Supplementary information for:

**Attribution of N$_2$O sources in a grassland soil with laser spectroscopy based isotopocule analysis**

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1. **N$_2$O fluxes with coupled flux chambers and GC-ECD**

![Graph showing N$_2$O fluxes at the intensively managed grassland site De-Fen](image)

SI Figure 1 N$_2$O fluxes at the intensively managed grassland site De-Fen determined with five automated chambers and N$_2$O analysis by GC-ECD. Vertical dashed lines indicate the mowing (blue) and the manure applications (red).

1.1 **Comparison of N$_2$O mole fractions and N$_2$O emission rates**

N$_2$O concentrations 2 m above ground analysed by TREX-QCLAS show a significant correlation (p-value < 0.05) with $f$ (N$_2$O) obtained with the coupled flux-chamber and GC-ECD (SI Figure 2).
SI Figure 2 Comparison of N₂O mole fractions measured with the TREX-QCLAS system and the N₂O fluxes measured with the coupled flux-chambers and GC-ECD system. The figure on the right depicts the comparison of noon-to-noon average values as obtained with the two measurement systems shown on the left. The r-squared value and the p-value are given.

2. Source signatures

2.1 Miller and Tans (2003) analysis

A Miller and Tans (2003) analysis as performed by Harris et al. (2017) was conducted to retrieve source signatures with an independent method in order to verify the Keeling (1958, 1961) plot-derived results. For the first third of the measurement period source signatures calculated with the Keeling (1958, 1961) plot approach did not pass the selection criteria due to lack of N₂O build up and Miller and Tans (2003) derived source signatures are rather scattered. In periods with reasonable N₂O fluxes, there is a very good agreement between the two methods.
2.2 Illustratory example for the SP vs. $\Delta\delta^{15}$N$_{\text{bulk}}$ and SP vs. $\Delta\delta^{18}$O plots

SI Figure 4 Illustration of the two concepts behind the two mapping approaches used in the main document. The source signatures of fungal denitrification- and nitrification-derived N$_2$O (FD/ N) and bacterial denitrification- and nitrifier denitrification-derived N$_2$O (BD/ ND) are indicated with rectangles according to the values given in Table 4. The shaded area represents the mixing region of the two domains. As exemplary values, the average source signatures for our measurements are given with the orange star. Red arrows denote the path of partial N$_2$O reduction to N$_2$, while black arrows indicate the direction of mixing with FD/ N-derived N$_2$O. Solid arrows indicate scenario 1 (first reduction, then mixing), while dashed arrows indicate scenario 2 (first mixing, then reduction). (a) SP versus $\Delta\delta^{15}$N map according to Koba et al. (2009), where $\Delta\delta^{15}$N = δ$^{15}$N-NO$_3$ – δ$^{15}$N-N$_2$O. (b) SP versus $\Delta\delta^{18}$O of soil-emitted N$_2$O according to Lewicka-Szczebak et al. (2017), where $\Delta\delta^{18}$O = δ$^{18}$O-N$_2$O – δ$^{18}$O-H$_2$O.

SI Figure 4 illustrates the SP vs. $\Delta\delta^{15}$N$_{\text{bulk}}$ and SP vs. $\Delta\delta^{18}$O plots with the average source signatures (given as orange stars). The two rectangles labelled with FD/ N and BD/ ND indicate the expected source signatures of fungal denitrification/ nitrification (FD/ N) derived N$_2$O and bacterial denitrification/ nitrifier-denitrification (BD/ ND) derived N$_2$O. Source signatures falling into the grey shaded area correspond to a N$_2$O mainly derived by a mix of the two process domains. Red arrows indicate the path of source-signature changes due to partial N$_2$O reduction, while black arrows indicate source signature changes due to mixing of N$_2$O originating from the two process domains. In principle, two scenarios are possible to interpret the measured source signatures (Lewicka-Szczebak et al., 2017). Scenario 1: BD/ ND derived N$_2$O is partially reduced to N$_2$, then the residual N$_2$O is mixed with FD/ N derived N$_2$O. Scenario 2: BD/ ND derived N$_2$O is mixed with FD/ N derived N$_2$O first and then partial N$_2$O reduction to N$_2$ occurs. The rate of N$_2$O reduction is calculated with the Rayleigh approach (described in detail in the main manuscript), while the rate of mixing is assumed linearly proportional to the length of the mixing vectors ($V_{\text{mix}}$).
2.3 N₂O-to-N₂ reduction rates of individual events determined with different approaches and using different scenarios

SI Figure 5  Left: Fraction of remaining N₂O after the N₂O reduction as estimated with different approaches and assuming different scenarios (rN₂O refers to residual N₂O after N₂O reduction to N₂; sc11 = Koba approach scenario 1, sc12 = Koba approach scenario 2, sc21 = Lewicka-Szczebak approach scenario 1, and sc22 = Lewicka-Szczebak approach scenario 2). Dashed lines correspond to the 1:1 line. While the blue fit corresponds to the linear regression of all data points (n=12), the red fit was carried out only for rN₂O values smaller than 0.4, i.e. for cases with high N₂O reduction rates. Right: distribution of the rN₂O values given with boxplots.

SI Figure 6  Fraction of remaining N₂O after N₂O reduction plotted against WFPS, where rN₂O has been calculated using different approaches and assuming different scenarios (rN₂O refers to residual N₂O after N₂O reduction to N₂. Explanation of suffix: sc11 = Koba approach scenario 1, sc12 = Koba approach scenario 2, sc21 = Lewicka-Szczebak approach scenario 1, and sc22 = Lewicka-Szczebak approach scenario 2)
SI Figure 7 Fraction of remaining N₂O after N₂O reduction plotted against ambient temperature, where rN₂O has been calculated using different approaches and assuming different scenarios (rN₂O refers to residual N₂O after N₂O reduction to N₂). Explanation of suffix: sc11 = Koba approach scenario 1, sc12 = Koba approach scenario 2, sc21 = Lewicka-Szczebak approach scenario 1, and sc22 = Lewicka-Szczebak approach scenario 2)

SI Figure 8 left: Fraction of N₂O originating from fungal denitrification or nitrification (rNit), determined based on the mapping approach according to Lewicka-Szczebak et al. (2017) (rNit2; referred to as approach 2) versus rNit as determined based on the mapping approach according to the Koba et al. (2009) approach (rNit1; referred to as approach 1). Right: boxplots of rNit1 and rNit2. The medians of rNit1 and rNit2 are 0.37 and 0.41, respectively, indicating 37 and 41 % of FD/N derived N₂O on the total emissions.
2.4 Contribution of FD/N and BD/ND to the total emissions

SI Figure 9 Blue bars indicate the fraction of FD/N derived N$_2$O on the total N$_2$O emissions for individual emission events, while red bars refer to the fraction of BD/ND derived N$_2$O.

3. FLEXPART-COSMO simulations with local micro meteorological inputs

SI Figure 10 Simulation of concentration accumulation events with FLEXPART-COSMO. Observation data were obtained with TREX-QCLAS (black), while Sim Local (red) and Sim Nest (green) refer to values simulated with FLEXPART-COSMO assuming horizontally homogenous fluxes of $f$(N$_2$O) in the local domain shown in Figure 1 and in a larger domain (16 km x 16 km), respectively. Fluxes were taken as the mean flux observed in the chamber measurements as shown in the lower panel.

3.1 Footprints of individual events
SI Figure 11 Individual footprints of the 12 accumulation events
4. References


