

# The isotopic composition of atmospheric nitrous oxide observed at the high altitude research station Jungfrauoch

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## 1. Project description

Nitrous oxide (N<sub>2</sub>O) is a potent greenhouse gas and a strong stratospheric ozone-depleting substance. Past measurements from several monitoring networks have shown a significant increase in atmospheric N<sub>2</sub>O mixing ratio, at a current growth rate of about 0.93 nmol mol<sup>-1</sup> a<sup>-1</sup>. On the global scale, given excessive nitrogen (N) fertilizer application, agriculture is known to be the largest and most important anthropogenic source of N<sub>2</sub>O (Reay et al., 2012). However, long-term observations of N<sub>2</sub>O in the unpolluted atmosphere have shown significant seasonal and interannual variabilities in N<sub>2</sub>O mixing ratios, which cannot yet be explained with transport models and emission inventories.

Isotopic signatures of atmospheric N<sub>2</sub>O can provide important constraints on N<sub>2</sub>O sources (Denk et al., 2017). The ratios of <sup>15</sup>N/<sup>14</sup>N and <sup>18</sup>O/<sup>16</sup>O in N<sub>2</sub>O are reported in  $\delta$  notation as  $\delta(^{15}\text{N}/^{14}\text{N})$  and  $\delta(^{18}\text{O}/^{16}\text{O})$ , and often abbreviated as  $\delta^{15}\text{N}^{\text{bulk}}$  (average for <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O) and  $\delta^{18}\text{O}$ , respectively. A large fraction of N<sub>2</sub>O emitted to the atmosphere originates from soil bacterial processes, which usually emit N<sub>2</sub>O that is more enriched in light (<sup>14</sup>N, <sup>16</sup>O) isotopes than the tropospheric background (Toyoda et al., 2017). Recently, site-specific composition of N<sub>2</sub>O isotopomers (site preference:  $\delta^{15}\text{N}^{\text{SP}}$ ), which denotes the difference of <sup>15</sup>N between the central (<sup>14</sup>N<sup>15</sup>N<sup>16</sup>O,  $\alpha$  position) and terminal (<sup>15</sup>N<sup>14</sup>N<sup>16</sup>O,  $\beta$  position) N atoms, has been applied to constrain sources contributing to atmospheric N<sub>2</sub>O (Yoshida and Toyoda, 2000).  $\delta^{15}\text{N}^{\text{SP}}$  of N<sub>2</sub>O is particularly effective for distinguishing between the major N<sub>2</sub>O production processes, i.e. nitrification and denitrification, generally referred to as aerobic and anaerobic N<sub>2</sub>O production, with high and low  $\delta^{15}\text{N}^{\text{SP}}$ , respectively (Sutka et al., 2006).

Trends of N<sub>2</sub>O isotopic compositions in the unpolluted atmosphere are useful for investigating regional and global N<sub>2</sub>O emission sources. For example, Park et al. (2012) reported that the increase in N<sub>2</sub>O mixing ratios over the last decades is accompanied by a

decrease in both  $\delta^{15}\text{N}^{\text{bulk}}$  and  $\delta^{18}\text{O}$ -N<sub>2</sub>O. However, interannual trends in  $\delta^{15}\text{N}^{\text{SP}}$  and seasonal variability of N<sub>2</sub>O isotopic composition are still largely uncertain and rarely reported in the literature.

The High Altitude Research Station Jungfrauoch (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. For 5 years starting from 2014, our project had collected ambient air at JFJ using flasks for determining the mixing ratios and isotopic compositions of N<sub>2</sub>O (biweekly/weekly). The N<sub>2</sub>O isotopic composition of flask samples was analysed at Empa using pre-concentration from ambient air followed by quantum cascade laser absorption spectroscopy (QCLAS) (Mohn et al., 2010) and mixing ratios were measured directly using QCLAS. Our flask measurements were accompanied by *in situ* continuous measurements of N<sub>2</sub>O mixing ratios at JFJ.

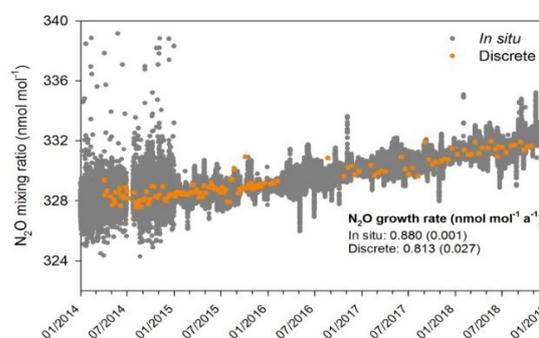


Figure 1. *In situ* and discrete measurements of atmospheric N<sub>2</sub>O mixing ratios at Jungfrauoch. *In situ* measurements were made with GC-ECD between April and December 2014. After that, OA-ICOS was the major analytical method. A sampling gap exists for discrete samples between February and August 2016. Annual N<sub>2</sub>O growth rates were determined by linear regressions.

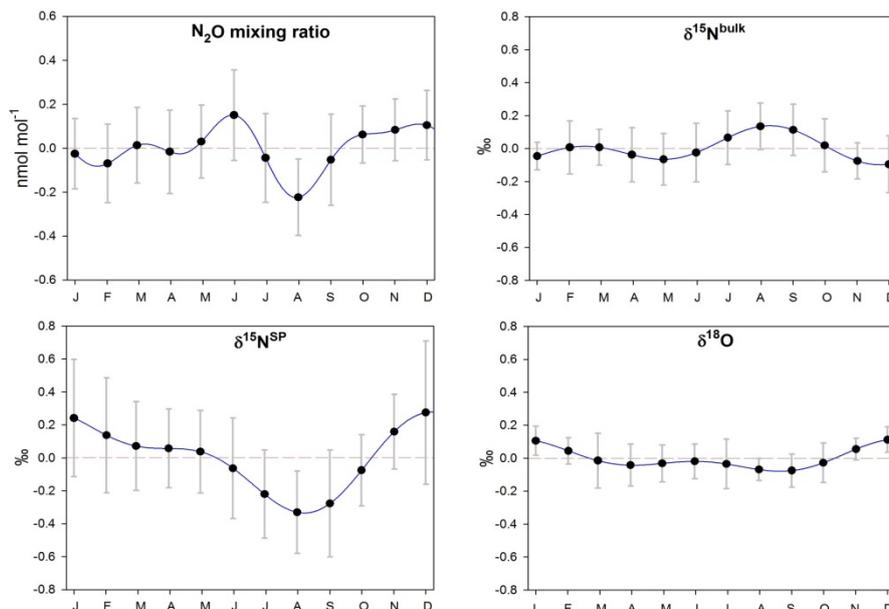


Figure 2. Seasonality of  $N_2O$  mixing ratio and isotopic composition. Detrended seasonality was derived from the nonlinear least-square model simulation for time-series, with error bars indicating one standard deviation of monthly residuals.

This study reports the first results of background  $N_2O$  isotopic measurements based on a laser spectroscopic technique, which achieved measurement repeatability of 0.10-0.20‰ for all isotopic compositions. We observed a linear growth of atmospheric  $N_2O$  at JFJ during the period 2014-2018 at  $0.880 \text{ nmol mol}^{-1} \text{ a}^{-1}$  (in situ measurements, Fig. 1). A point-to-point comparison of discrete and in situ measurements showed good agreement. The deseasonalised trend of  $\delta^{15}N^{bulk}$  showed a significant decrease (data not shown;  $-0.052 \pm 0.012 \text{ ‰ a}^{-1}$ ), suggesting that atmospheric  $N_2O$  increase is primarily attributed to isotopically light anthropogenic sources. However, for  $\delta^{15}N^{SP}$  and  $\delta^{18}O$  of  $N_2O$ , no significant interannual trend was found for the 5-year data-series.

The online measurements of  $N_2O$  mixing ratios at JFJ showed a clear early summer maximum and late summer minimum (Fig. 2). Such seasonal pattern is similar to those observed at other background stations with long-term monitoring of atmospheric  $N_2O$ . One explanation of the late-summer minimum is a strong influence of the stratosphere-troposphere exchange (STE) process in this period, which transports  $N_2O$ -depleted but isotopically ( $^{15}N$ ) enriched air downward from the stratosphere into the troposphere (Decock and Six, 2013). During the late summer at JFJ, we find strong enrichment of  $^{15}N$  in atmospheric  $N_2O$  according to the detrended seasonality of the whole dataset (Fig. 2). However, this explanation doesn't support the seasonal pattern of  $\delta^{15}N^{SP}$  at JFJ, which appeared to show a minimum in July-August.  $N_2O$  emission inventories for Switzerland were simulated based on a regional inverse model (data not shown), indicating that highest  $N_2O$  emission (mainly from soils) occurs in May to July at JFJ. Hence, we attributed the low  $\delta^{15}N^{SP}$  found in late summer to a pronounced influence from soil emission, which even overwrites the isotopic effect from the STE process.

The footprint analyses based on air mass residence times revealed that air masses received from regions with strong anthropogenic fingerprints display higher  $N_2O$  mixing ratios and lower delta values (Yu et al., 2019). This further supports that seasonality of  $N_2O$  mixing ratios and isotopic composition observed at JFJ is partly regulated by the influence of the planetary boundary layer. We also estimated the average isotopic signature of anthropogenic  $N_2O$

sources with a two-box model to be  $-8.6 \pm 0.6 \text{ ‰}$  for  $\delta^{15}N^{bulk}$ ,  $34.8 \pm 3 \text{ ‰}$  for  $\delta^{18}O$  and  $10.7 \pm 4 \text{ ‰}$  for  $\delta^{15}N^{SP}$ . Our study suggests that seasonal variation of  $N_2O$  isotopic composition determined with long-term measurements is crucial for evaluating interannual trends of atmospheric  $N_2O$  and its global sources.

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**Internet data bases**

<https://www.empa.ch/web/s503/emissions-and-isotopes?inheritRedirect=true>  
<https://www.empa.ch/web/s503/global-atmosphere-watch>  
<https://www.empa.ch/web/s503/nabel>  
<https://www.empa.ch/web/s503/flexpart-cosmo>

**Collaborating partners / networks**

Paul Krummel, Ray Langenfelds and Paul Steele, CSIRO Marine and Atmospheric Research, Aspendale, Australia

**Scientific publications and public outreach 2019****Refereed journal articles and their internet access**

Harris, S.J., J. Llisberg, L. Xia, J. Wei, K. Zeyer, L. Yu, B. Wolf, B.F.J. Kelly, D.I. Cendón, T. Blunier and J. Six, N<sub>2</sub>O isotopocule measurements using laser spectroscopy: analyzer characterization and intercomparison, *Atmos. Meas. Tech. Discuss.*, 1–84, 2019. <https://doi.org/10.5194/amt-2019-451>

Yu, L., E. Harris, S. Henne, S. Eggleston, M. Steinbacher, L. Emmenegger, C. Zellweger and J. Mohn, The isotopic composition of atmospheric nitrous oxide observed at the high-altitude research station Jungfrauoch, Switzerland, *Atmos. Chem. Phys. Discuss.*, 2019. <https://www.atmos-chem-phys-discuss.net/acp-2019-829/>

**Conference Papers**

Yu, L., E. Harris, E. Ibraim, M. Steinbacher, S. Henne, L. Emmenegger, C. Zellweger and J. Mohn, Partitioning N<sub>2</sub>O sources with isotopes: from ground to atmosphere, DASIM Conference - tracing Denitrification, Giessen, Germany, March 12-14, 2019.

Yu, L., E. Harris, S. Henne, M. Steinbacher, L. Emmenegger, C. Zellweger and J. Mohn, Seasonal patterns and trends of N<sub>2</sub>O isotopes observed in the unpolluted atmosphere, American Geoscience Union Fall Meeting, San Francisco, USA, December 9-13, 2019.

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