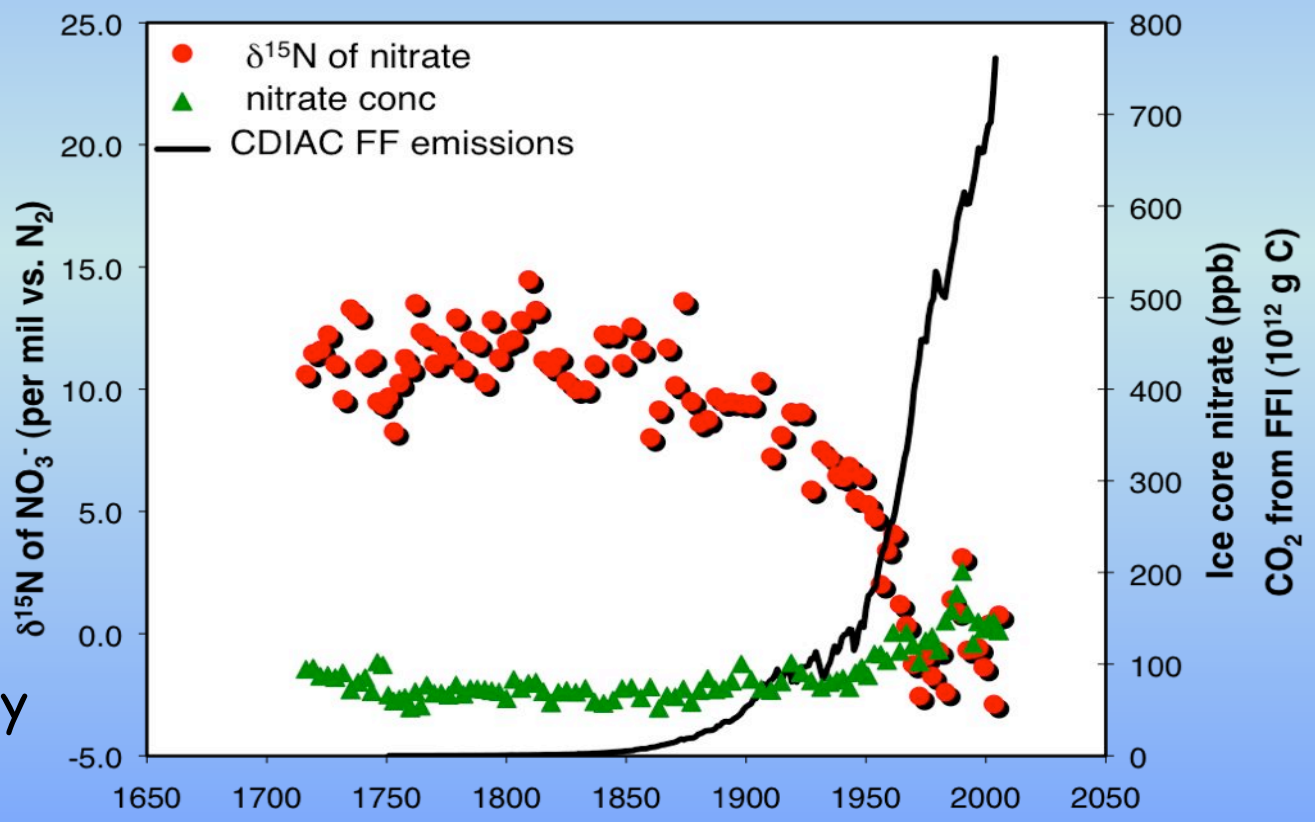
- Recent ice (11-14 m depth) shows similar seasonality to modern snow studies:
  - ↑ $\delta^{15}N$ in **summer**
  - ↓ $\delta^{15}N$ in **winter**
- Limited measurements on pre-industrial ice show no clear seasonality in $\delta^{15}N$



Hastings et al., *Science*, 2009

$\delta^{15}N$ of NO_3^- in recent Greenland ice

- A clear (negative) trend is found in $\delta^{15}N$ of NO_3^- in recent ice
- This trend closely follows estimates of fossil fuel burning over the last 250 years
- Can we quantitatively interpret changes in NOx sources?

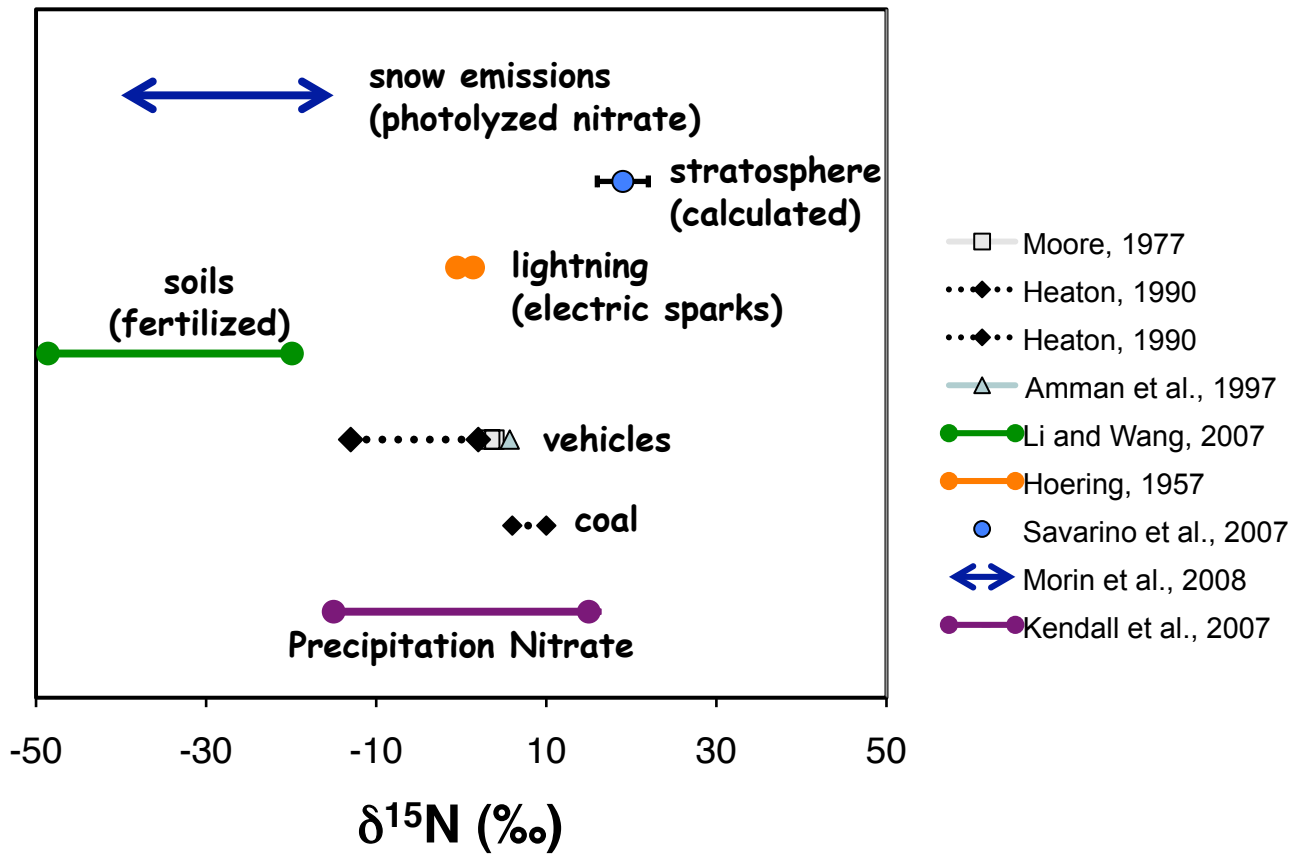


Hastings et al., *Science*, 2009

$\delta^{15}N$ of atmospheric NO_3^-: NO_x Source Signatures?

- NOx from fossil fuels combustion has not been measured recently and there is no published data in N. America

- $\delta^{15}N$ of NOx from biomass burning ??



Conclusions/Implications

- $\delta^{15}N$ of atmospheric NO_3^- shows a clear decrease (-12‰) since 1750 based on results from a Greenland ice core

- The change in $\delta^{15}N$ is best explained by a significant change in the source of NO_3^-, namely the addition of nitrogen oxides (NOx) from fossil fuel combustion

- To use the $\delta^{15}N$ of NO_3^- in ice to quantify NOx source changes we need to know the isotopic source signatures of all NOx sources

- The relatively short lifetime of NOx/NO_3^- should allow us to develop regional pictures of source and chemistry variations over both recent and climate-relevant timescales

- Interpretation of other isotopic records that are impacted by atmospheric NO_3^- should account for variations over time in the isotopic composition of NO_3^-