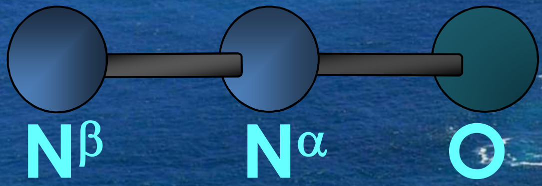
The Isotopic Composition of Nitrous Oxide: Of Microbes and Men



The 5th Asia-Pacific GAW Workshop
on Greenhouse Gases
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The Cape Grim Baseline Air Pollution Station in Tasmania

nature geoscience

LETTERS

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Trends and seasonal cycles in the isotopic composition of nitrous oxide since 1940

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"Fertilizer use responsible for increase in nitrous oxide in atmosphere" UC Berkeley News April 2, 2012

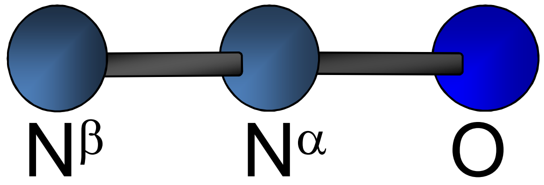
"Fertilizer linked to greenhouse gas rise" United Press International April 2, 2012

UPI.com OVER 100 YEARS OF JOURNALISTIC EXCELLENCE

"Confirming that the N_2O increase is largely due to fertilizer." is not a surprise! There are "much more" which are difficult to distill down to a press release….

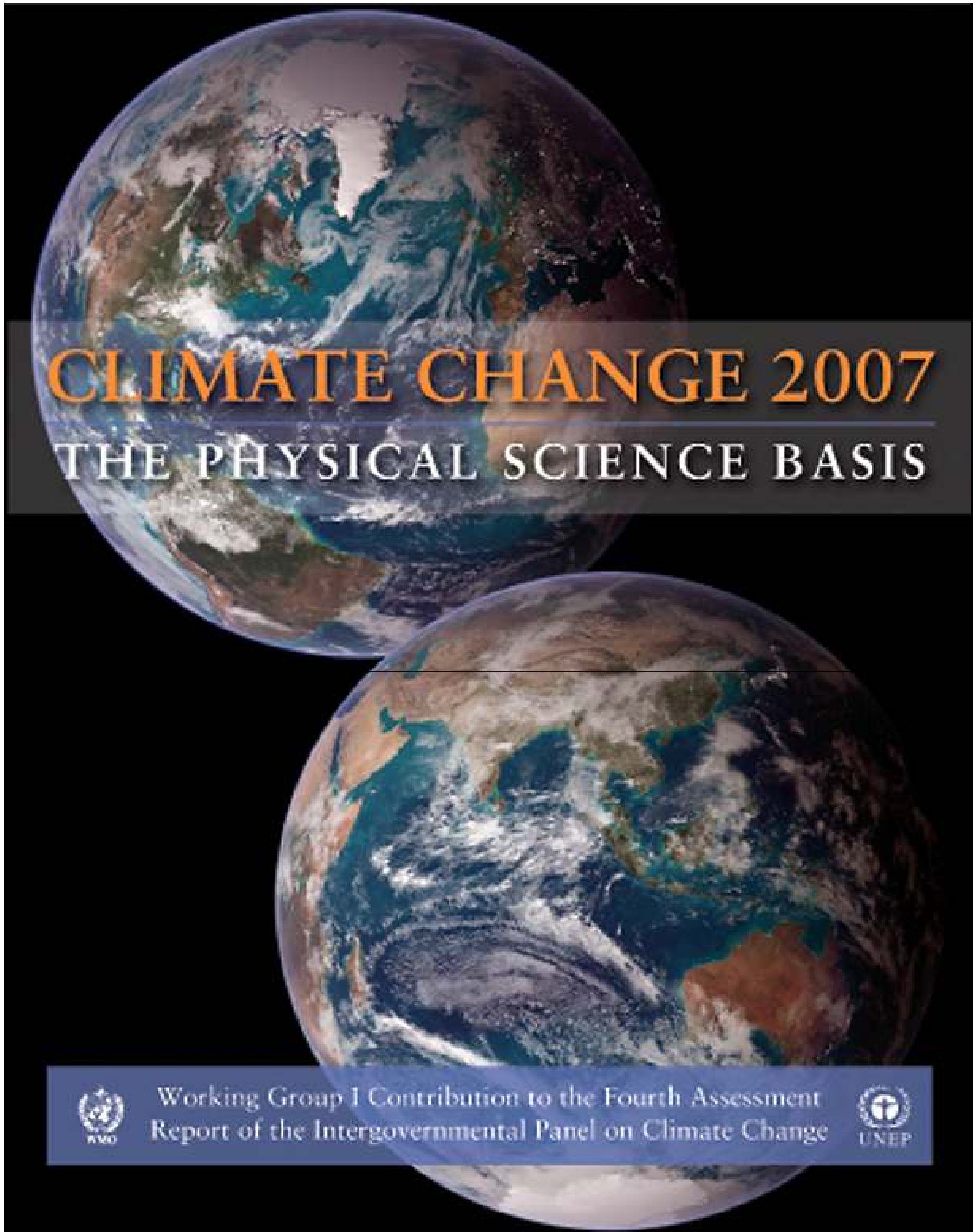
Implications for Trends in the Relative Contributions of Microbial N_2O Production Processes:

Learning from Measurements of the Atmospheric N_2O Isotopic Compositions since 1940



Sunyoung Park (Kyungpook National University), Philip Croteau, Kristie Boering (UC Berkeley); Ray Langenfelds, Paul Steele, Paul Kummel, Cathy Trudinger, David Etheridge, Paul Fraser (CSIRO Marine and Atmospheric Research); Tibisay Perez (IVIC, Venezuela); Kyung-Ryul Kim (SNU)

The 5th Asia-Pacific GAW Workshop on Greenhouse Gases



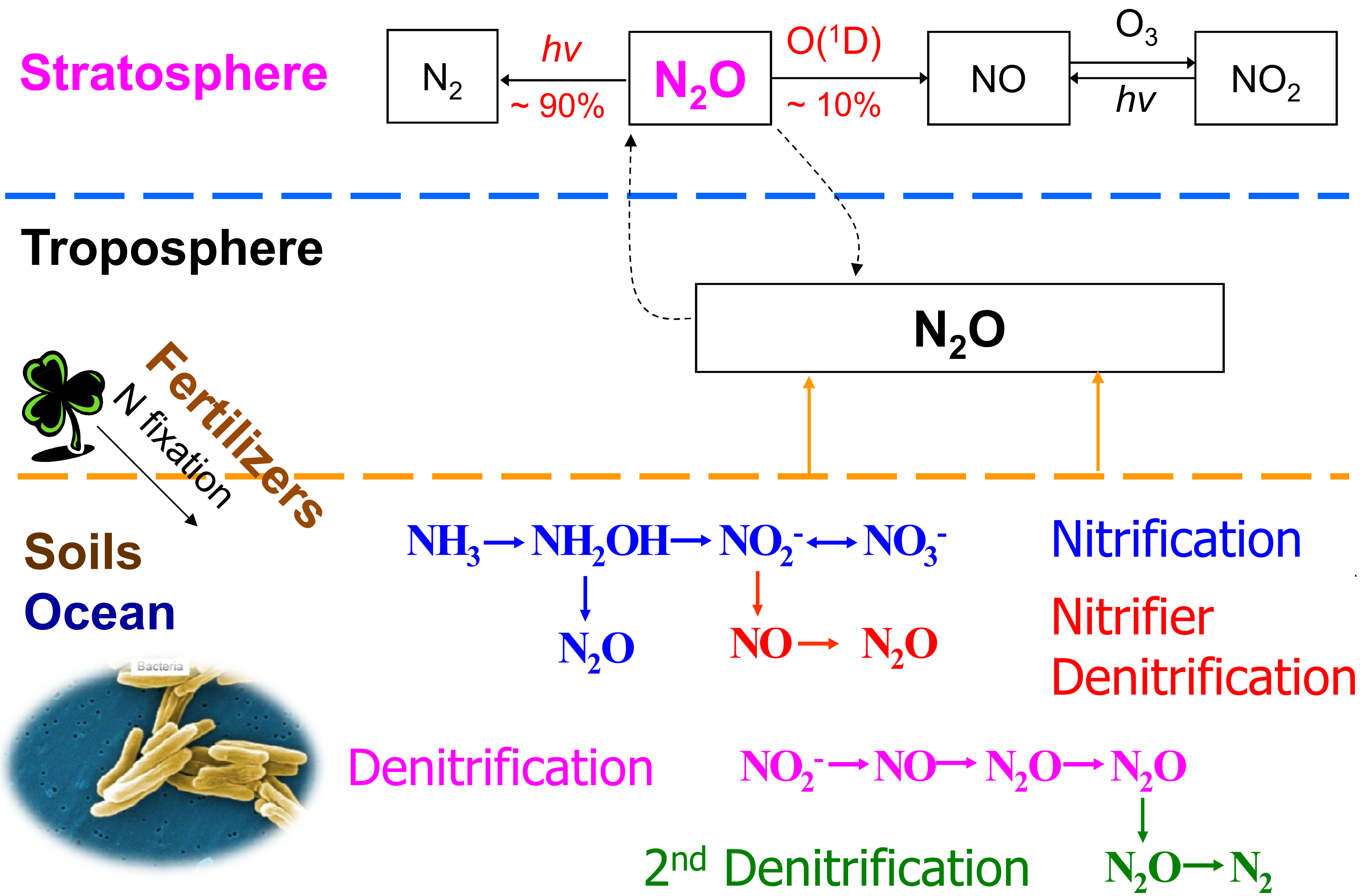
IPCC (2007) "Warming is unequivocal, and most of the warming of the past 50 years is very likely (90%) due to increases in greenhouse gases."

Kyoto Protocol

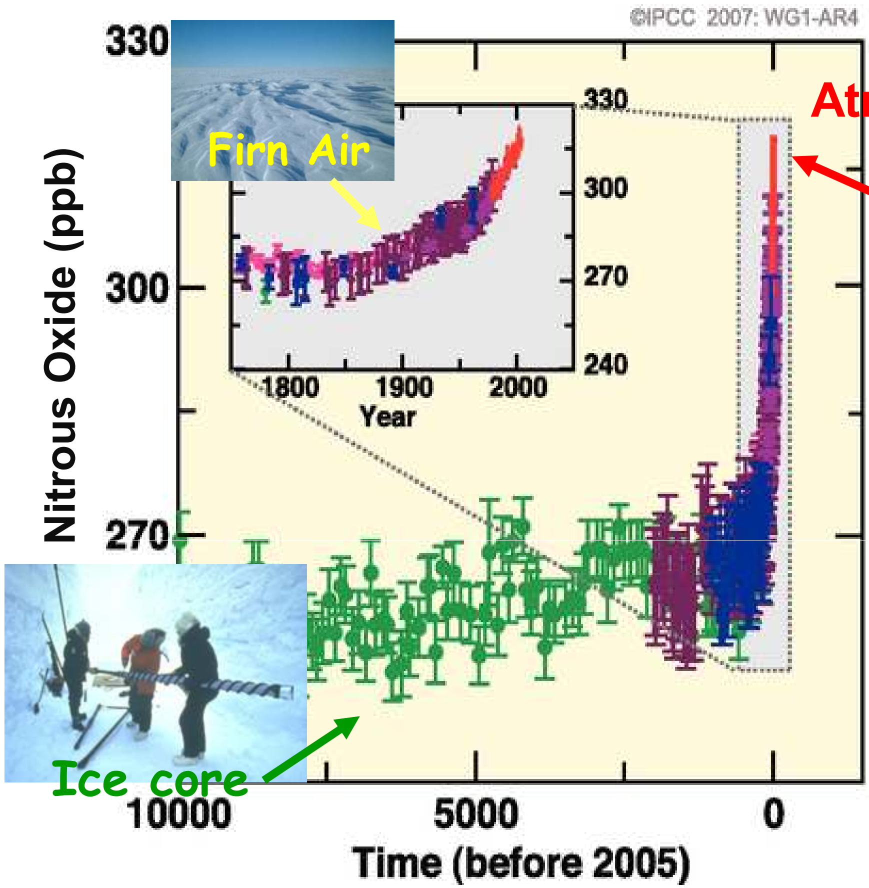
"The greenhouse gases are CO_2, CH_4, N_2O, SF_6, HFCs, and PFCs"

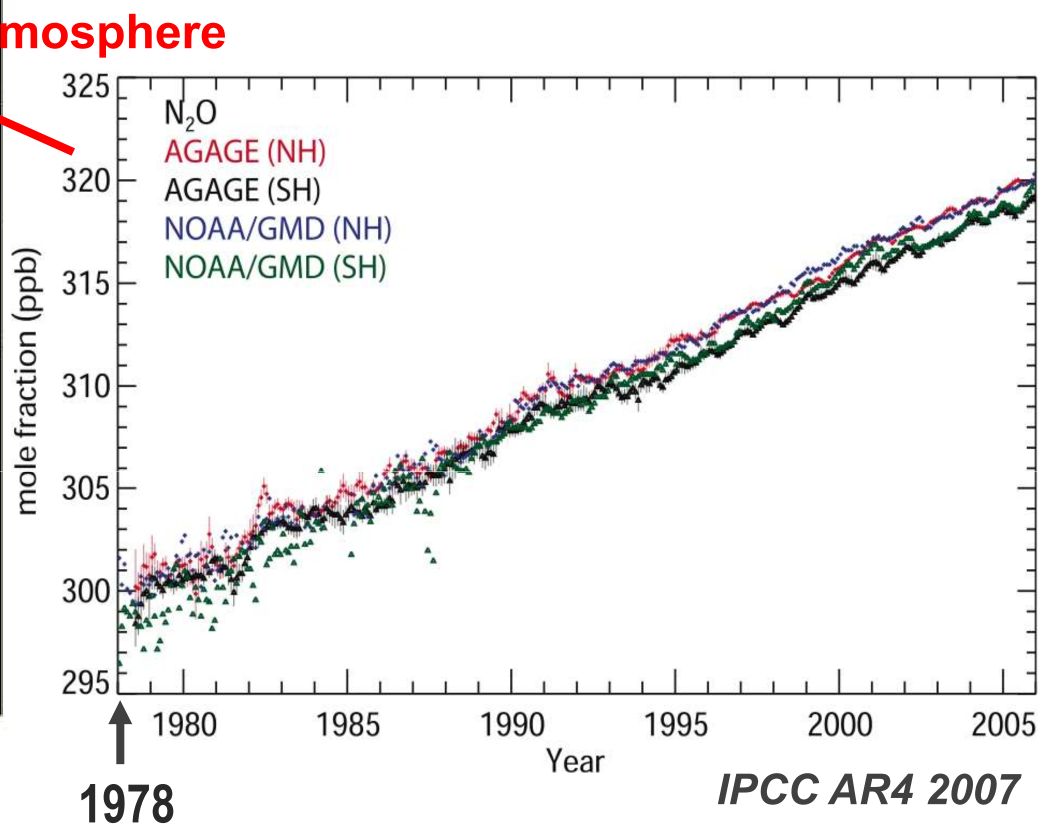
N_2O Sources and Sinks

Greenhouse gas and ozone depleting substance



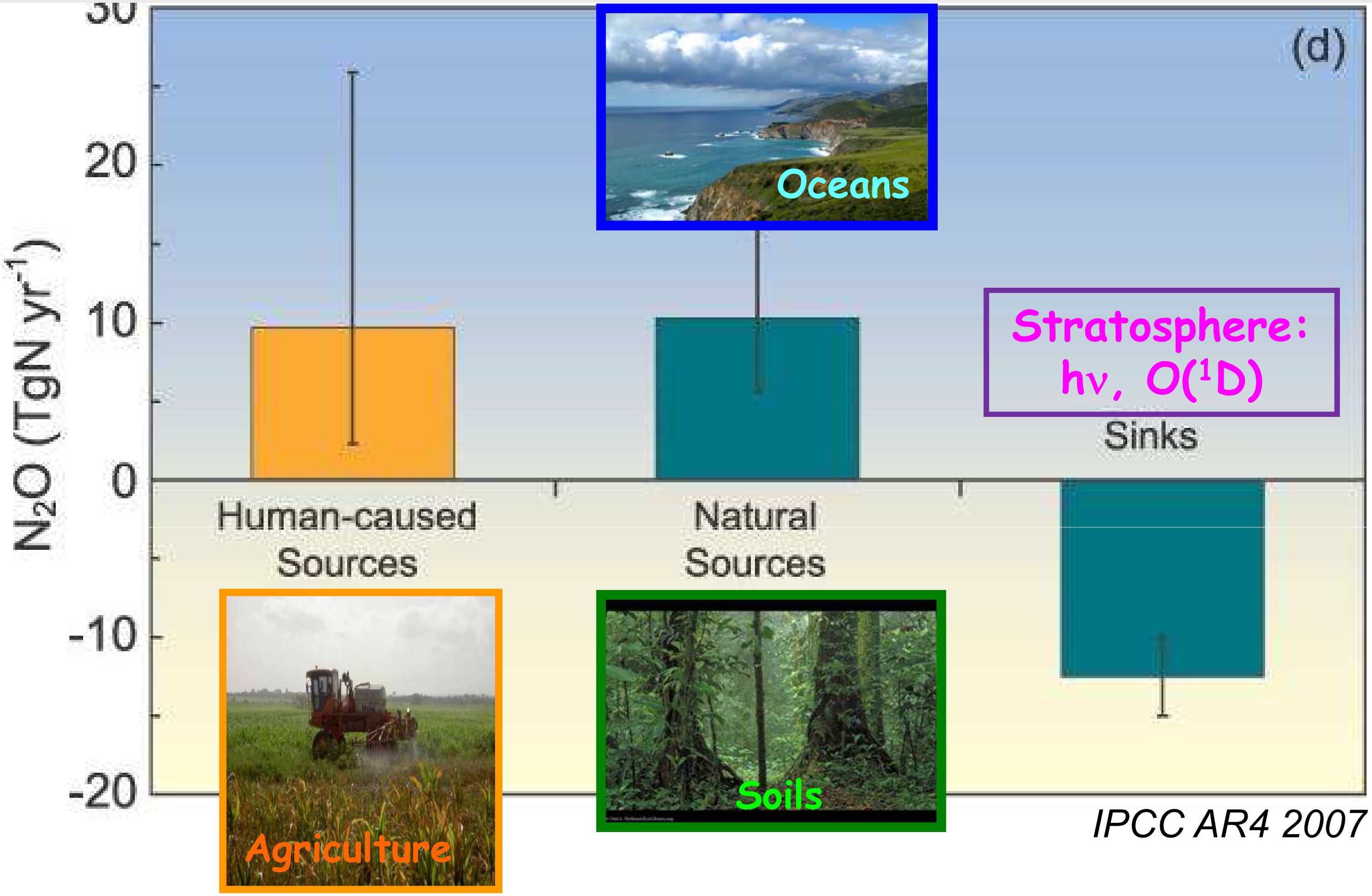
Increasing N_2O concentrations





- Continuing imbalance between *sources and sinks* over time; ***a microbe-human link!***

Global N_2O Budget



IPCC AR4 2007

- Currently, sources exceed sinks by ~ 3 to 5 $TgNyr^{-1}$
- Large uncertainties (± 50% or worse) and qualitative understanding in source fluxes

⇨ An additional tool: **Stable isotopic compositions**

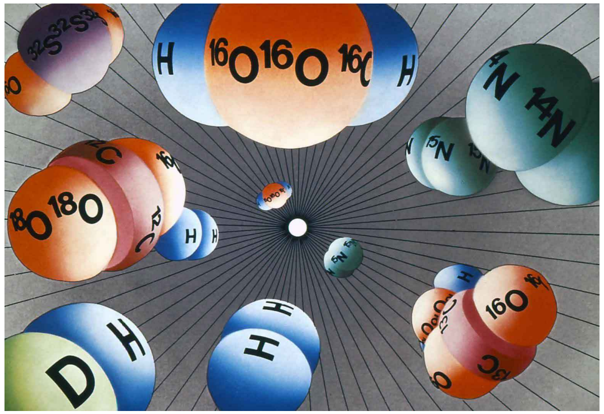
Isotopic composition of N_2O

- Relative abundances:

$^{14}N^{14}N^{16}O$ (mass 44) :	99.4_ _ %
$^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$ (mass 45) :	0.4_ _ %
$^{14}N^{14}N^{18}O$ (mass 46) :	0.2_ _ %

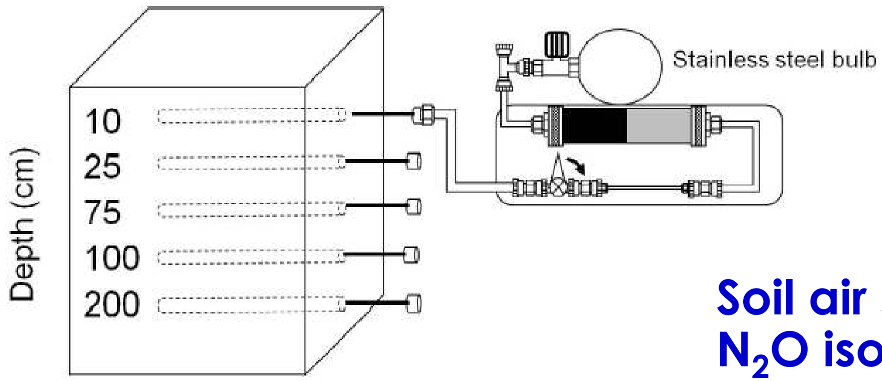
- Diffusion, Phase Changes, Chemical Reactions (including metabolic reactions) act to alter the relative abundances – typically in the decimal places noted in red above ! ***"Isotope Effects" "Isotope Fractionation"***

⇨ *Distinct isotopic signatures of sinks and sources are fingerprints!*

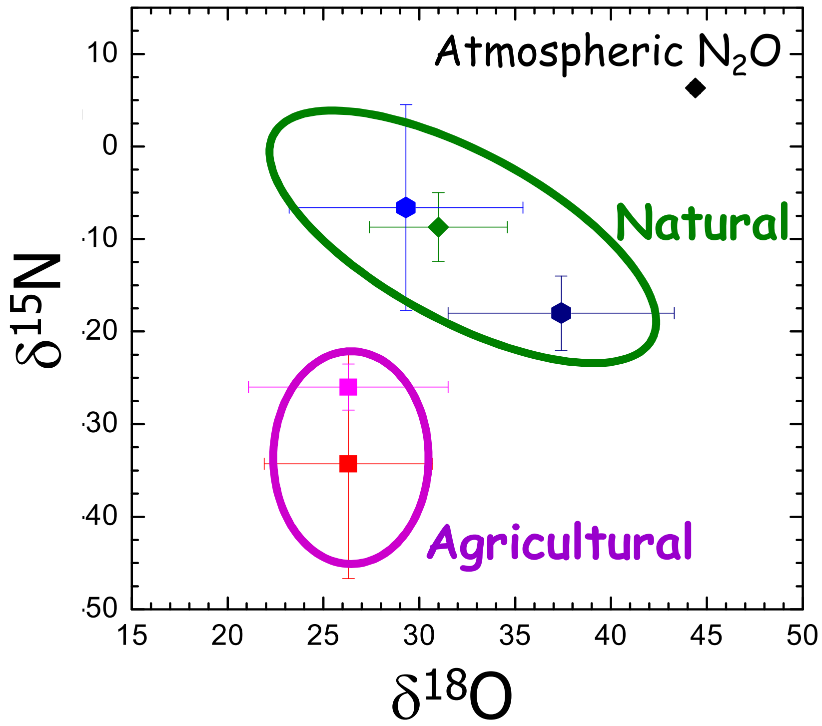


Natural vs. Agricultural soils

Amazon National Forest, Brazil vs. Fertilized Corn Field in Venezuela



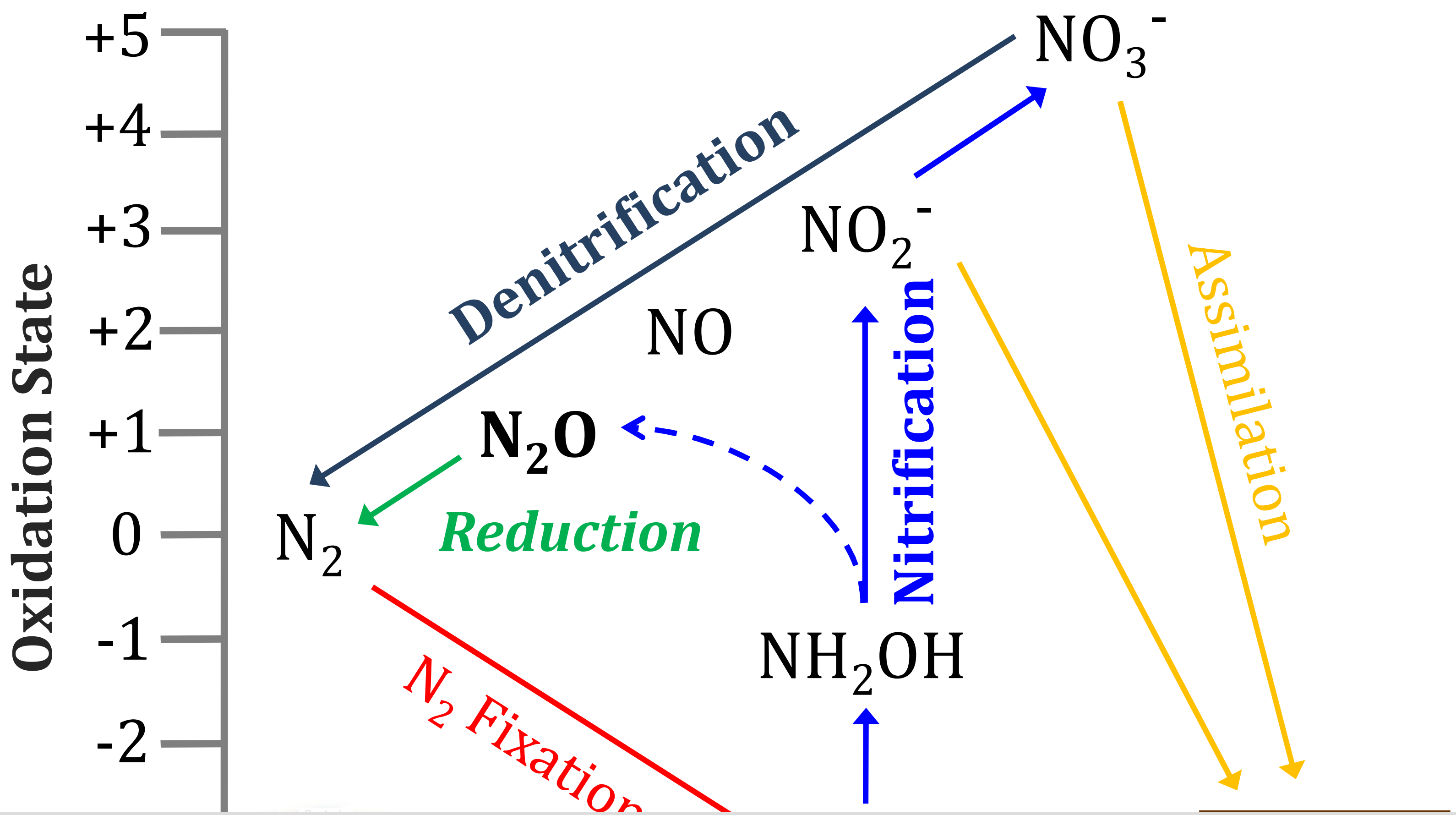
Soil air sampling system for N_2O isotope analysis



- Larger emission of N_2O from N-fertilized agricultural soils and isotopically more depleted N_2O than from natural forest soils

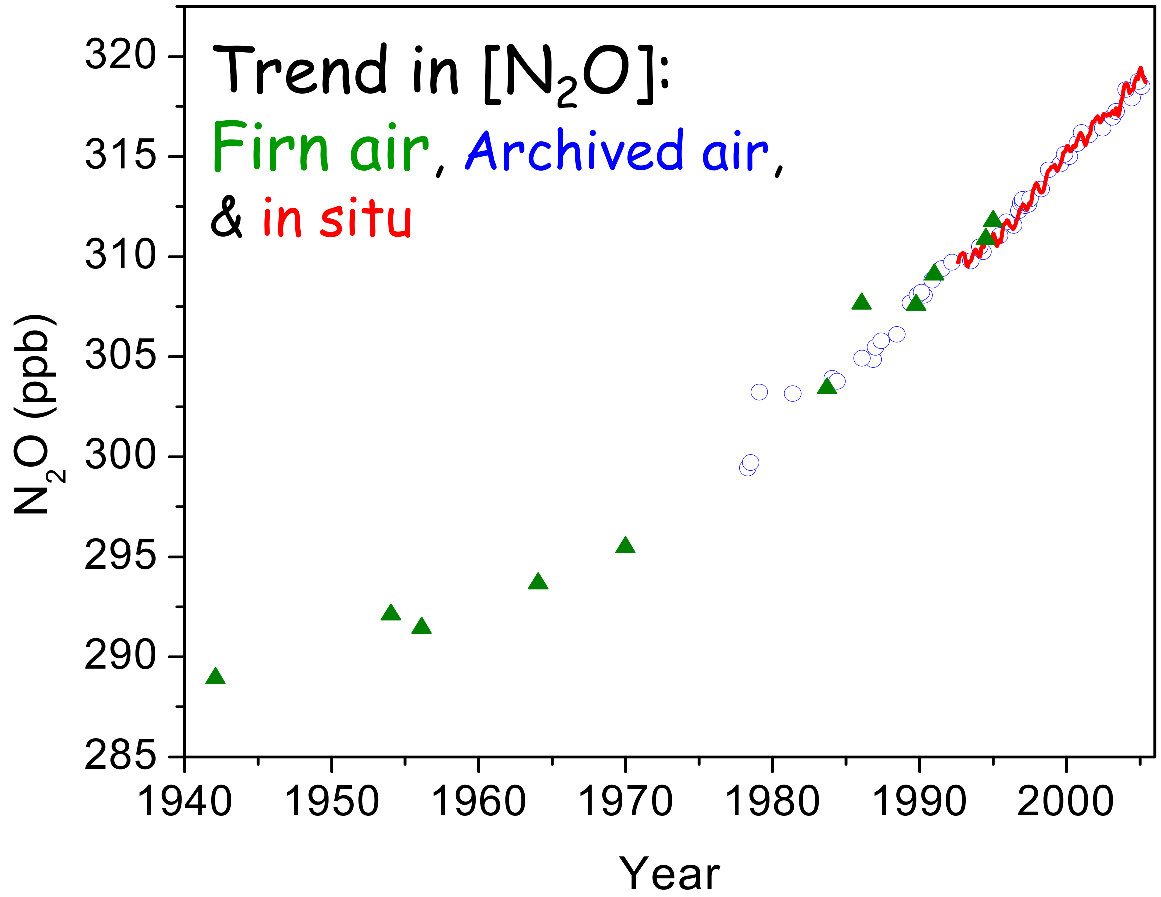
Park et al., Global Biogeochemical Cycles, 2011

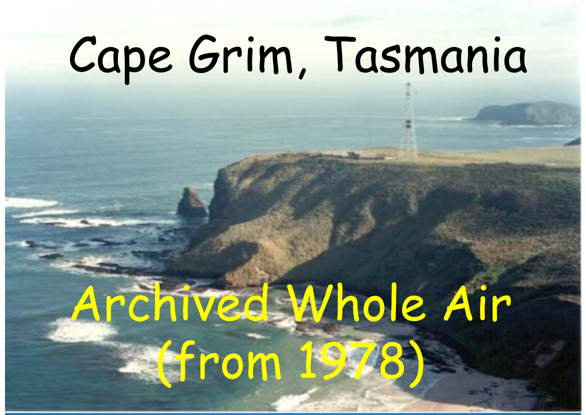
NITROGEN CYCLE



If we have significant contribution of global fertilization to the observed increase in N_2O concentration, we could expect a decreasing trend in isotopic compositions

Trend in atmospheric N_2O isotopic compositions:
Investigating "integrated" N_2O sources

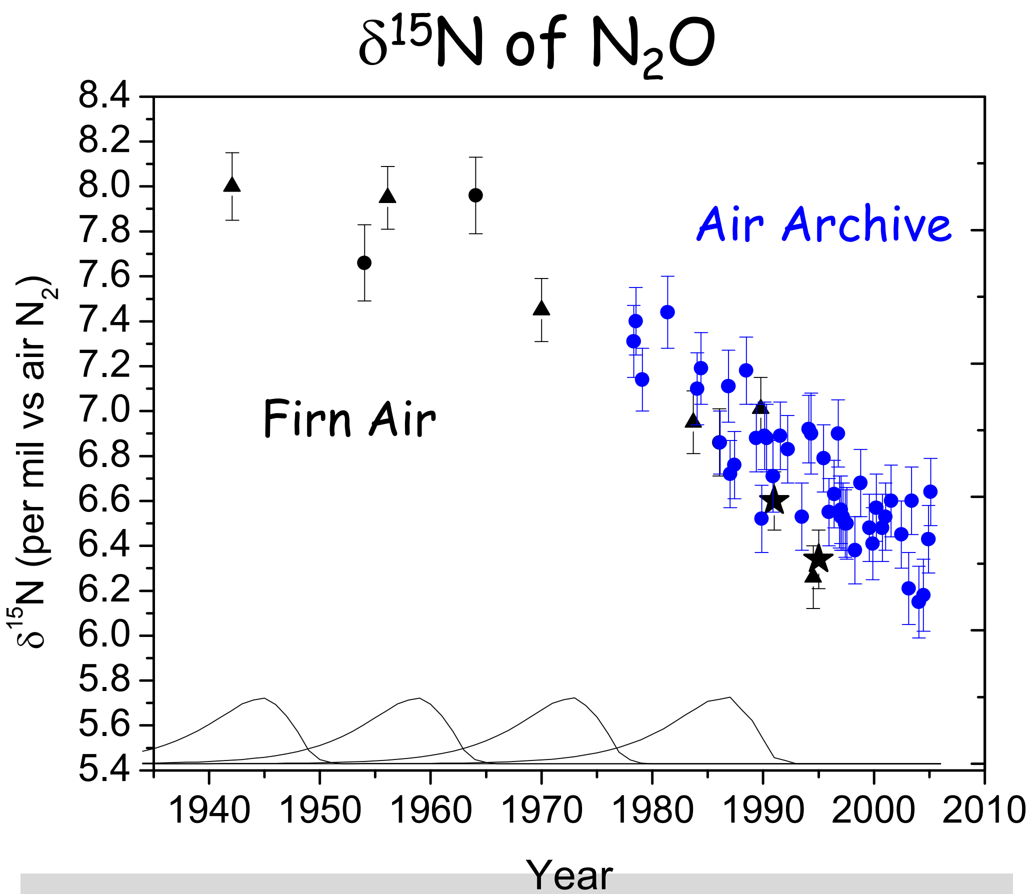


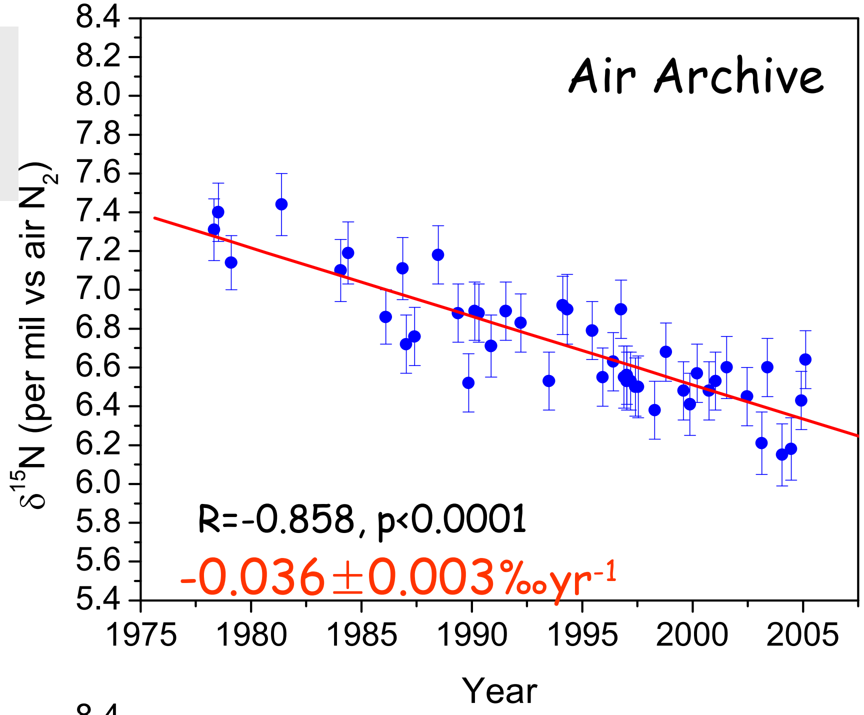


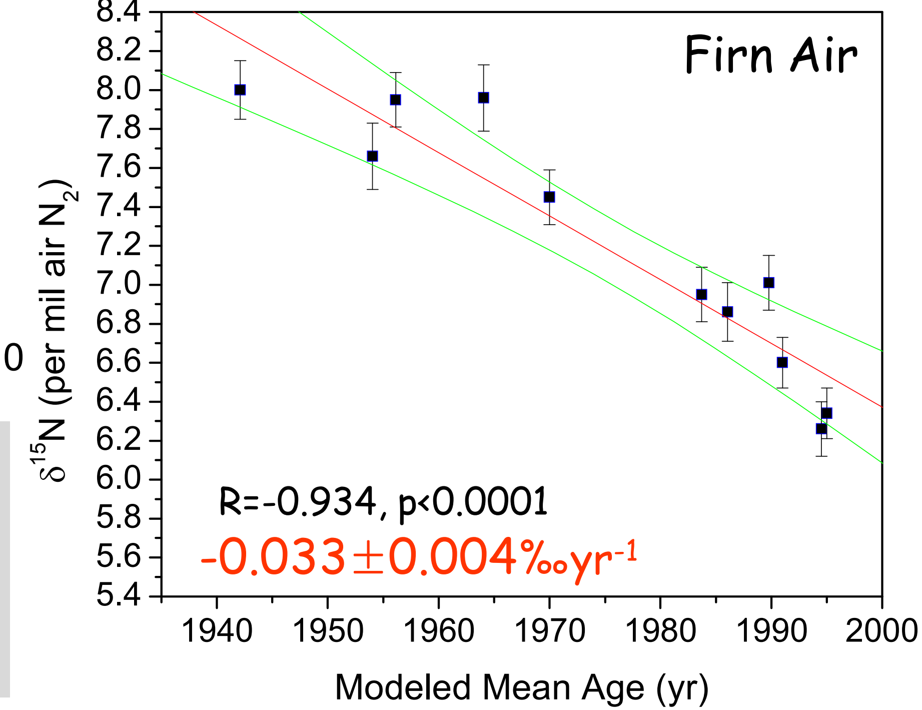
- Isotopic compositions of N_2O ($\delta^{18}O$, $\delta^{15}N$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$) measured by continuous-flow IRMS at UC Berkeley

Park et al, Nature Geoscience, 2012

Observed trend in N_2O isotope composition for the last 65 years



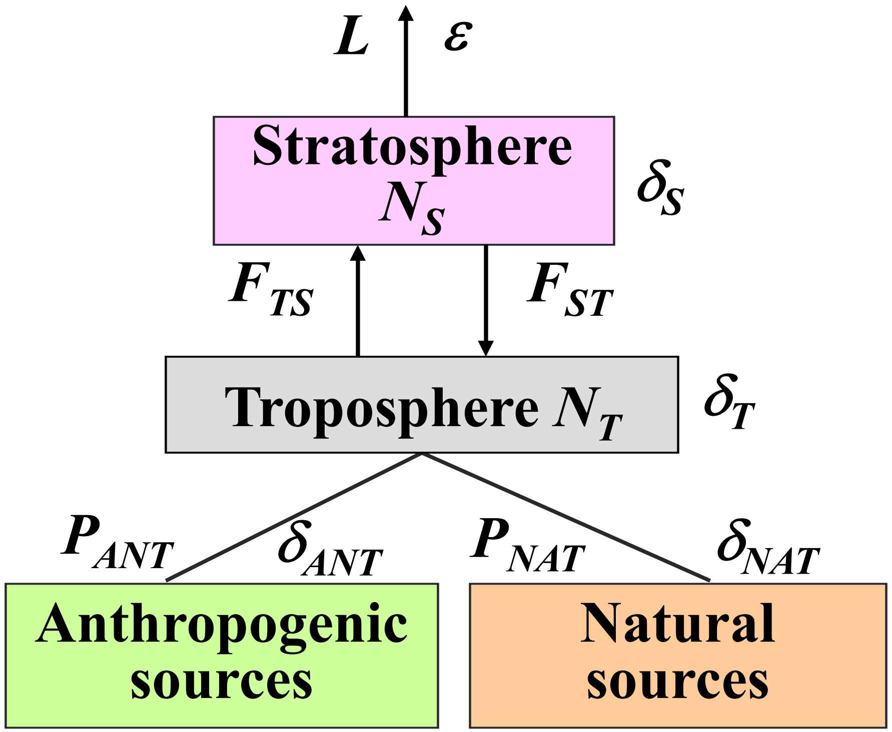




- Significant negative trends: Atmospheric N_2O is increasingly depleted in ^{15}N and ^{18}O, as expected from light sources. *N_2O "Suess effect"*

Natural vs. Anthropogenic N_2O sources?

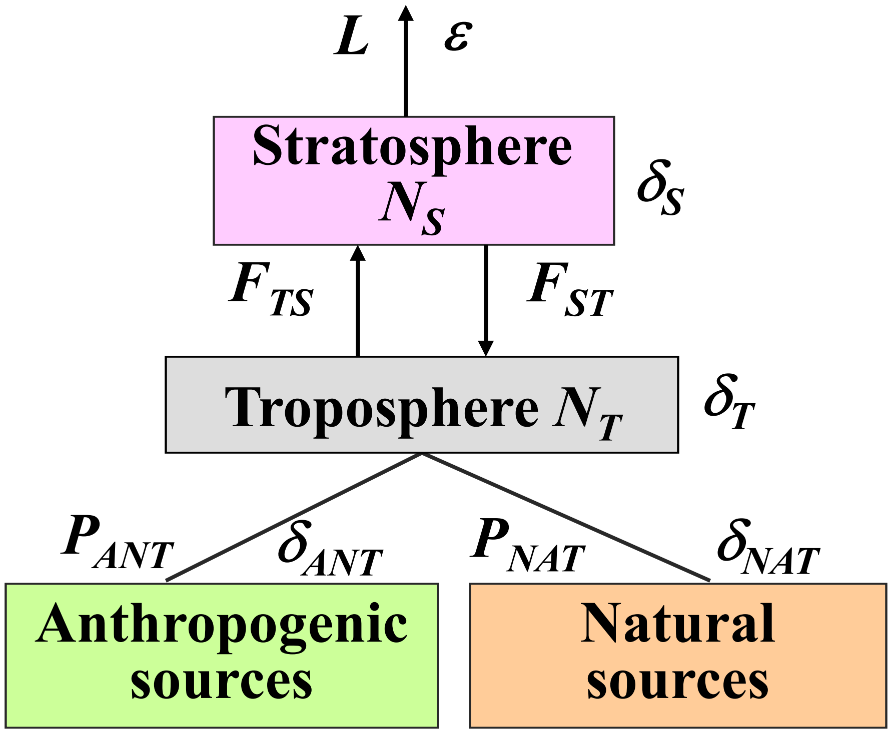
Two Box Model

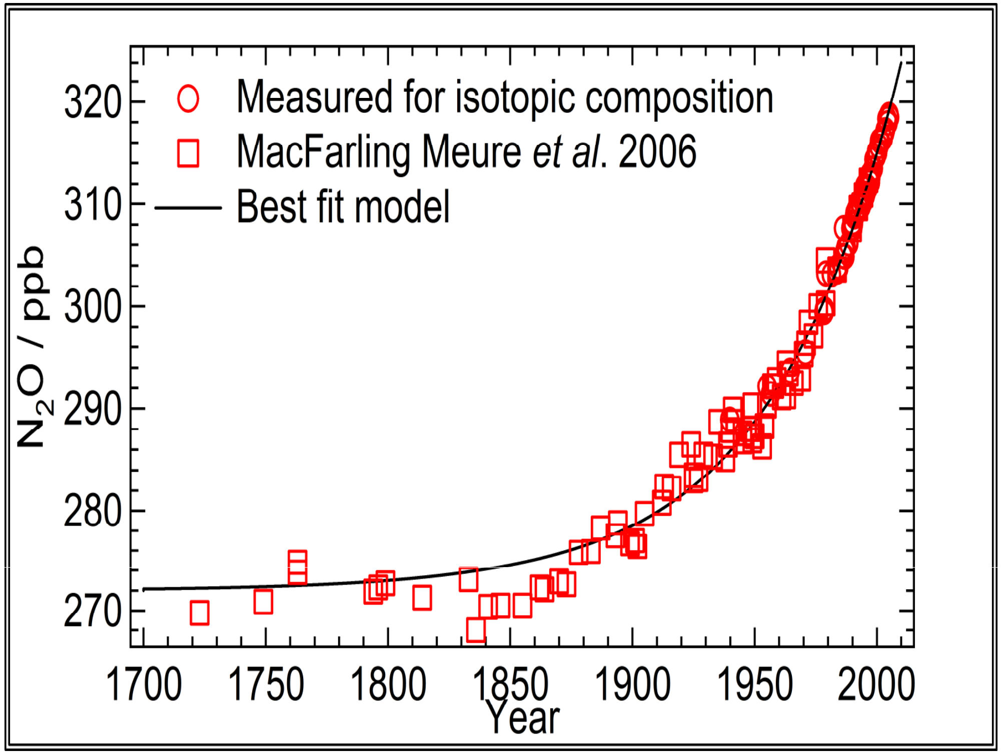


L: Minschwaner et al., 1993;
F_{TS} and F_{ST}: Holton et al., 1995;
ε and δ_S: Park et al., 2004

Park et al, Nature Geoscience, 2012

Two Box Model

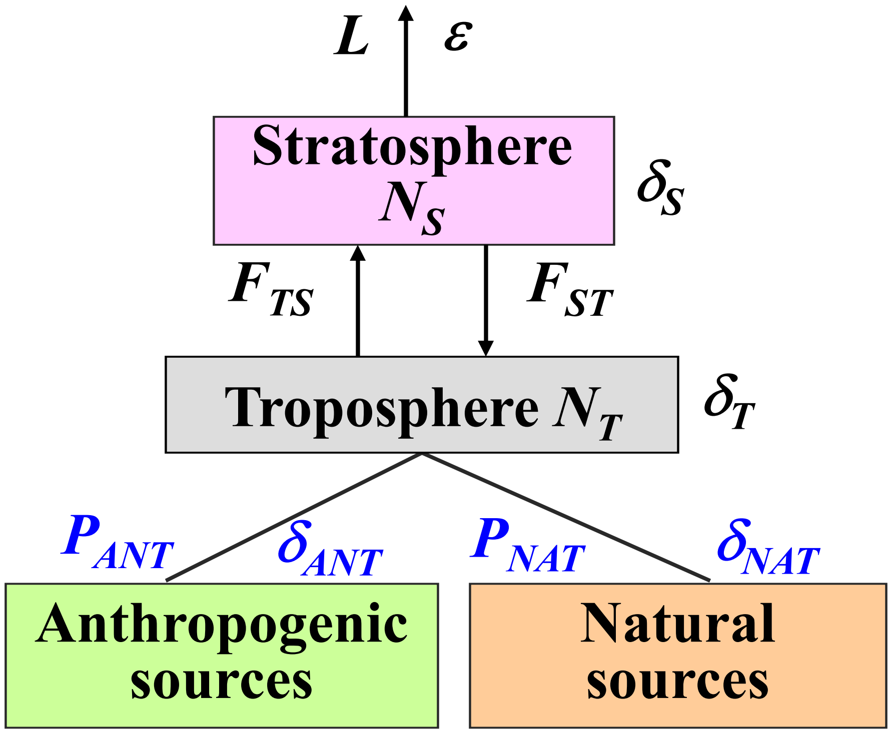


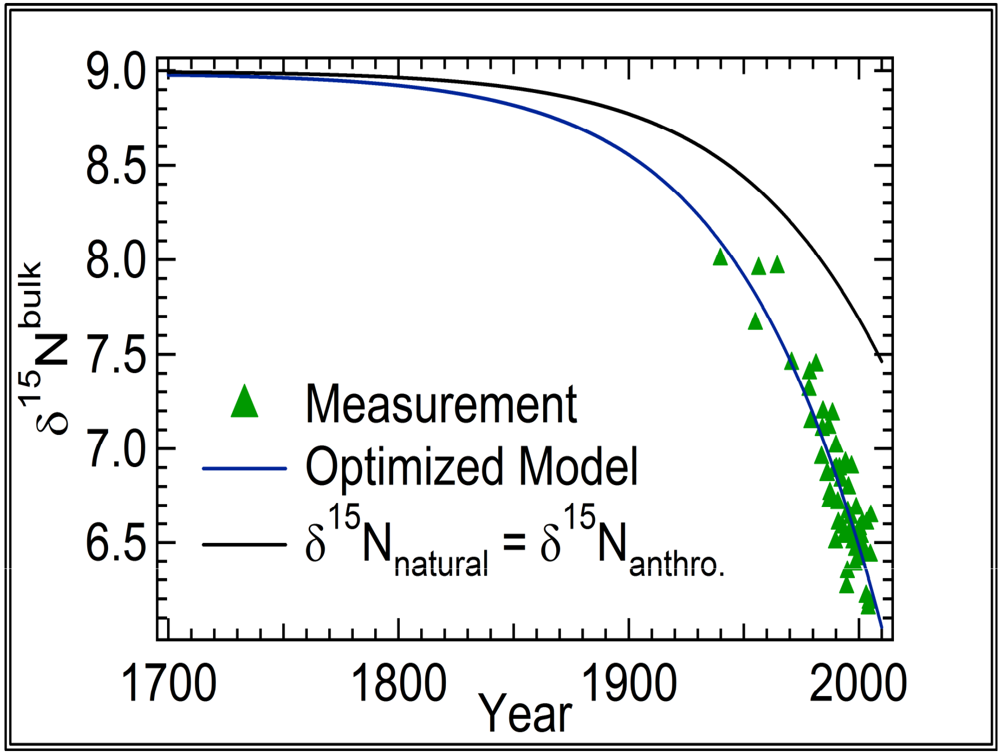


$P_{NAT} = 11.1(\pm 5)\ TgNyr^{-1}$ and $P_{ANT} = 6.6(\pm 5)\ TgNyr^{-1}$

Park et al, Nature Geoscience, 2012

Two Box Model





	Anthropogenic	Natural
$\delta^{15}N$	–15.6 (±1.2)	–5.3 (±0.2)

Park et al, Nature Geoscience, 2012

Model Summary: Implied Global Averages

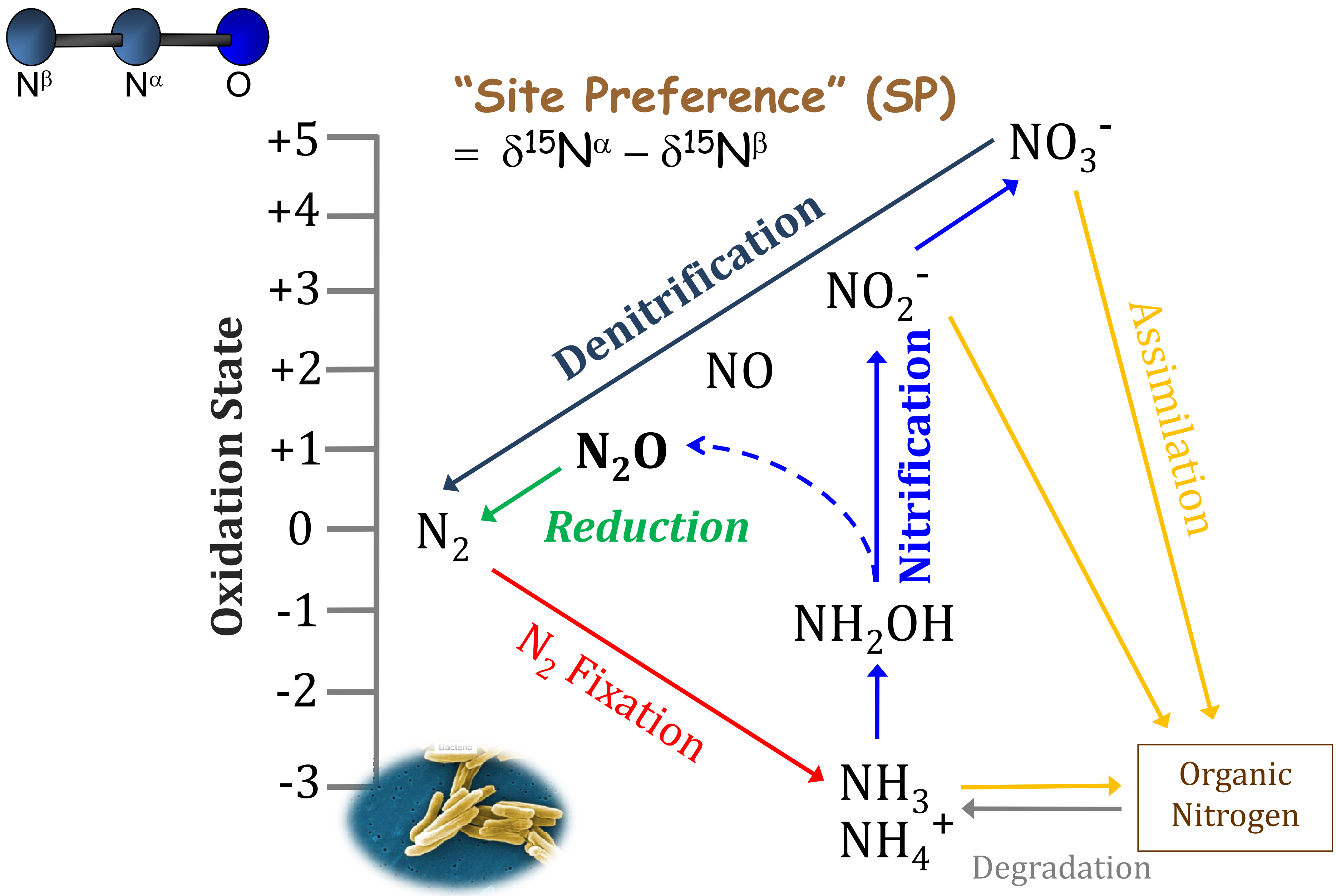
Isotopologue	**Linear Trend** (‰/yr) Deseasonalized Archive Data	δ_{ANT} (‰) Box Model	δ_{NAT} (‰) Box Model
$\delta^{15}N$	-0.035 (±0.002)	-15.6 (±1.2)	-5.3(±0.2)
$\delta^{18}O$	-0.022 (±0.004)	32.0 (±1.3)	32.0 (±0.2)
$\delta^{15}N^{\alpha}$	-0.026 (±0.013)	-7.6 (±6.2)	-3.3 (±1.0)
$\delta^{15}N^{\beta}$	-0.046 (±0.015)	-20.5 (±7.1)	-7.5 (±1.1)
Site Preference	+0.028 (±0.028)	13.1 (±9.4)	4.2 (±1.5)

- The trends imply an anthropogenic source that is isotopically lighter than the average of the natural sources, consistent with agricultural emissions of N_2O playing a large role.

Park et al, Nature Geoscience, 2012

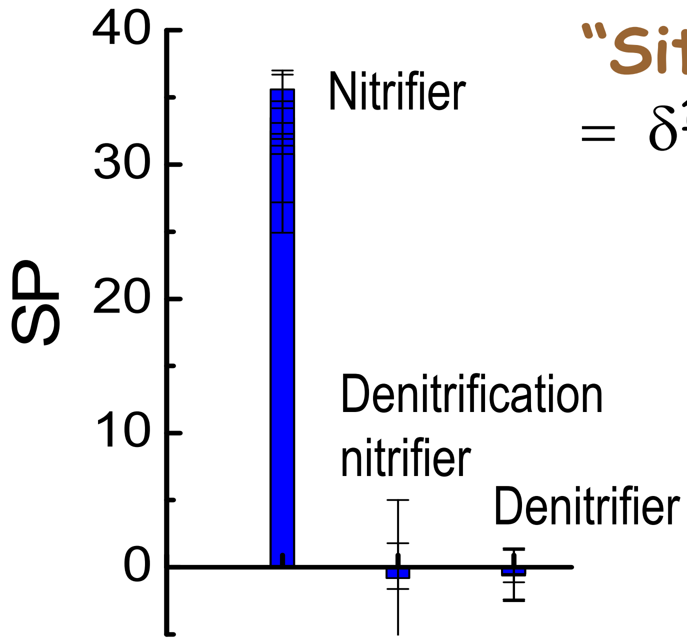
Nitrification vs. Denitrification ?

Nitrification vs. Denitrification



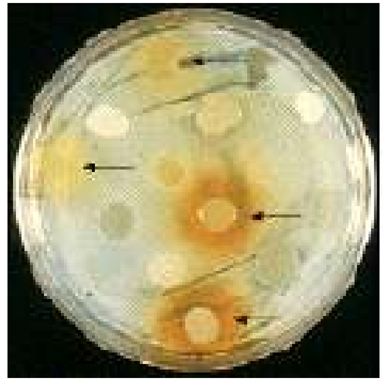
Nitrification vs. Denitrification

- <u>Pure bacteria cultures in lab</u>



"Site Preference" (SP)

$= \delta^{15}N^{\alpha} - \delta^{15}N^{\beta}$



M. capulatus, N. europaea, N. multiformis, M. trichosporium, P. chloropaphis, P. aureofaciens, P. stutzeri, and P. denitrificans
[Stuka et al., 2003, 2006, Ostrom et al., 2007]

"SPs of ~33‰ and ~0‰ are characteristic of nitrification and denitrification, respectively, and provide a basis to quantitatively apportion N_2O" - Stuka et al., 2006

(We refer to nitrification as the <u>oxidation of ammonia</u>, whereas, denitrification refers <u>nitrate or nitrite reduction</u> regardless of whether or not reduction is carried out by nitrifying or denitrifying bacteria)

Model Summary: Implied Global Averages

Isotopologue	**Linear Trend** (‰/yr) Deseasonalized Archive Data	δ_{ANT} (‰) Box Model	δ_{NAT} (‰) Box Model
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SP of anthropogenic N_2O > SP of natural N_2O

Estimates of the relative contributions of nitrification and denitrification to *global* microbial N_2O production

(1) $SP_{NAT} = F_{Nit\_NAT} \cdot SP_{Nit} + (1 - F_{Nit\_NAT}) \cdot SP_{Denit} = 4.2 \pm 1.5$ ‰

$SP_{ANT} = F_{Nit\_ANT} \cdot SP_{Nit} + (1 - F_{Nit\_ANT}) \cdot SP_{Denit} = 13.1 \pm 9.4$ ‰

$SP_{Nit} = 33 \pm 5$‰ $SP_{Denit} = 0 \pm 5$‰

Fraction of Nitrification in Anthropogenic N_2O (F_{Nit_ANT}) = 40(±29)%;

Fraction of Nitrification in Natural N_2O (F_{Nit_NAT}) = 13(±5)%

← *Nitrification fraction in preindustrial time*

(2) Given $P_{NAT} = 11.1(\pm 5)$ $TgNyr^{-1}$ and $P_{ANT} = 6.6(\pm 5)$ $TgNyr^{-1}$

$$F_{Nit\_Total} = (F_{Nit\_NAT} \cdot P_{NAT} + F_{Nit\_ANT} \cdot P_{ANT}) / (P_{NAT} + P_{ANT})$$

$$= 23 \pm 13 \%$$

The fraction of all N_2O from the nitrification is 23(±13)% at the present time.

Estimates of the relative contributions of nitrification and denitrification to *global* microbial N_2O production

The relative contribution of nitrification versus denitrification to global microbial N_2O production has increased by ~10% from preindustrial times to the present.

Some caveats:

I. All N_2O is produced by nitrification and denitrification.

II. SP has not been altered by N_2O reduction and fungal activities.

III. Bacteria culture measurements of SP during N_2O production from nitrification (33±5‰) vs. denitrification (0±5‰) are globally relevant. Oceanic and soil bacteria behave similarly.

- *Process-based observations of N_2O isotopic compositions produced from oceanic bacteria at higher precision must help further quantify how N_2O production processes have changed over time.*

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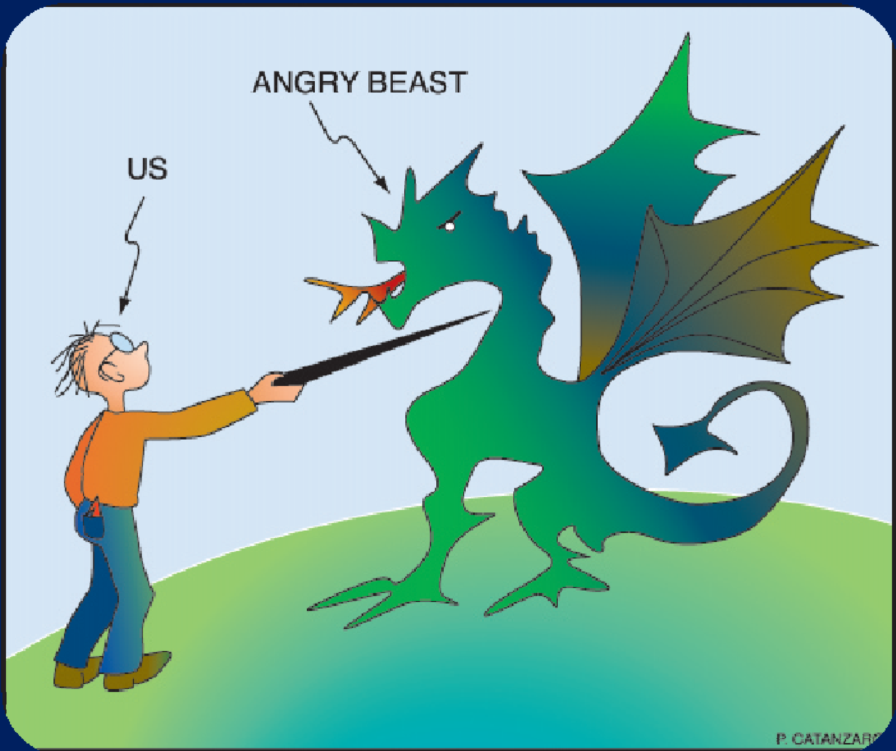
"much more"

- ✓ Increasing trend in the N_2O site preference (SP) suggests that the relative contribution of nitrification to *global* microbial N_2O production has increased from 13% in 1700 to 23% in 2005, in combination with the microbial SP values.
- ✓ Seasonal and interannual variations in N_2O isotopic compositions are detectable, and **contribution of oceanic source component** to the N_2O variations may be inferred from the seasonality.
- ✓ Additional long-term observations of N_2O isotopic compositions at higher precision must help further quantify how N_2O production processes have changed over time.

- Increase of greenhouse gases due to human activities has and will continue to have an impact on climate; while important details remain to be worked out.
- More observations and analysis of natural greenhouse gases and their isotopic compositions at higher precision must help complete our mechanistic understanding of their biogeochemical cycles.

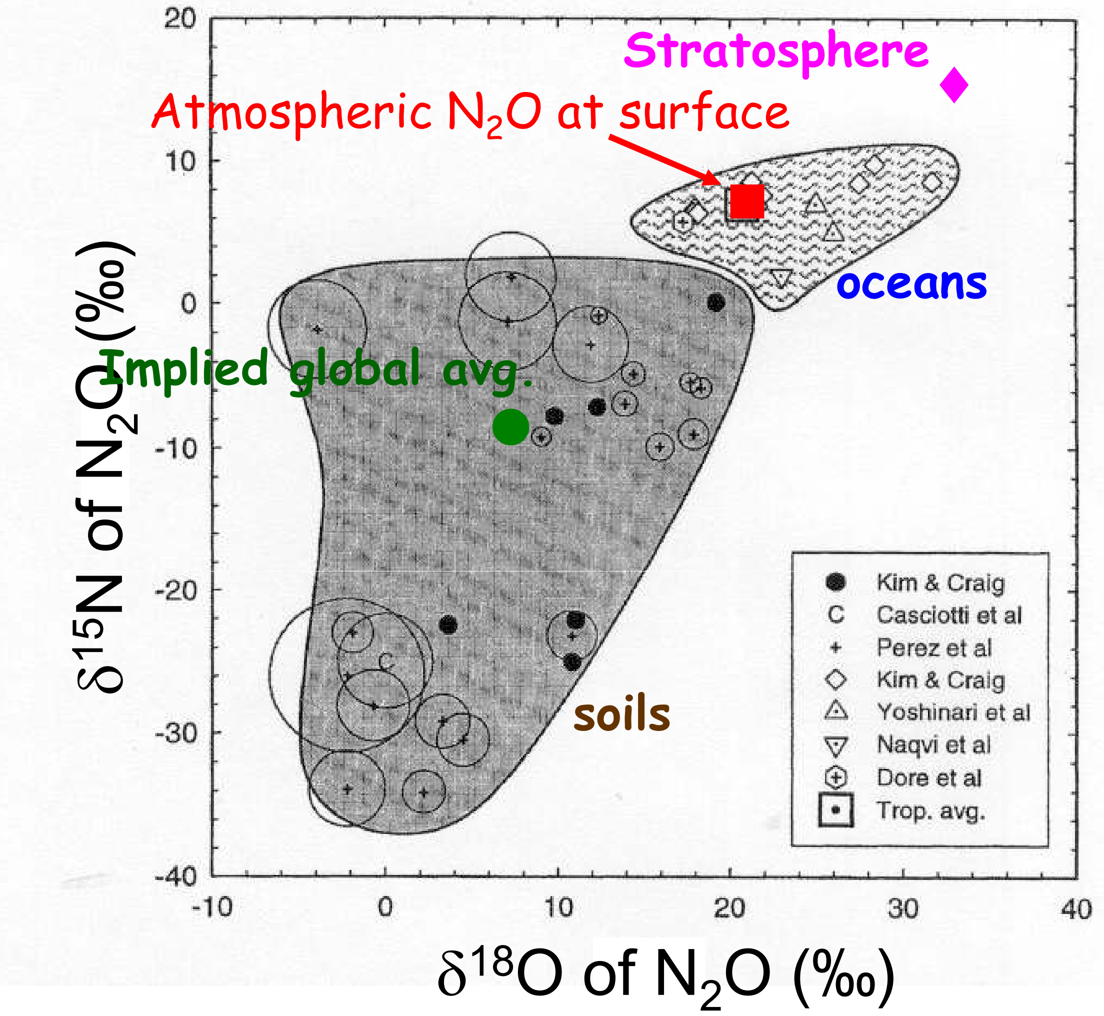


" By adding greenhouse gases to the atmosphere we are poking an angry beast!"

– Wallace Broecker

감사합니다

N_2O Isotopes



From Rahn & Wahlen 2000

Light sources:
Enzymatic microbial processes in **soils** & **oceans**

Burning and manufacturing sources:
Residual N_2O of burning plumes is slightly depleted, but similar to atmospheric N_2O

Heavy sinks:
Photolysis and reaction w/O(^{1}D) in **stratosphere** (large kinetic isotope effect)

"Top-down approach"
Implied global average
for surface sources

- Isotopic compositions of N_2O sources are left as the remaining largest uncertainties in the global N_2O isotope budget.

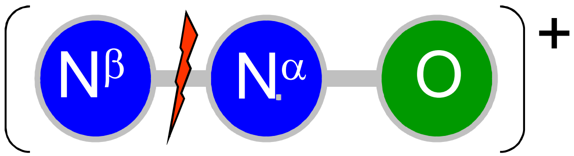
Isotopic composition of N_2O

- Measure on an isotope ratio mass spectrometer the mass-to-charge ratios 45/44 and 46/44 for N_2O^+

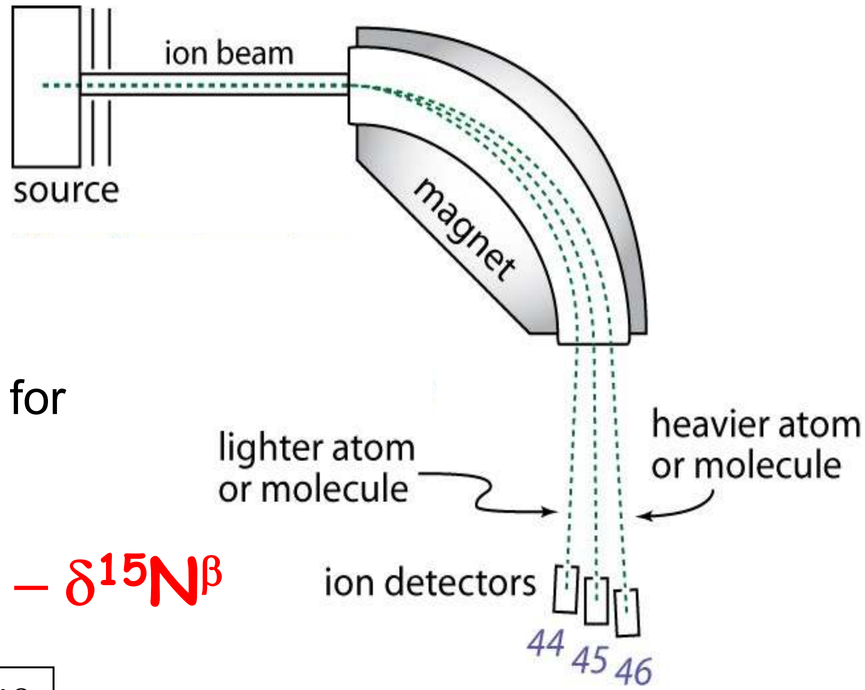
$$\delta^{15}N = \left[\frac{(^{15}N/^{14}N)_{sample}}{(^{15}N/^{14}N)_{std}} - 1 \right] * 1000$$

in parts per thousand
or "per mil" ≡ ‰
And similarly for $\delta^{18}O$…

"Site-Specific" Isotopic Composition of N_2O



- Measure the mass-to-charge ratio 31/30 for the NO^+ fragment ion from N_2O^+



Site Preference (SP) $= \delta^{15}N^{\alpha} - \delta^{15}N^{\beta}$

→ $\delta^{15}N$, $\delta^{18}O$, $\delta^{15}N^{\alpha}$, and $\delta^{15}N^{\beta}$