

Using data science to unravel isotopic data and quantify N₂O production and consumption pathways

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Nitrous oxide (N₂O) is a strong greenhouse gas and the most important stratospheric ozone-depleting substance emitted in the 21st century [9, 7]. The primary global source of N₂O is production during N cycling by microbiota in soils. Anthropogenic activities, in particular fertiliser use leading to an increase in available N [13], have caused an increase in N₂O mole fraction from 260-270 parts per billion in air (ppb) in the preindustrial era to 331.7 ppb today [2]. Particularly concerning is the acceleration in growth rate seen in the last few decades (Fig. 1). The causes of increasing N₂O emissions, which cannot be explained by rising fertiliser use, are poorly known and could relate to the impact of climate change on different N₂O production and consumption pathways.

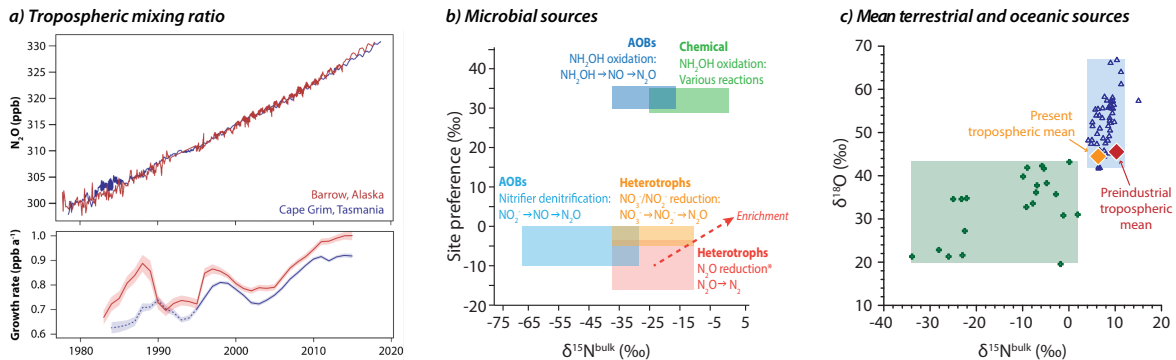


Figure 1: *a)* Tropospheric N₂O mixing ratio (top panel) and growth rate of the mixing ratio (bottom panel) from Barrow, Alaska, and Cape Grim, Tasmania. Barrow data is attributed to the NOAA flask monitoring program [2] and Cape Grim data is from the AGAGE monitoring network [8]. *b)* Microbial sources of N₂O, with isotopic signatures from [12, 11, 15, 16, 17, 5, 4]. *c)* Isotopic ranges for natural terrestrial (blue) and oceanic (green) sources of N₂O, compared to the preindustrial average tropospheric isotopic composition [10] and the present-day average tropospheric isotopic composition [14].

N₂O is produced by microbes in soil and water primarily during nitrification, an oxic process where N₂O is released as a by-product, and denitrification, an anoxic process with N₂O as an obligate intermediate. Additionally, heterotrophic denitrification can consume N₂O and release N₂ under low oxygen conditions [1]. The balance between these pathways influences N₂O emission strength, as well as fertilizer N use efficiency, total N losses, and N volatilization and leaching. N₂O isotopic composition can be used distinguish between production and consumption pathways and thus infer the relative rates of nitrification and denitrification [3]. The linear N₂O molecule has two distinct positions for isotopic substitution, ¹⁴N¹⁵N¹⁶O (α) and ¹⁵N¹⁴N¹⁶O (β). The ‘bulk’ ¹⁵ isotopic composition ($\delta^{15}\text{N}^{\text{bulk}}$) refers to the average isotopic composition at these positions, whereas the N₂O ‘site preference’ (SP) describes the difference in ¹⁵N isotopic composition

between the two positions. SP and $\delta^{15}\text{N}^{\text{bulk}}$ can be used to distinguish between sources, as shown in the examples in Figure 1. However, consumption alters the isotopic composition of the remaining N_2O (Figure 1b); moreover, variability in substrate isotopic composition, high measurement uncertainty, and unknown minor N_2O reactions make the quantitative extraction of production pathways from isotope data challenging [18, 3].

The recently developed FRAME (isotope FRactionation And Mixing Evaluation) interface is a much needed first step towards a robust community tool to quantify N_2O production and consumption pathways from isotopic data including clearly defined quantification of uncertainty (github.com/malewick/frame). FRAME uses a Markov Chain Monte Carlo approach to simultaneously determine mixing between N_2O from different sources as well as the extent of reduction, with an estimate of uncertainty. This modelling approach has been designed and validated for identification of N_2O production pathways and quantification of N_2O reduction progress in soil incubation experiments [6]. However, FRAME can currently only be applied to discrete datasets; analysis of mixing between pathways across a timeseries generated from a field or laboratory experiment is not possible. Within this MSc project, FRAME will be extended to allow the analysis of timeseries data, accounting for varying timescales of autocorrelation in the different inputs: Contributions of different pathways are expected to vary on an hourly to daily timescale, while isotopic endmembers and fractionation factors will vary on timescales of weeks to months.

Additional information

- **What will you learn?**

- Markov Chain Monte Carlo implementation in Python
- Different approaches to account for temporal autocorrelations within the MCMC (or other) optimization framework
- Data science applications to key questions in biogeoscience and climate research

- **Requirements:**

- Good knowledge of Python or R
- Experience with MCMC and/or timeseries data an advantage
- A strong interest in environmental science

- **Supervisors and collaborators:**

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