Isotopic measurements of greenhouse gases at mountain sites: *Opportunities and challenges*

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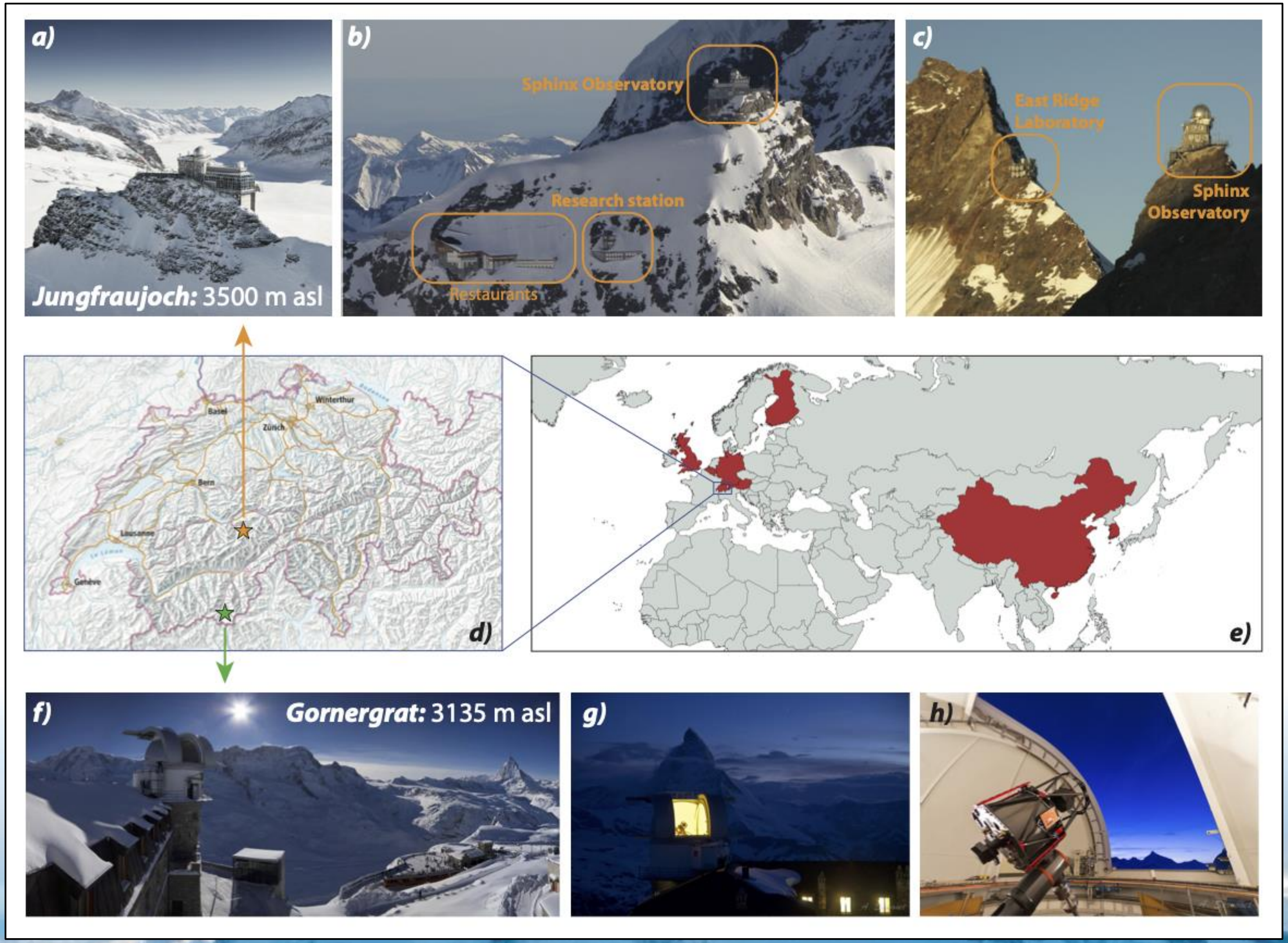

- Support high-altitude scientific research, including environmental monitoring and long-term datasets

Measuring clean air

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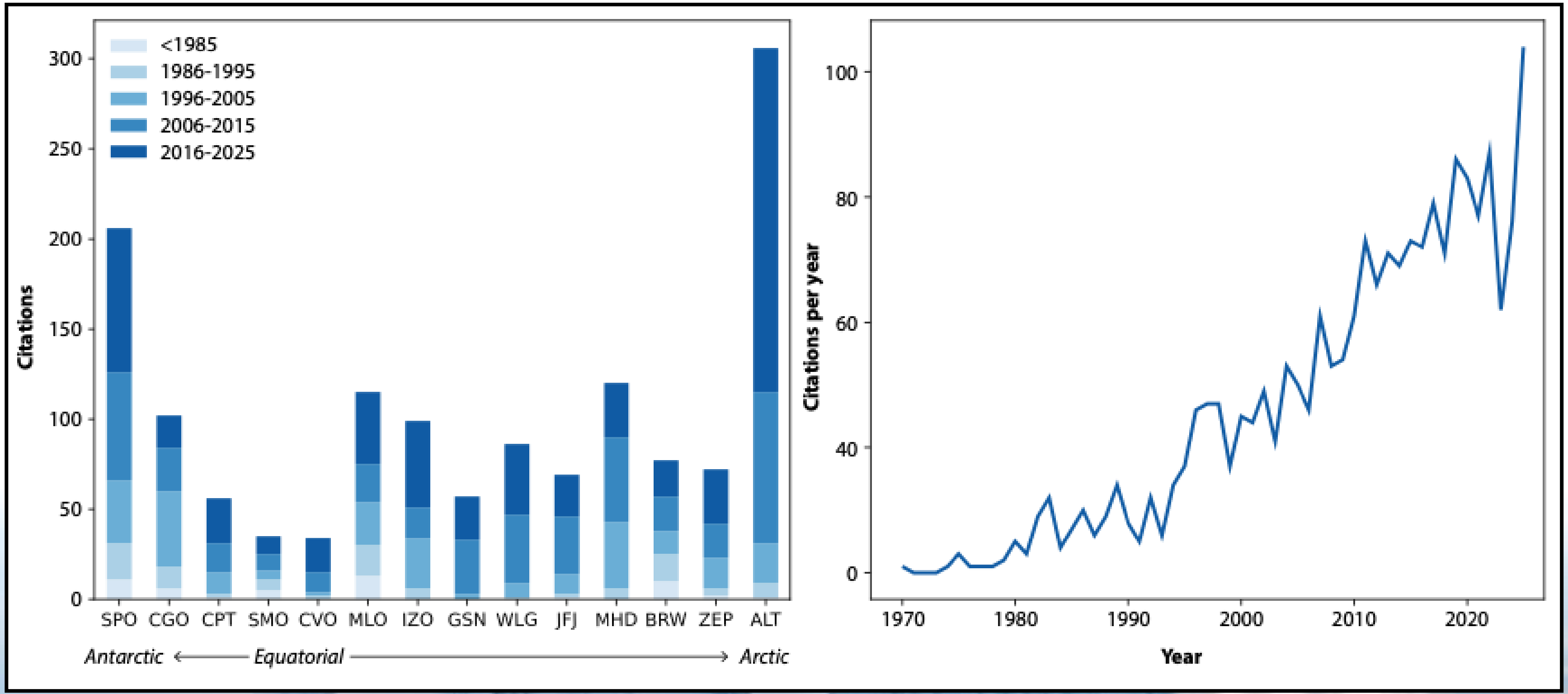
- Background and baseline stations allow us to understand large-scale changes in atmospheric processes and biogeochemical cycles



- Measurements and interest began in the 1970s following WMO's BAPMoN program, eventually becoming GAW

Mountain sites: Diverse laboratories

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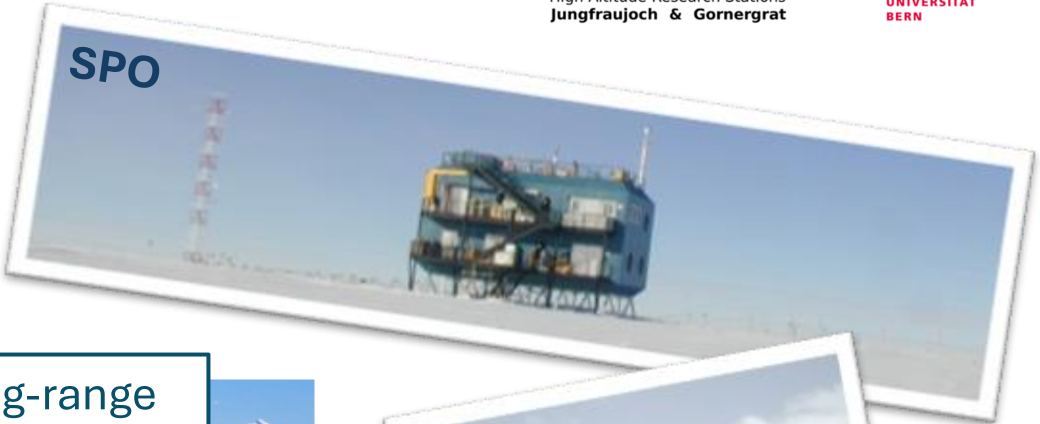

Images: CSIRO (Cape GRIM), AMOF (Cape Verde), NOAA (South Pole), https://www.railbookers.com/destinations/europe/switzerland/bern (Thun)

Nitrogen cycle: Major research questions

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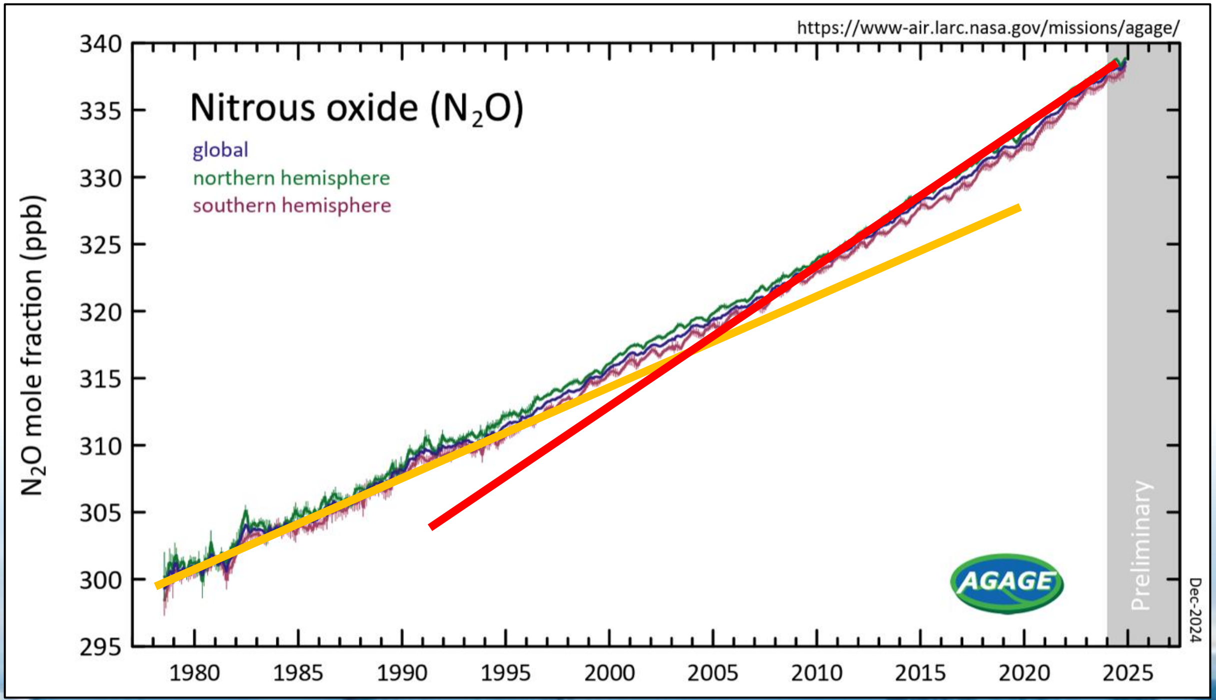
- Why are N_2O emissions accelerating?
  - Increasing N inputs or climate feedbacks?
- Nitrogen losses: Changing in a changing climate?



- <2000: ~0.6 ppb / year
- >2015: ~1.0 ppb / year

Nitrogen cycle: Major research questions

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- Why are N_2O emissions accelerating?
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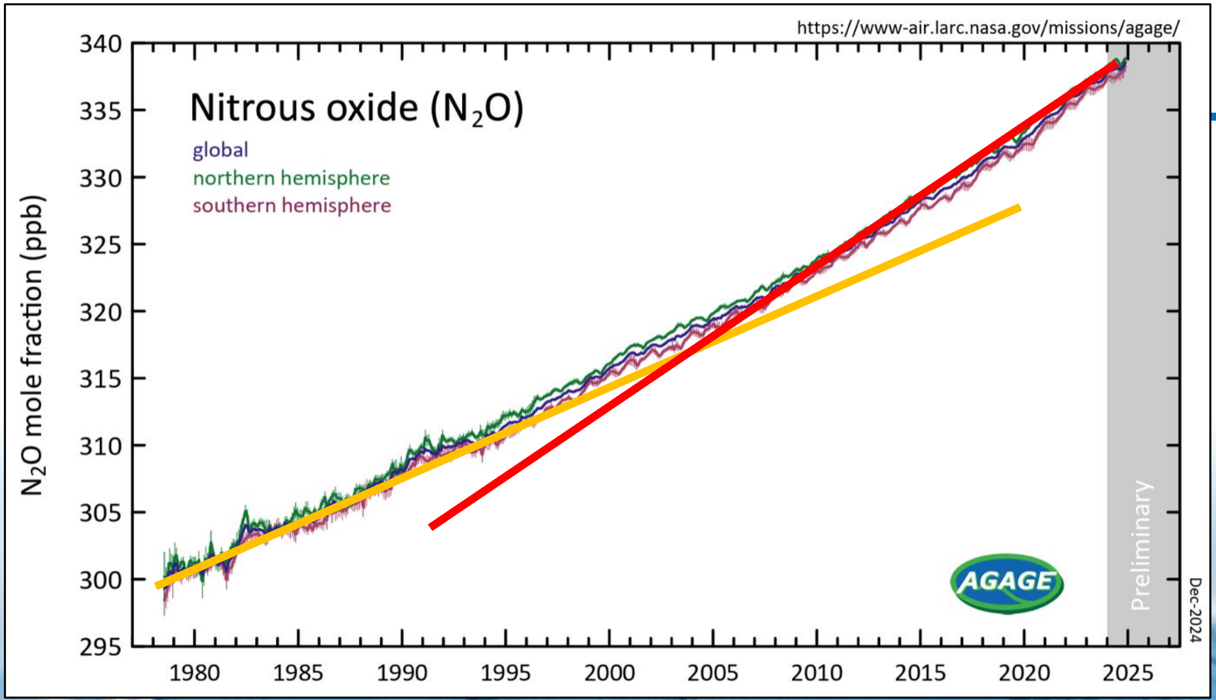
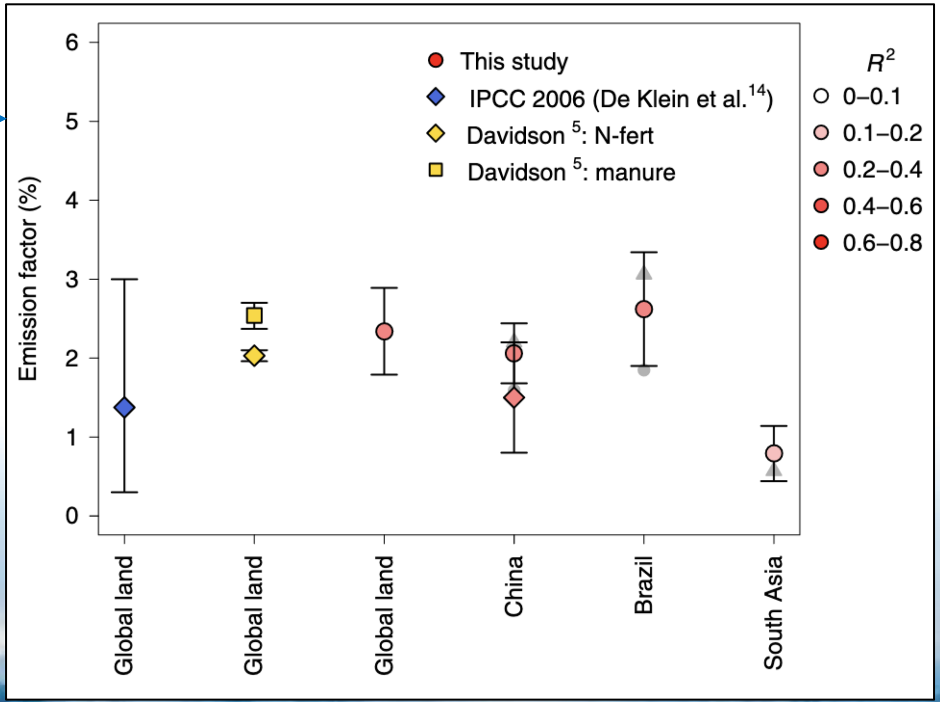
Global average emission factors





Thompson et al. (2019) 10.1038/s41558-019-0613-7

Using isotopes for biogeochemistry

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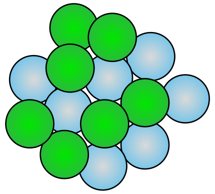
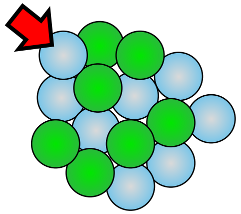
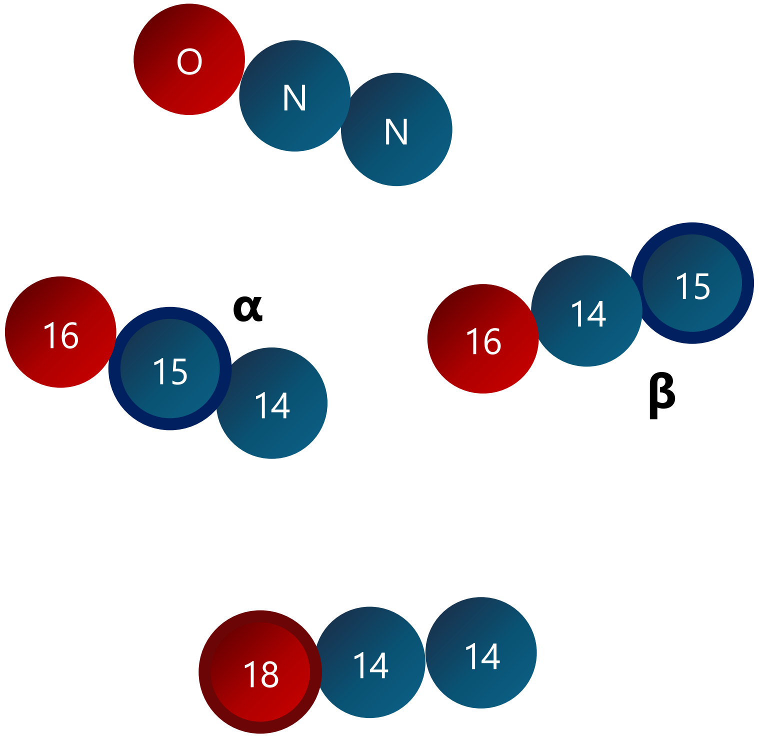
- Isotopes give us information about sources, sinks and processes

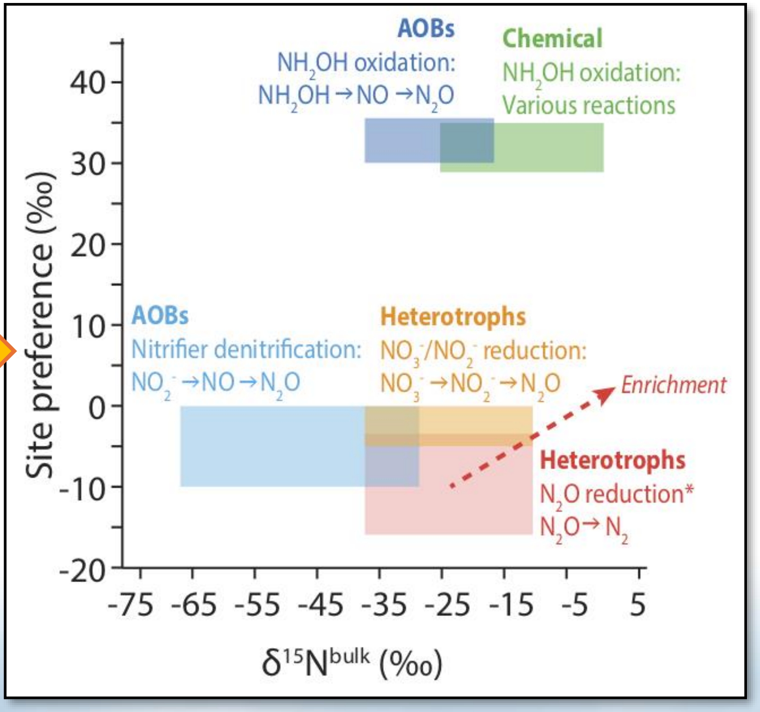


^{14}N: 7 protons,
7 neutrons



^{15}N: 7 protons,
8 neutrons





Many views on the same question

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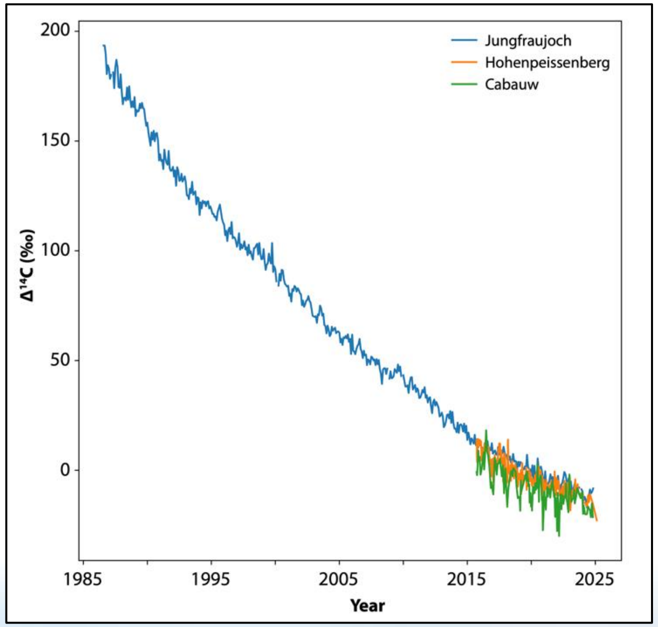
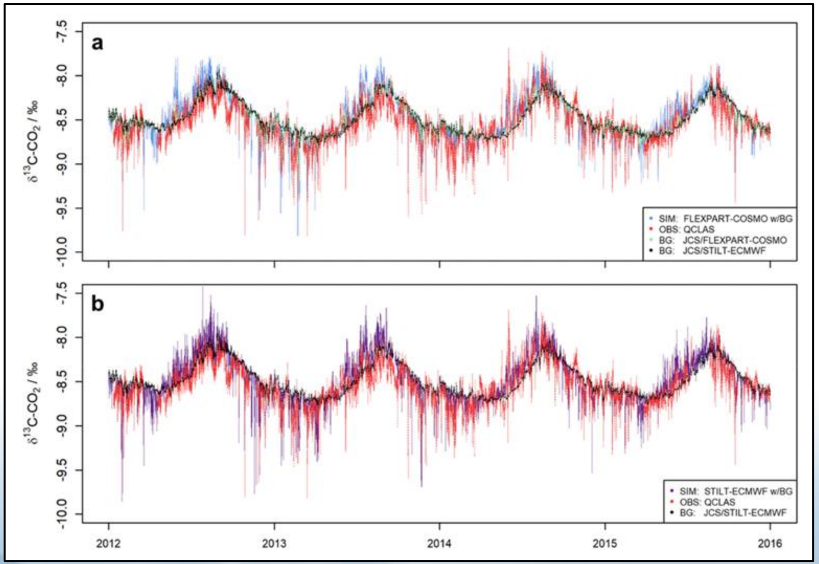
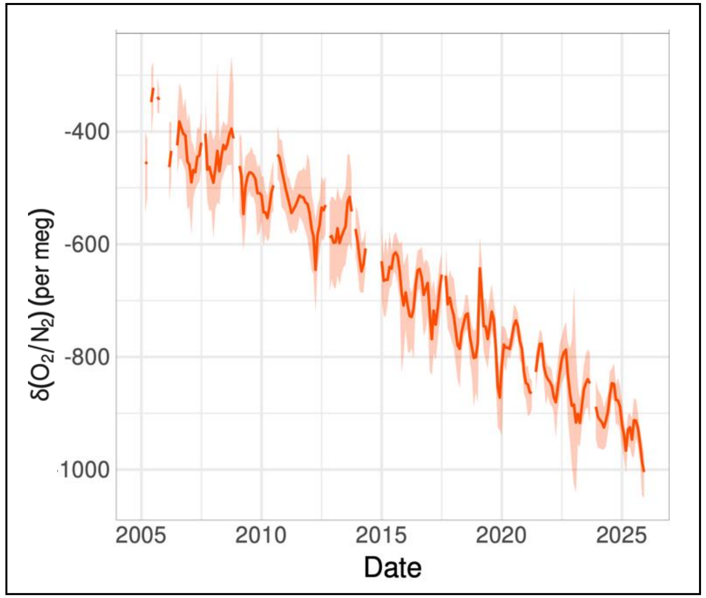
- Using isotopes and other novel tracers allows us to investigate the same question from different angles:



[14]C: Quantifying fossil fuel CO_2

[13]C: Estimating contributions from different sources and sinks



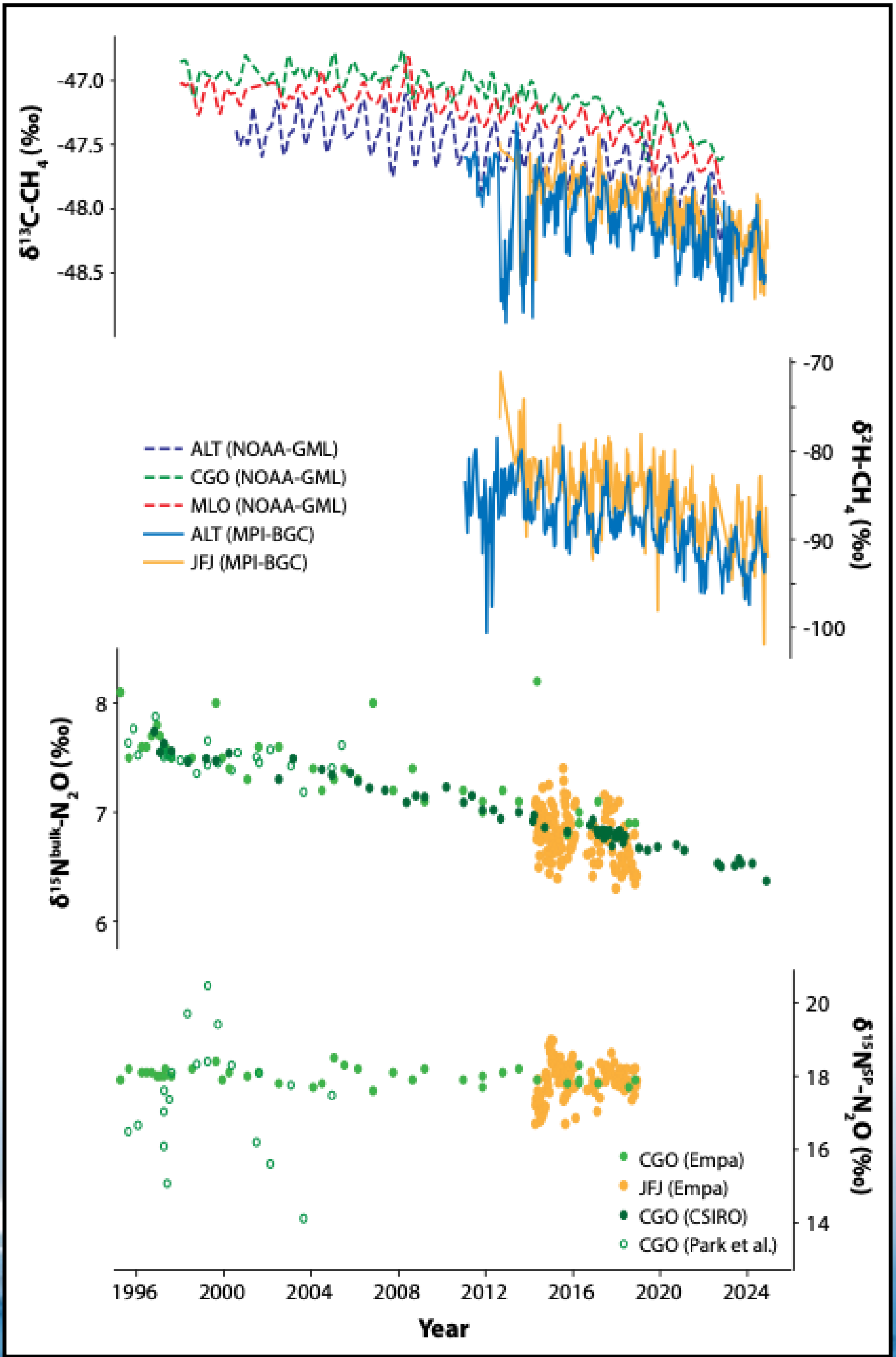


O_2: Quantifying fossil fuel CO_2 and oceanic and biogenic sources and sinks

Images from HFSJG Activity Report, 2025: Harris et al., Grange et al., and Pieber et al. (2022) doi.org/10.5194/acp-22-10721-2022

Isotopes at background stations

- Isotopic timeseries are primarily from flask sample programs
- **CO_2:** Solid understanding of isotopic trends at many sites
- **CH_4:** Clear trends at some sites, particularly for $\delta^{13}C$-CH_4
- **N_2O:** Few sites, clear trend in $\delta^{15}N^{bulk}$, no spatial patterns resolved



How do we measure isotopic composition?

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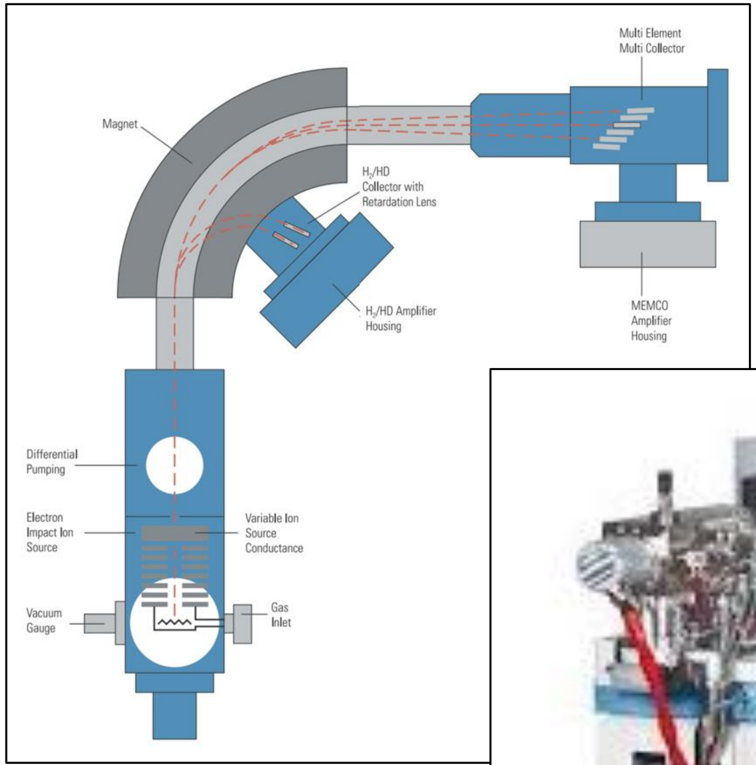

Images: Thermo Fisher MAT253, 2020

- **IRMS:** Separates isotopes based on mass to charge ratio – requires large, heavy instrumentation

✓ Precise, well understood, small sample sizes

✗ Not (easily) field deployable, cannot distinguish isotopomers

How do we measure isotopic composition?

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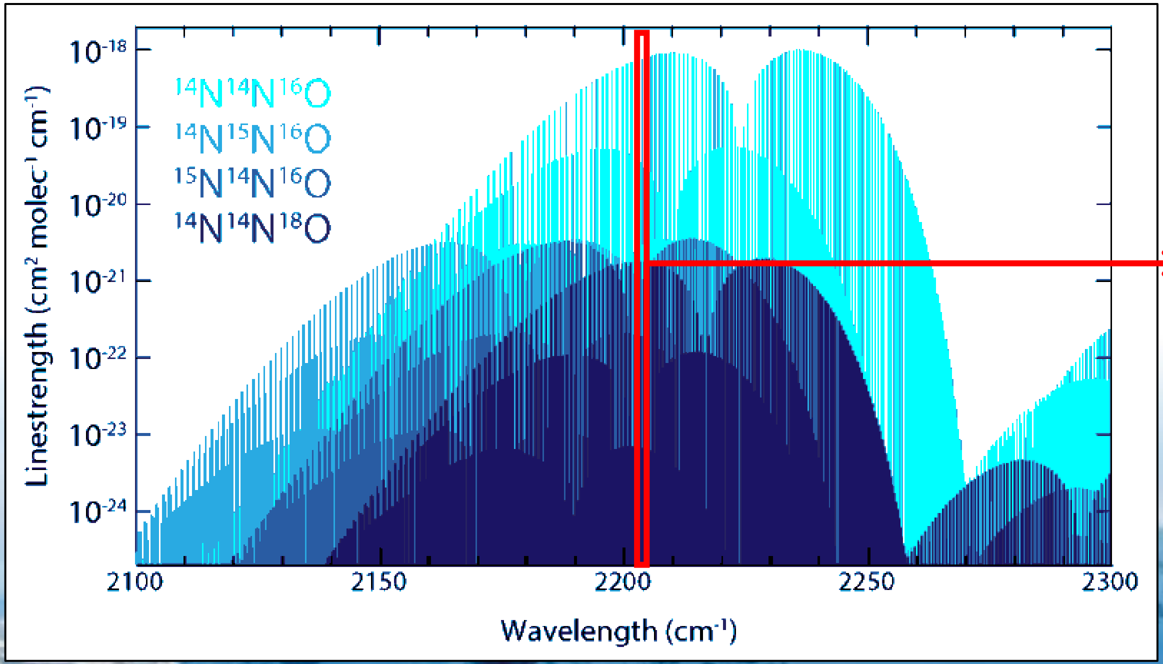
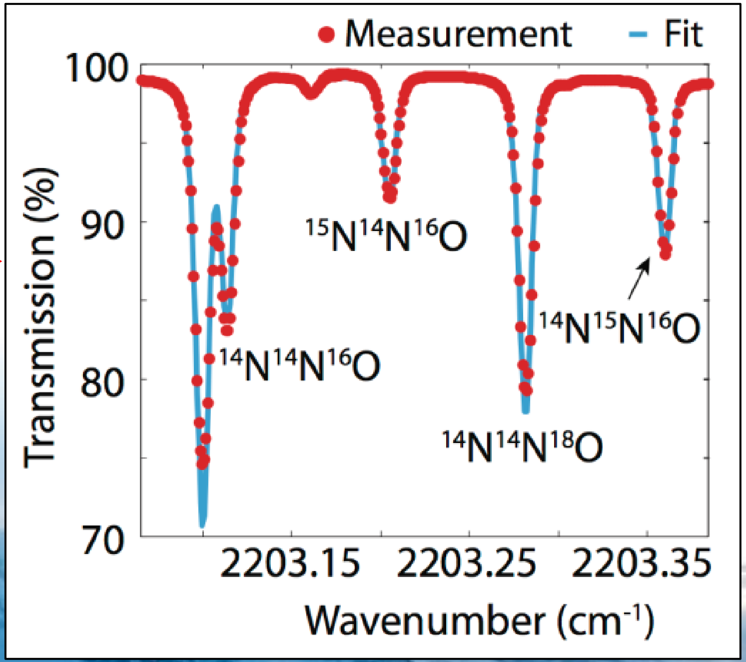
- **Spectroscopy** techniques use specific absorption bands in the mid-IR to quantify different isotopocules

✓ Field deployable, online, quantification of isotopomers

✗ Interferences, corrections, drift, sample size

From Harris et al. (2014) *Analytical Chemistry*, 10.1021/ac403606u





Measuring isotopes at mountain sites

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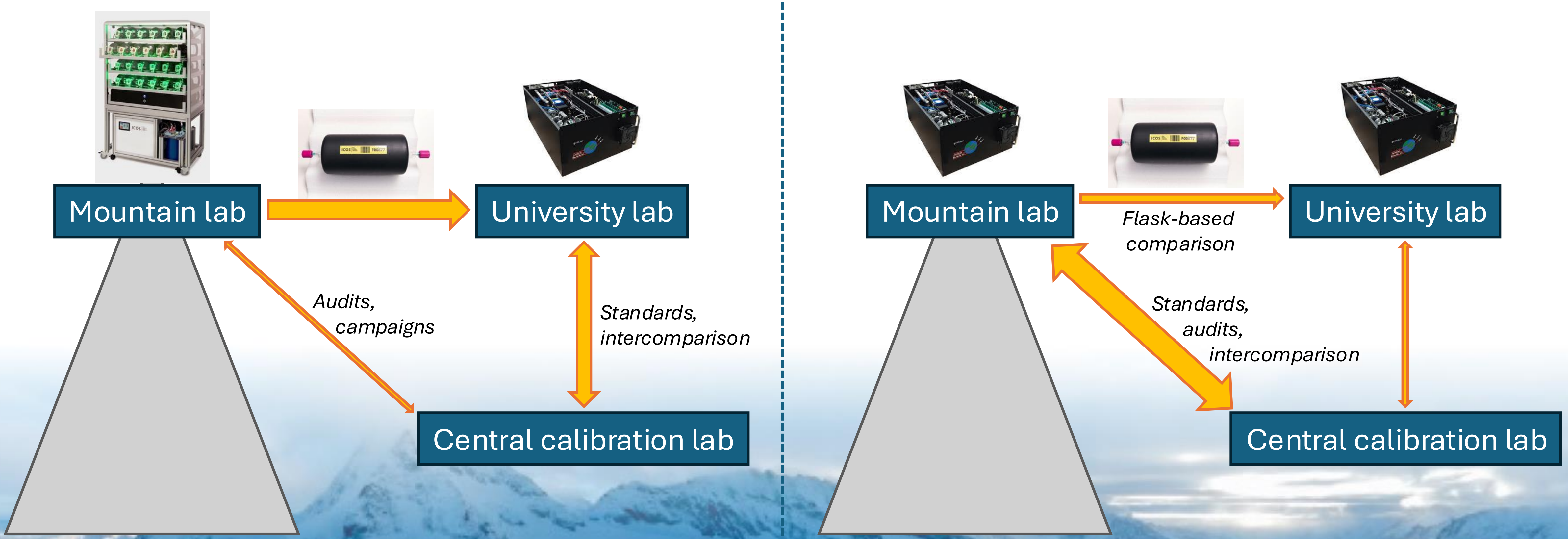
- Small signals, difficult logistics → calibration is challenging

Calibration and measurements simpler,
better intercomparability

Logistics simpler, measurements difficult,
better time resolution



Images: ICOS (https://www.icos-cal.eu/fcl/sampler/support); Aerodyne Research

Measuring isotopes at mountain sites

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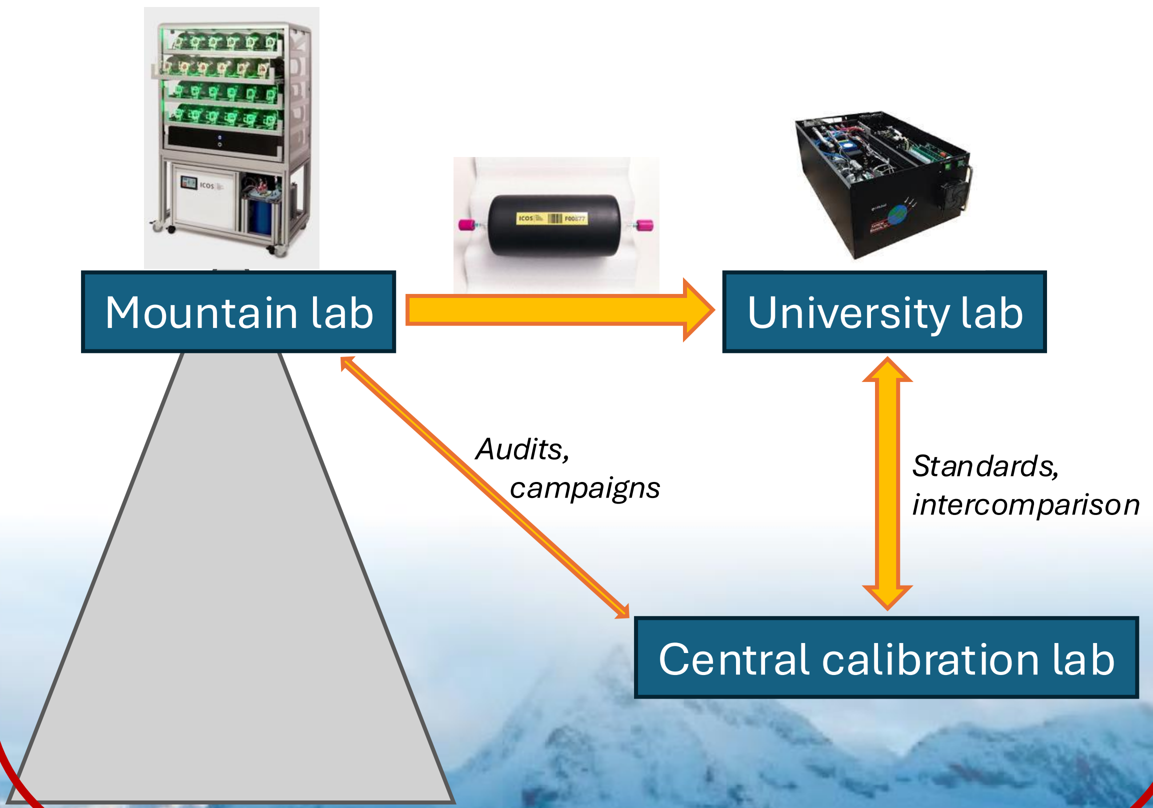

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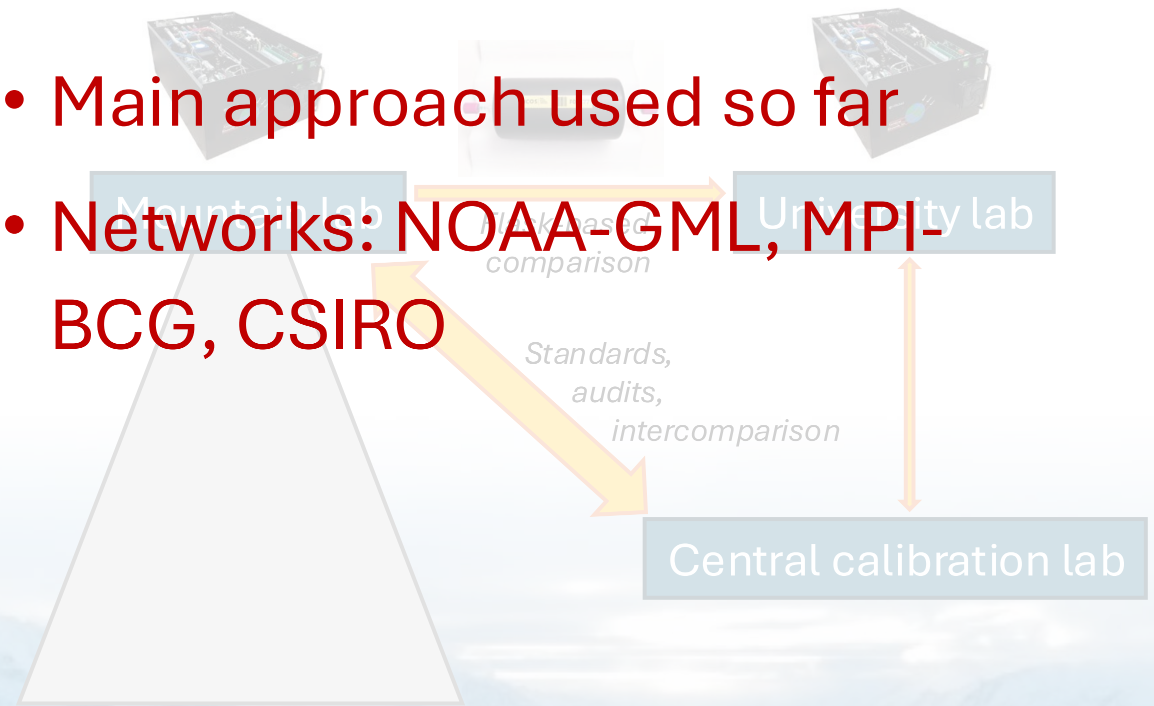

- Main approach used so far
- Networks: NOAA-GML, MPI-BCG, CSIRO

Images: ICOS (https://www.icos-cal.eu/fcl/sampler/support); Aerodyne Research

Interpreting isotopic data from mountain sites

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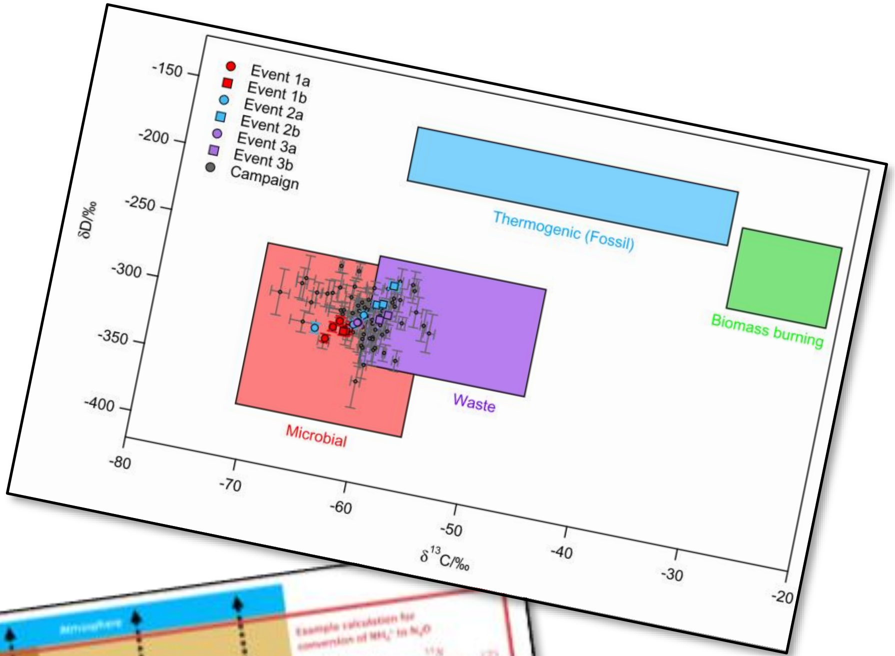
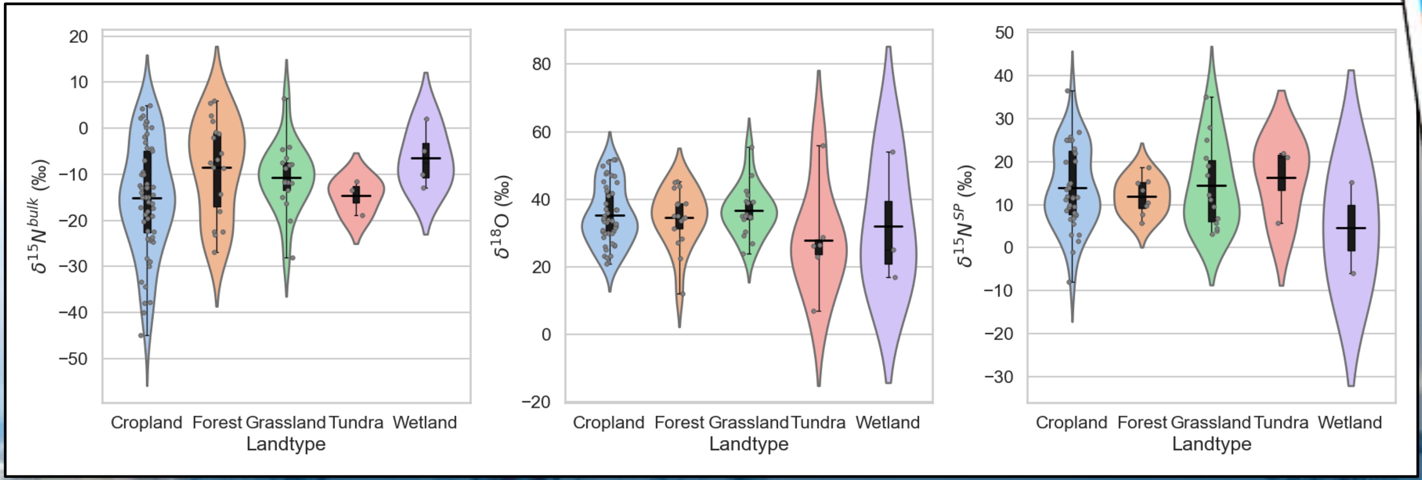
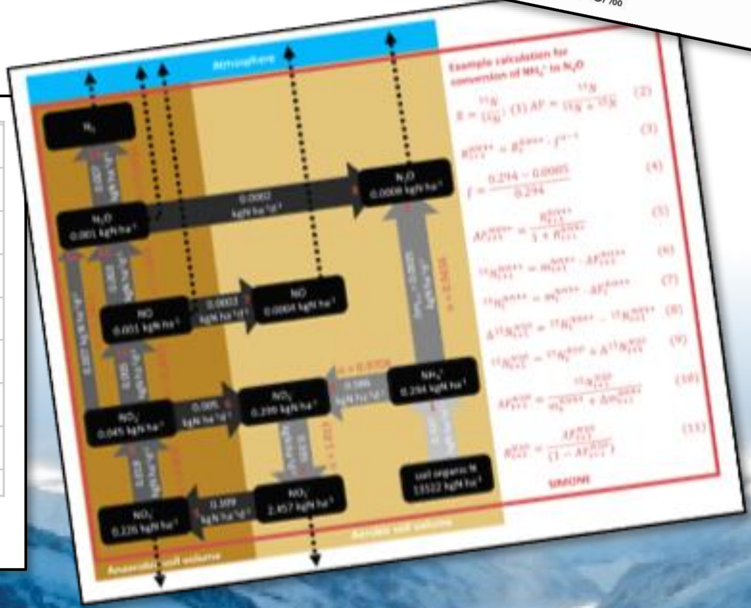
- Data analysis remains challenging…
  - Modelling mountain sites is always challenging
  - Source end members are poorly constrained
  - Processes are even more difficult to model
- Handling of error and uncertainty is key







Li et al. (2025) in preparation

Röckmann et al. (2016) 10.5194/acp-16-10469-2016; Denk et al. (2019) Ecology

Case study: N_2O isotopes at Jungfraujoch

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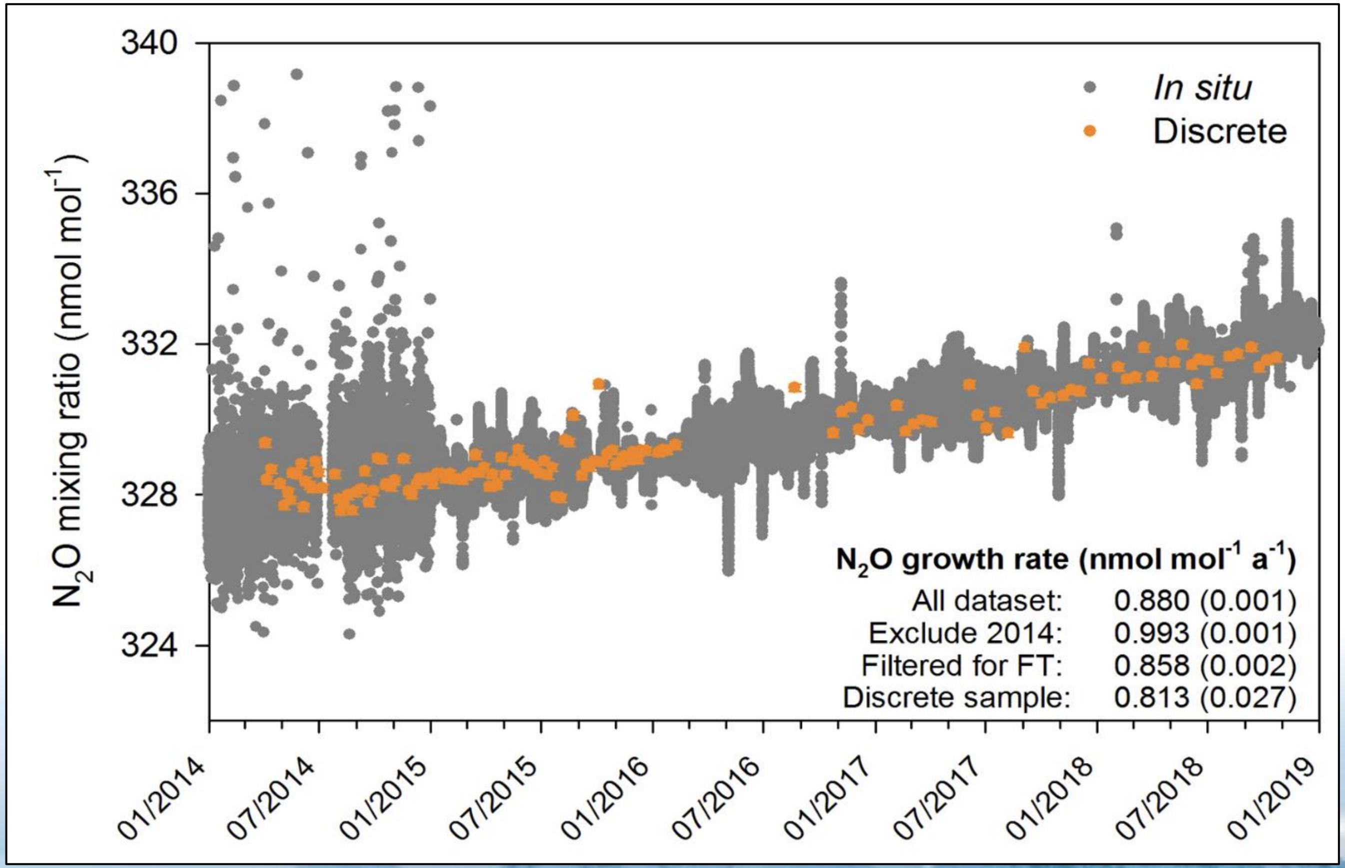
- N_2O mixing ratio has been measured at Jungfraujoch since 2004



Yu et al. (2019) doi: 10.5194/acp-19-12141-2019

- **Increasing** at a rate of ~0.9 ppb / y mainly due to agriculture
- Can we see a change in the isotopic composition?
- What does this tell us about sources and sinks?

Case study: N_2O isotopes at Jungfraujoch

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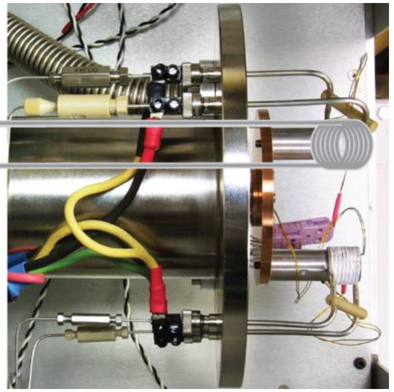
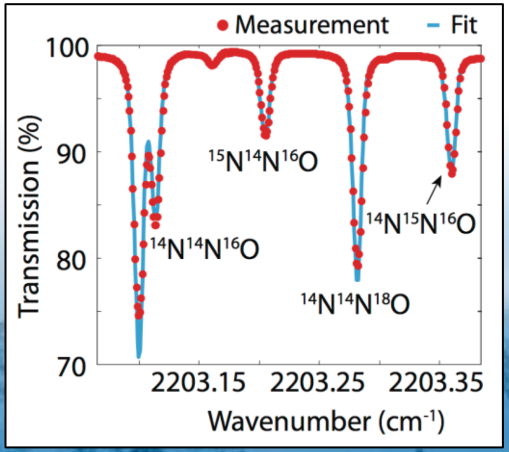
- Trace gases have low concentrations, eg. N_2O = 335 parts per billion in air
- *Preconcentration* is used to trap N_2O and reach >10 ppm in a laser cell

Ambient air (flask):
~335 ppb N_2O



HayeSepD:
Trap at –105°C
Warm to 45°C



Case study: N_2O isotopes at Jungfraujoch

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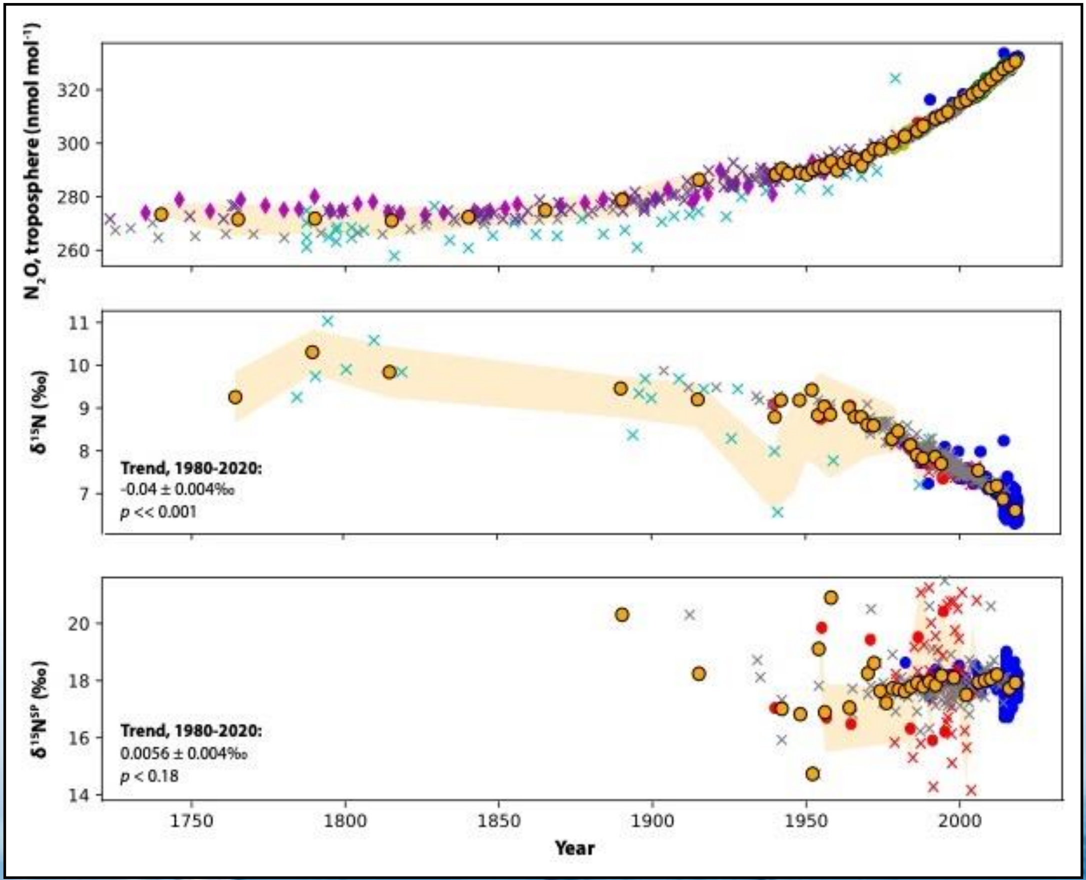
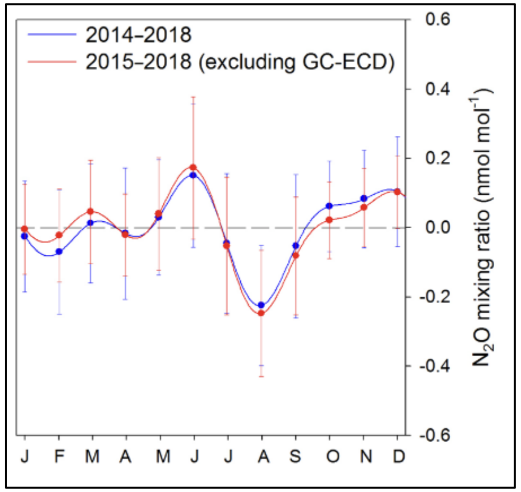
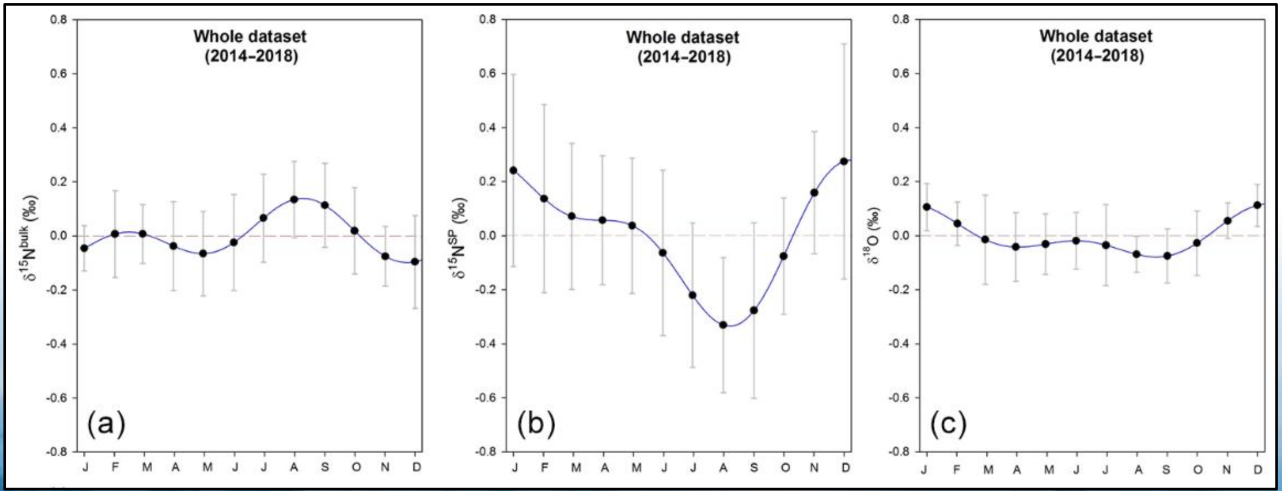
- δ^{15}N trend reflects the light anthropogenic source



- Seasonal N_2O cycle suggested stratospheric intrusions in summer

- Isotopes agree somewhat...





Case study: N_2O isotopes at Jungfraujoch

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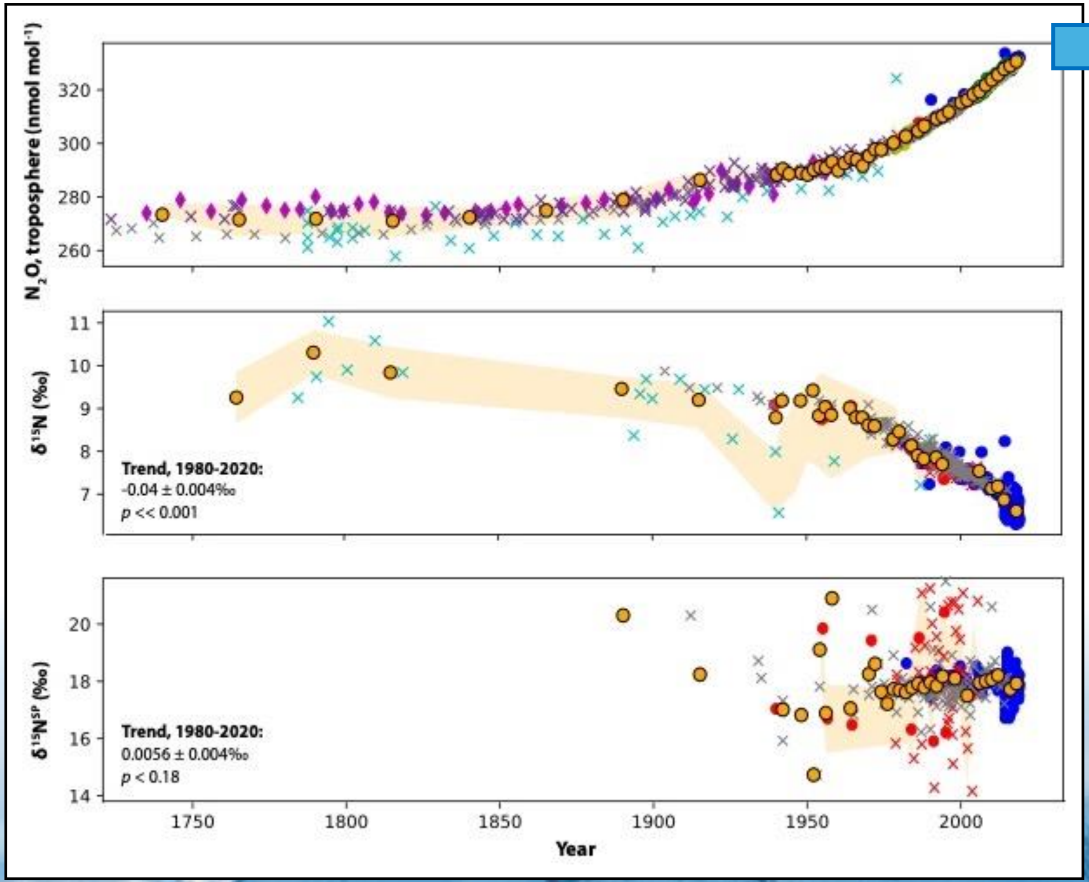
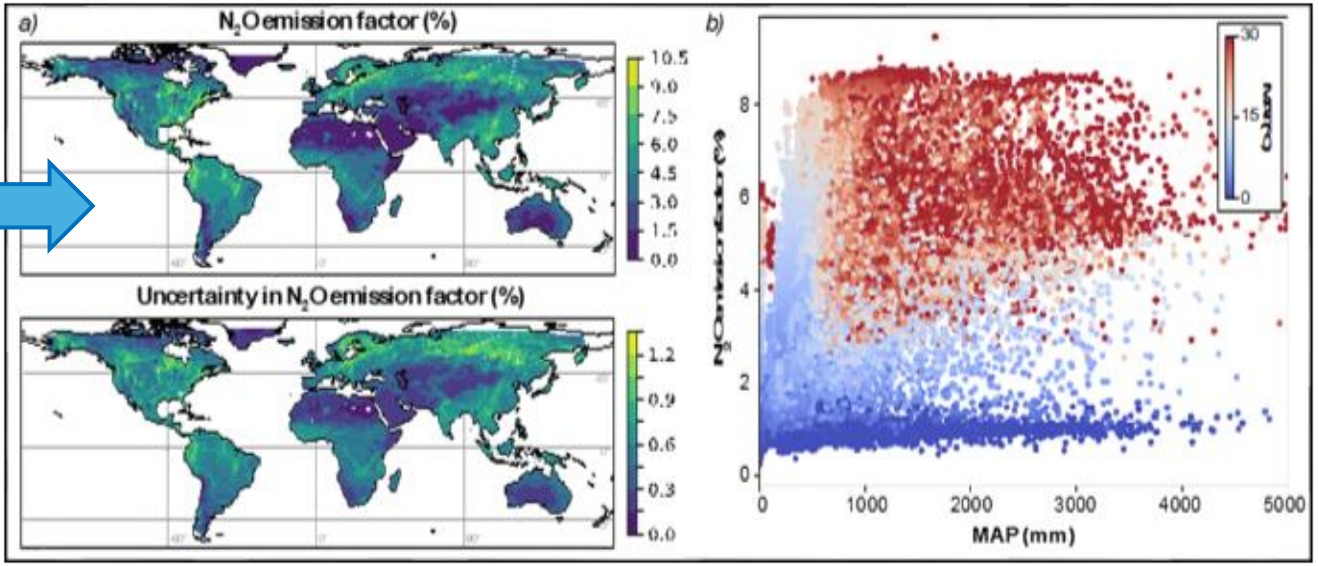
- $\delta^{15}N$ trend reflects the light anthropogenic source





- $\delta^{15}N$ of soil can be combined with isotopic trends to map global emissions
- Increasing emissions from subtropical regions could be driving global increases

Conclusions

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- Background measurements allow us to understand large-scale variability in transport, biogeochemical cycles, and anthropogenic emissions of **trace gases**
- Mixing ratios can be used to quantify total sources, but isotopes and novel tracers give us information and **sources, sinks and processes**
- Measurements can be made ***in situ*** or using **flask sampling**, which improves intercomparability or time resolution respectively
  - With both methods, small signals make calibration a major challenge
- Currently, isotopic timeseries are only adequate for CO_2
- *Isotopes at background sites offer many opportunities, despite many challenges!*