Isotopic composition of N₂O at Jungfraujoch High Alpine Station

Joachim Mohn[1], Longfei Yu[1], Sarah Eggleston[1], Stephan Henne[1], Martin Steinbacher[1], Christoph Zellweger[1]

[1] Laboratory for Air Pollution / Environmental Technology, Empa – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

joachim.mohn@empa.ch

1. Project description

Nitrous oxide (N_2O) and methane (CH_4) are important trace gases in the atmosphere with global warming potentials of 265 and 28 times that of CO_2, respectively. Coupled with their current atmospheric concentrations, these gases are the most important greenhouse gases after water vapour and CO_2. Furthermore, N_2O is the strongest ozone-depleting substance emitted in the 21st century [1, 2].

Atmospheric mixing ratios of N_2O are rising at a rate of 0.2-0.3% per year globally due to anthropogenic emissions. The sources are dominated by disperse and highly variable agricultural soil emissions, which, combined with the long lifetime of N_2O, makes source apportionment – and thus mitigation – challenging. Although the total global source and sink strengths for N_2O are relatively well-constrained, individual source contributions and the factors causing seasonality and interannual variability in N_2O mixing ratio 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 CH_4 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 modelling [7] or measurements of the isotopic signature of CH_4 [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 centre 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 N_2O (biweekly/weekly) and CH_4 (monthly) at JFJ using flask sampling with high precision offline analysis. Initially focusing solely on N_2O measurements, CH_4 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 N_2O 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 N_2O isotopic composition of flask samples is analysed 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 CH_4 and $\delta^{13}C$-CH_4 were analysed by Isotope-Ratio Mass Spectrometry (IRMS) at RHUL until April 2017; from May 2017 until December 2018, CH_4 mixing ratios, $\delta^{13}C$-CH_4 and δD-CH_4 were measured at Empa by laser spectroscopy. Until now, we have monthly/bi-weekly analysed atmospheric N_2O and CH_4 isotopes from JFJ over a period of about four years, making this a unique isotopic dataset for greenhouse gases at a background measurement station in Europe.

The online measurements show a distinct trend in N_2O mixing ratio of +1.2 ppb y^{-1}, higher than the global average of 0.8 ppb y^{-1} [11]. $\delta^{15}N^{bulk}$ of N_2O shows a decrease over the study period, likely due to ^{15}N-depleted anthropogenic sources [12]. However, we observe no clear interannual tendency for $\delta^{15}N$ site preference (SP) and $\delta^{18}O$ of N_2O. Surprisingly, our dataset demonstrates significant seasonal patterns for $\delta^{15}N^{bulk}$ and SP, which might reflect seasonal
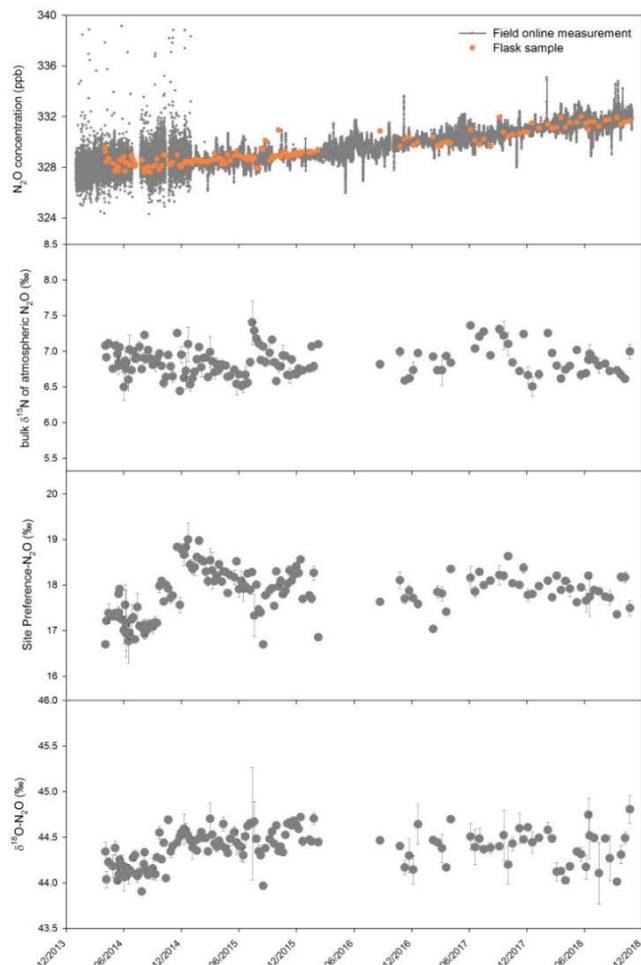
Figure 1. N₂O mixing ratios (dark grey: online measurements per 10 minutes; orange: flasks); $\delta^{15}N_{bulk}$, $\delta^{18}O$ and site preference of atmospheric N₂O (flasks) from February 2014 to October 2018 at JFJ. Standard deviations are given for replicate measurements. Sampling issues between February and August 2016 are responsible for the data gap in flask measurements.

variation in N₂O production processes in the Northern Hemisphere. Stratospheric intrusion of isotopically enriched air could be another contributor to the observed seasonal pattern. The seasonal pattern observed at JFJ combined with long-term trends from Cape Grim will therefore improve our understanding of global trends of N₂O cycle.

CH₄ mixing ratios and $\delta^{13}C$-CH₄ values are generally anti-correlated, indicating emissions of ^{13}C-depleted CH₄ sources. Similarly, δD-CH₄ is negatively associated with CH₄ mixing ratios. We observe a seasonal pattern in CH₄ mixing ratios over the four-year period. However, this is not shown within the isotopic measurements, likely due to low sampling frequency. Keeling plot analyses indicates a main emission source with $\delta^{13}C$-CH₄ = -51 ‰ and δD-CH₄ = -333 ‰.

References

1. IPCC (2014) Climate Change 2014: Synthesis Report. IPCC, Geneva, Switzerland, 151 pp.
2. Ravishankara et al. (2009) *Science,* 326(5949): 123-125
3. Ishijima et al. (2009) *Tellus B*, 61: 408–415.
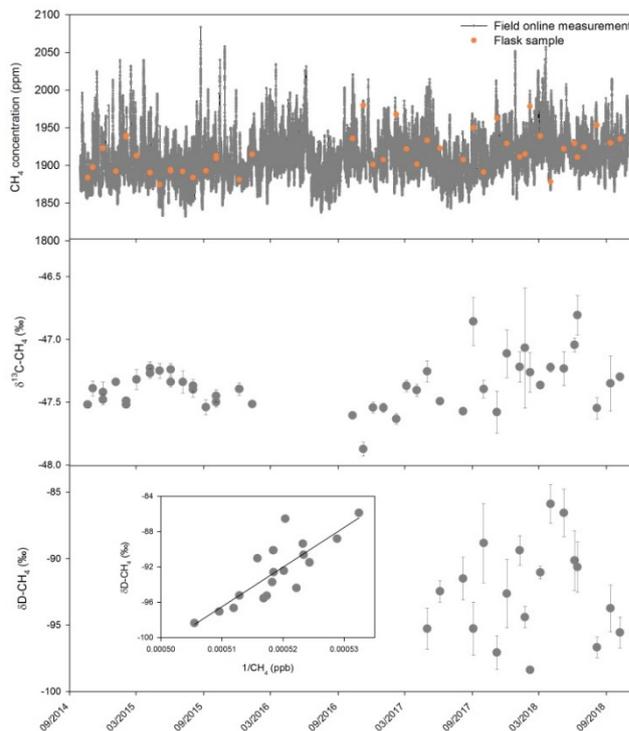4. Thompson et al. (2014) *Atmospheric Chemistry and Physics*, 14: 1801–1817.

Figure 2. CH₄ mixing ratios (dark grey: online measurements per 10 minutes; orange: flask samples) and $\delta^{13}C$-CH₄ (flasks) from October 2014 to November 2018, and δD-CH₄ (flasks) from May 2017 to November 2018; keeling plot for δD-CH₄ is included within the lower figure; standard deviations are shown. Sampling issues between February and August 2016 are responsible for the data gap in flask measurements.

5. Rigby et al. (2012) *Journal of Geophysical Research: Atmospheres*, 117: doi:10.1029/2011JD017384.
6. Hiller et al. (2014) *Biogeosciences*, 11: 1941-1959.
7. Bergamaschi et al. (2015) *Atmospheric Chemistry and Physics*, 15: 715-736.
8. Lowry et al. (2001) *Journal of Geophysical Research: Atmospheres*, 106: 7427-7448.
9. Henne et al. (2016) *Atmospheric Chemistry and Physics*, 16(6): 3683-3710.
10. Mohn et al. (2012) *Atmospheric Measurement Techniques*, 5: 1601-1609.
11. World Meteorological Organization and Global Atmospheric Watch (2017) *WMO/GAW Greenhouse Gas Bulletin*, 13.
12. Toyoda et al. (2013) *Journal of Geophysical Research: Atmospheres*, 118: doi:10.1002/jgrd.50221.

Collaborating partners / networks

Paul Krummel, Ray Langenfelds and Paul Steele / CSIRO Marine and Atmospheric Research, Aspendale, Australia
Euan Nisbet / Royal Holloway, University of London

Address

Laboratory for Air Pollution and Environmental Technology
Empa
Überlandstrasse 129
CH-8600 Dübendorf

Contacts

Dr. Joachim Mohn
e-mail: joachim.mohn@empa.ch

Dr. Sarah Eggleston
e-mail: sarah.eggleston@empa.ch

Dr. Longfei Yu
e-mail: longfei.yu@empa.ch.