

Name of research institute or organization:

Laboratory for Air Pollution and Environmental Technology, Empa

Title of project:

Isotopic composition of N₂O at Jungfraujoch High Altitude Station

Part of this programme:

SNF Project 200021_163075: Assessment of the global N₂O budget based on seasonal and long-term isotope measurements at Jungfraujoch and the Cape Grim Air Archive

SNF Project 200021_150237: N₂O from the Swiss midlands: regional sources and hot spots. Integrated Carbon Observation System (ICOS)

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Project description:

Nitrous oxide (N₂O) and methane (CH₄) are important trace gases in the atmosphere with global warming potentials of 265 and 28 times that of CO₂, respectively. Coupled with their current atmospheric concentrations, these gases are the most important greenhouse gases after water vapor and CO₂. Furthermore, N₂O is the strongest ozone depleting substance emitted in the 21st century [1, 2].

Atmospheric mixing ratios of N₂O are rising at a rate of 0.2-0.3% per year globally due to anthropogenic emissions. The sources are dominated by dispersed and highly variable agricultural soil emissions, which, combined with the long lifetime of N₂O, makes source apportionment – and thus mitigation – challenging. Although the total global source and sink strengths for N₂O are relatively well-constrained, individual source contributions and the factors causing seasonality and interannual variability in N₂O concentration and growth rate are poorly known [3, 4]. Isotope measurements combined with modelling show great potential to unravel sources and processes; however, data is currently sparse and interpretation is often limited by precision [5].

Methane emissions have varied over the past decades, and source attribution remains uncertain. According to bottom-up inventory estimates, anthropogenic methane emissions in Central Europe are dominated by the agricultural sector, mainly produced by ruminants, natural gas distribution and waste management, e.g. landfills [6]. Remaining CH₄ emissions are from natural and semi-natural sources. However, these estimates are based on statistical data and are associated with large uncertainties. Therefore, validation through an independent technique, e.g. inverse emission modeling [7] or measurements of the isotopic signature of CH₄ [8], is essential. Although independent national inverse modelling emission estimates are highly desirable for the validation of GHG reporting, they remain the exception and require dense observational networks and high resolution modelling [9].

The High Altitude Research Station Jungfraujoch (JFJ, 3580 m above sea level), located in the center of Europe on the northern ridge of the Swiss Alps, is well-suited for long-term monitoring of tropospheric background air and for studying the transport of anthropogenic or biogenic tracers from the boundary layer to the free troposphere. These projects aim at determining the mixing ratios and isotopic compositions of both N₂O (biweekly/weekly) and CH₄ (monthly) at JFJ using flask sampling with high precision offline analysis. Initially

focusing solely on N₂O measurements, CH₄ samples were incorporated into this project in October 2014, thanks to a partnership developed with Prof. Euan Nisbet at Royal Holloway, University of London (RHUL). In 2015-16, the N₂O project was extended to include analogous measurements from the Cape Grim (Tasmania) air archive, to compare the isotopic trends observed at JFJ to this important southern hemispheric baseline site (SNF Project 200021_163075). The N₂O isotopic composition of flask samples is analyzed at Empa using pre-concentration from ambient air followed by quantum cascade laser absorption spectroscopy (QCLAS) [10], and mixing ratios are measured directly using QCLAS. Mixing ratios of CH₄ and δ¹³C-CH₄ are analyzed by Isotope-Ratio Mass Spectrometry (IRMS) at RHUL. In total, 157 N₂O and 39 CH₄ samples have been collected from JFJ since the project was initiated in April 2014, making this a unique isotopic dataset for greenhouse gases at a background measurement station in Europe.

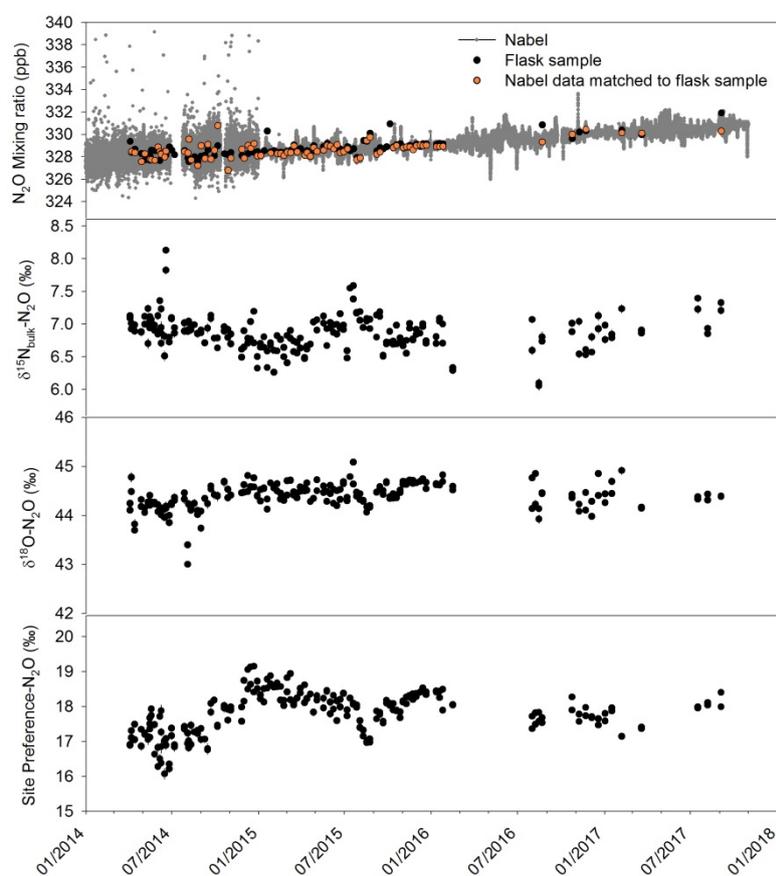


Figure 1. N₂O mixing ratios (grey and orange: continuous measurements; black: flasks); δ¹⁵N_{bulk}, δ¹⁸O and site preference of atmospheric N₂O (flasks) during the period of 2014-2017 at JFJ. Standard deviations are given for replicate measurements. Note that the measurements for mixing ratios in flasks are not yet completed for this period. Furthermore, sampling problems between February and August 2016 are responsible for the data gap in flask measurements.

The continuous data show a distinct trend in N₂O mixing ratio of +1.2 ppb y⁻¹, higher than the global average of 0.8 ppb y⁻¹ over the period 2015-2016 [11]. δ¹⁵N_{bulk} of N₂O decreased over the study period, likely due to ¹⁵N-depleted anthropogenic sources [12]. However, we observe no clear interannual tendency for δ¹⁵N site preference (SP) and δ¹⁸O of N₂O. Surprisingly, our dataset demonstrated significant seasonal patterns for δ¹⁵N_{bulk} and SP, which might reflect seasonal variation in N₂O production processes in the Northern Hemisphere. Stratospheric intrusion of isotopically enriched air could be another contributor to the observed seasonal pattern. Completing the dataset for 2017 and comparing with seasonal and long-term trends

from Cape Grim will further improve our understanding of hemispheric difference and global trends of N₂O cycle.

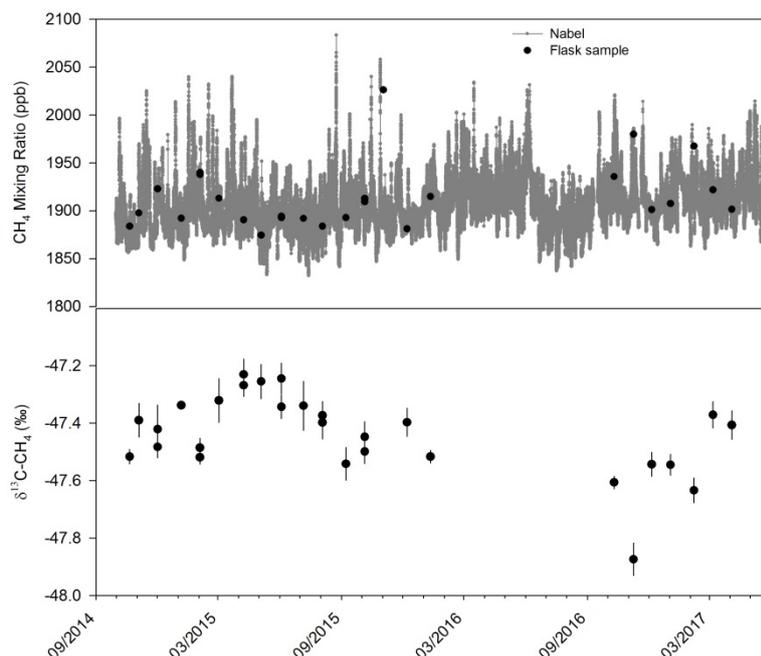


Figure 2. CH₄ mixing ratios measured in situ (grey line) and in flask samples (black points) and δ¹³C-CH₄ in flask samples between October 2014 and April 2017; standard deviations are shown in the figure. Note that sampling issues between February and August 2016 are responsible for the data gap in flask measurements.

CH₄ mixing ratios and δ¹³C-CH₄ values are generally anti-correlated, indicating emissions of ¹³C-depleted CH₄ sources. Variations in CH₄ mixing ratios and isotope ratios are rather small, as samples were only collected on a regular basis and not triggered by emission events. A Keeling plot analysis indicates a main emission source with δ¹³C-CH₄ = -55 ‰ (*r*² = 0.56). We plan to continue regular flask sampling at JFJ for CH₄ isotopic analysis. Additionally, we will add intensive sampling campaigns for emission events and FT conditions. Furthermore, flask samples will be analyzed for δD-CH₄ by QCLAS to better characterize emission sources.

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Key words:

Nitrous oxide, methane, greenhouse gas, flask sampling, isotopic composition, seasonal variability

Collaborating partners/networks:

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Scientific publications and public outreach 2017:

Refereed journal articles and their internet access

Harris, E., L. Emmenegger, J. Mohn, Using Isotopic Fingerprints to Trace Nitrous Oxide in the Atmosphere, Highlights of Analytical Sciences in Switzerland, *Chimia*, **71**, 46, doi:10.2533/chimia.2017.46, 2017.

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