

Real-time measurement of site specific N₂O isotopic composition above intensively managed grassland reveals controls on N₂O source processes

Institute for Meteorology and Climate Research, Atmospheric Environmental Research (IMK-IFU)

^{1,2}Wolf B., ³Decock C., ³Merbold L., ¹Tuzson B.,
¹Emmenegger L., ¹Mohn J.

¹ Karlsruhe Institute of Technology (KIT), Germany

² Empa, Laboratory for Air Pollution and Environmental Technology,
Swiss Federal Laboratory for Materials Science and Technology,
Switzerland

³Institute of Agricultural Sciences, ETH Zürich, Switzerland

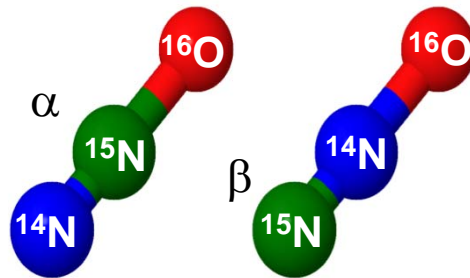
benjamin.wolf@kit.edu



Motivation

- N_2O is a potent GHG mainly produced by nitrification, nitrifier denitrification or denitrification
- $\geq 60\%$ of anthropogenic emissions attributed to food production (Syakila & Kroeze 2011) \rightarrow atmospheric mole fraction increases
- development of mitigation strategies pertinent BUT: which source process needs to be controlled to tailor target-oriented strategies?
- relative contribution of N_2O source processes to bulk emission uncertain

N₂O isotopomers



$$SP = \delta^{15}N_{\alpha} - \delta^{15}N_{\beta}$$

■ N₂O isotopomers carry process information: processes with

- preference for α-position (N₂O_N; SP ~ 33 ‰*)
 - nitrification, abiotic N₂O production, fungal denitrification
- low preference (N₂O_D; SP ~ -2 ‰*)
 - (nitrifier) denitrification

→ SP can be used to separate N₂O_N and N₂O_D

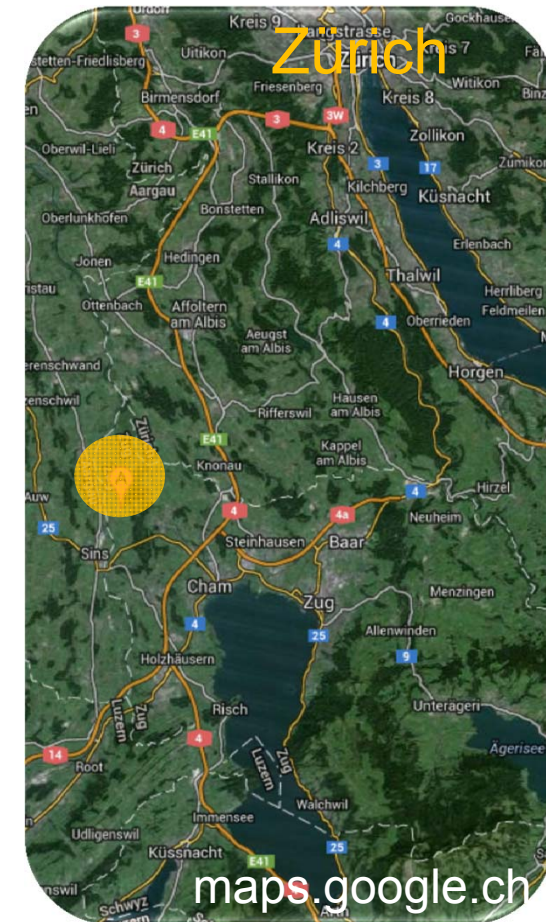
* SP values for N₂O_N and N₂O_D according to Decock and Six 2013

Sampling site & specific aims

- site specific measurements predominately lab based
- intensively managed grassland site (ETH site Chamau)
- eddy covariance & chamber measurements

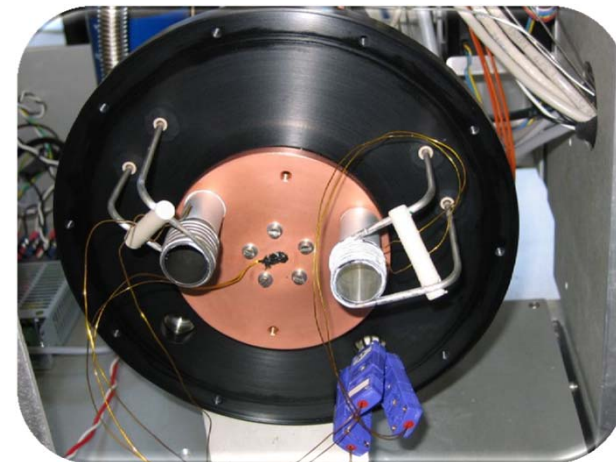
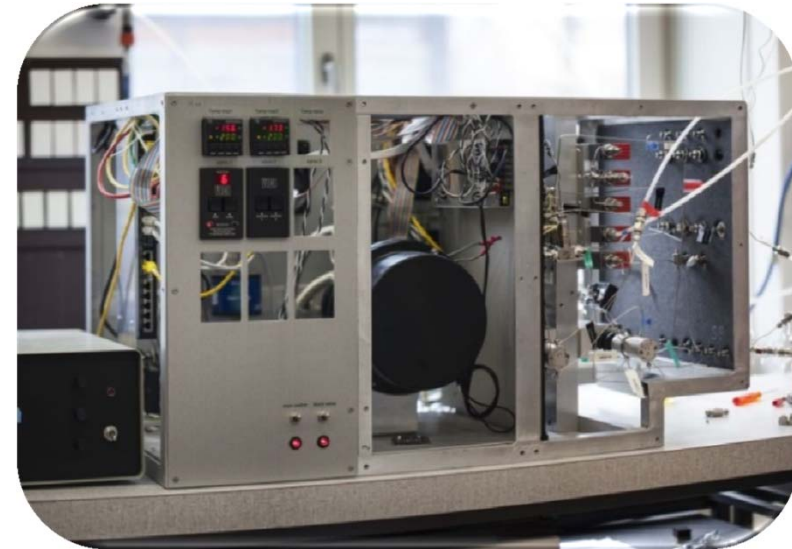


- study
 - dynamics of N₂O site specific isotopic composition
 - effects of environmental drivers and management



Isotopomer analysis

- until recently exclusively IRMS measurements (not field deployable)
- quantum cascade laser absorption spectroscopy (QCLAS) allows online analysis of N_2O isotopic composition in the field
- ambient air N_2O concentration too low for precise on-line measurement of isotope ratios
- N_2O of ~ 8 liters ambient air is adsorbed on a HayeSepD trap
- desorption in low synthetic air flow increases concentration to 50ppm



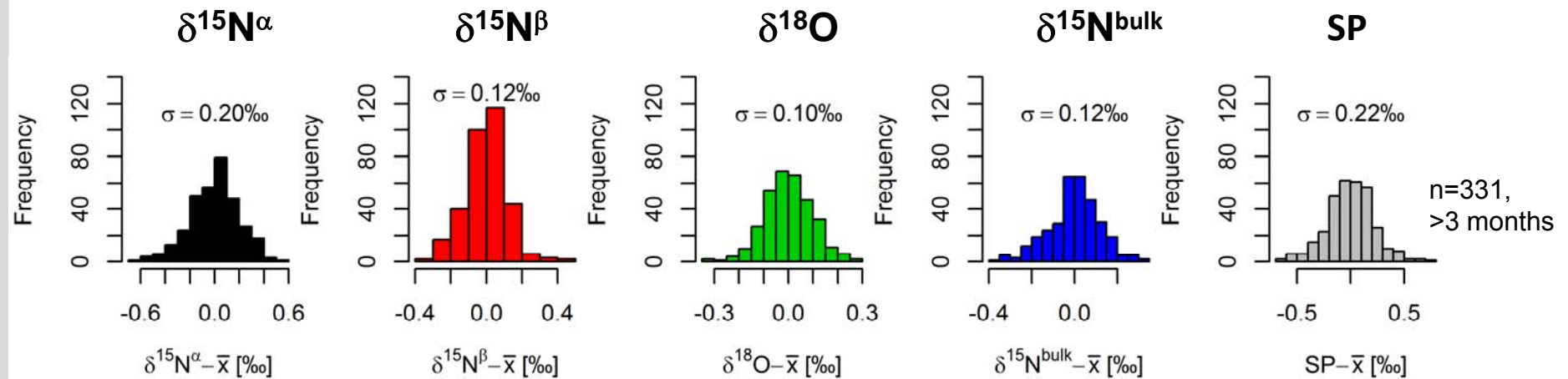
System performance



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Surface layer measurements



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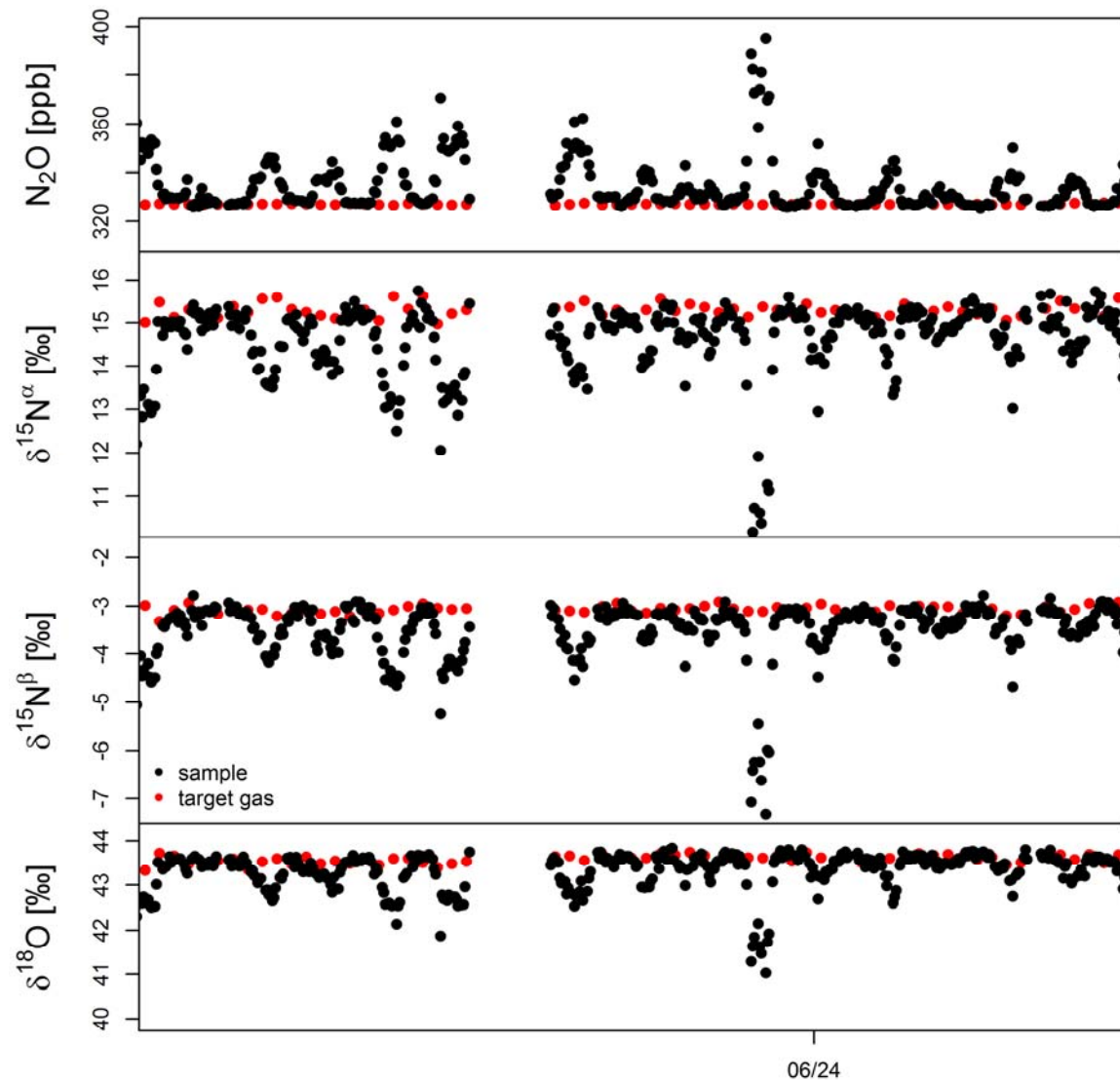


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- ambient air sample (inlet @ 2m height)
- compressed air sample

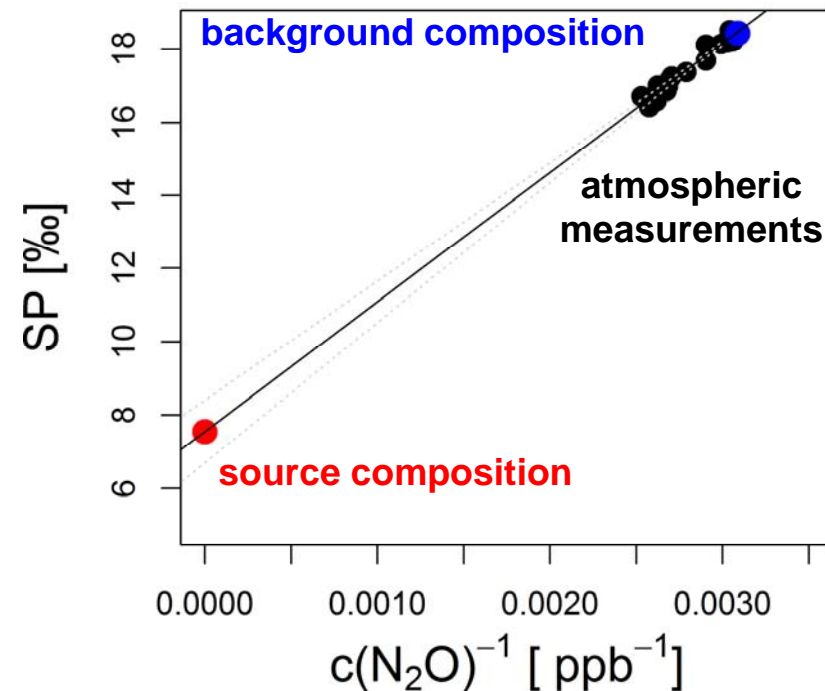
■ C_{input} : diurnal cycle of atmospheric N_2O (source strength and stability)

■ depletion of δ -values with increasing concentration



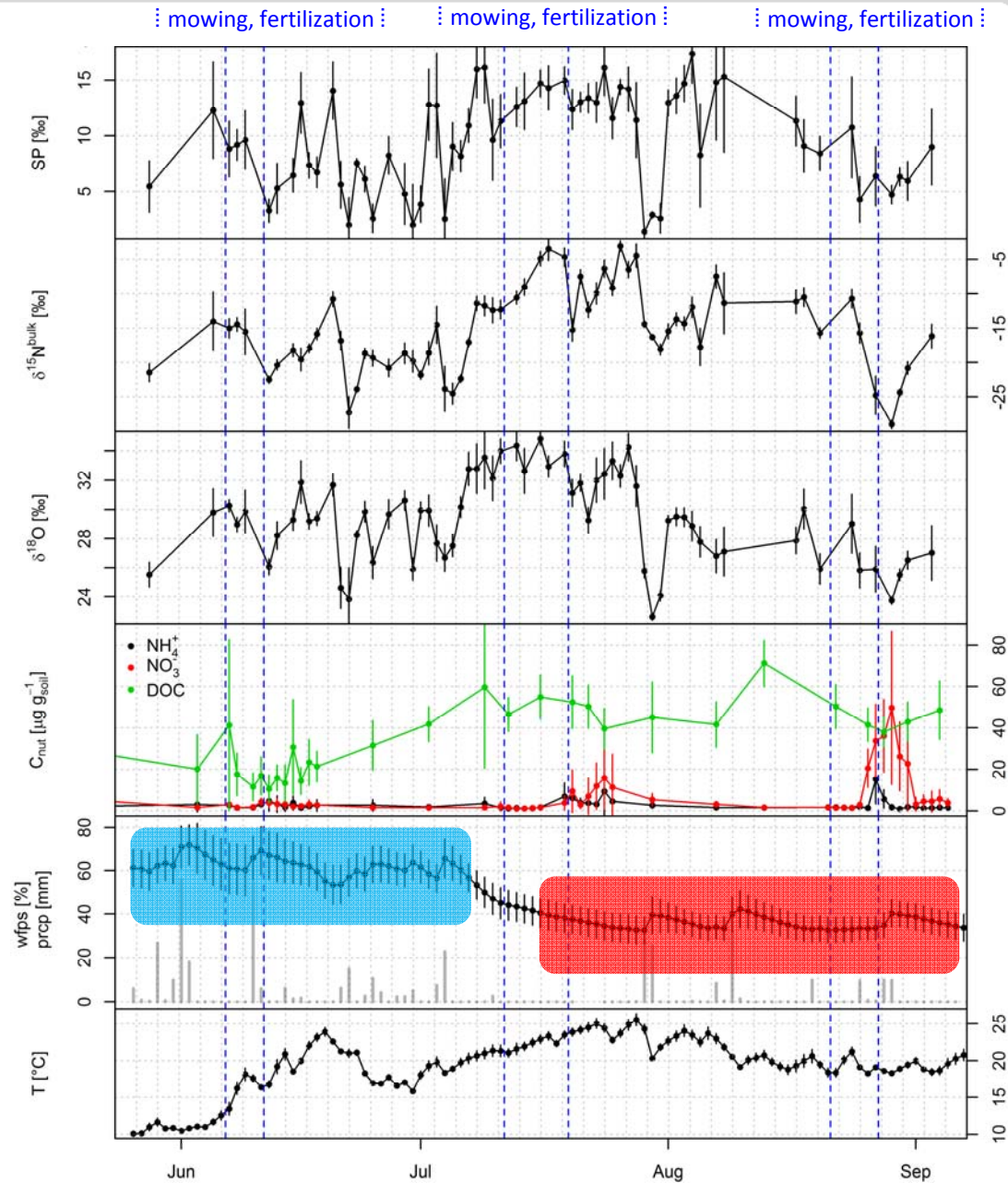
Keeling-plots for SP, $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$

- atmospheric isotopic composition in surface layer reflects combination of **source** and **atmospheric background composition**
- **source** composition equals intercept when noon-to-noon atmospheric isotopic composition is plotted versus inverse concentration



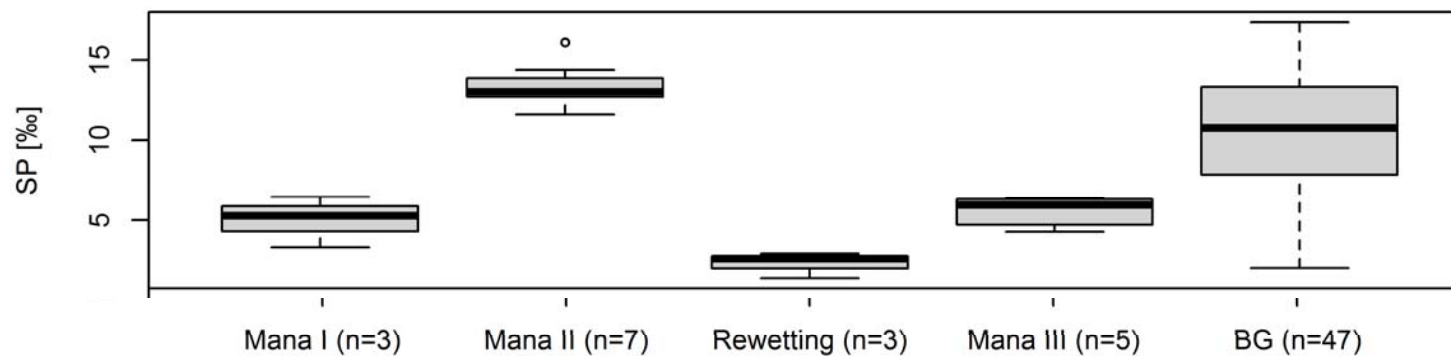
Isotopic composition: soil-emitted N₂O

- SP between 1 and 17‰
- large (short term) variation
- management actions & rewetting event decreased SP
- correlations of N₂O isotopic composition highest with
 - temperature
 - DOC (dissolved organic carbon)
- r² below 30%
- «wet» and «dry» period



Event based data aggregation

- classes: Manal – Manall, rewetting, all others (BG)
- variability during events like management or rewetting low
- isotopic composition very variable when no obvious drivers



- isotopic composition significantly different for dry/wet phases
 - SP lower during wet phase, higher during dry phase
- larger contribution from nitrification?

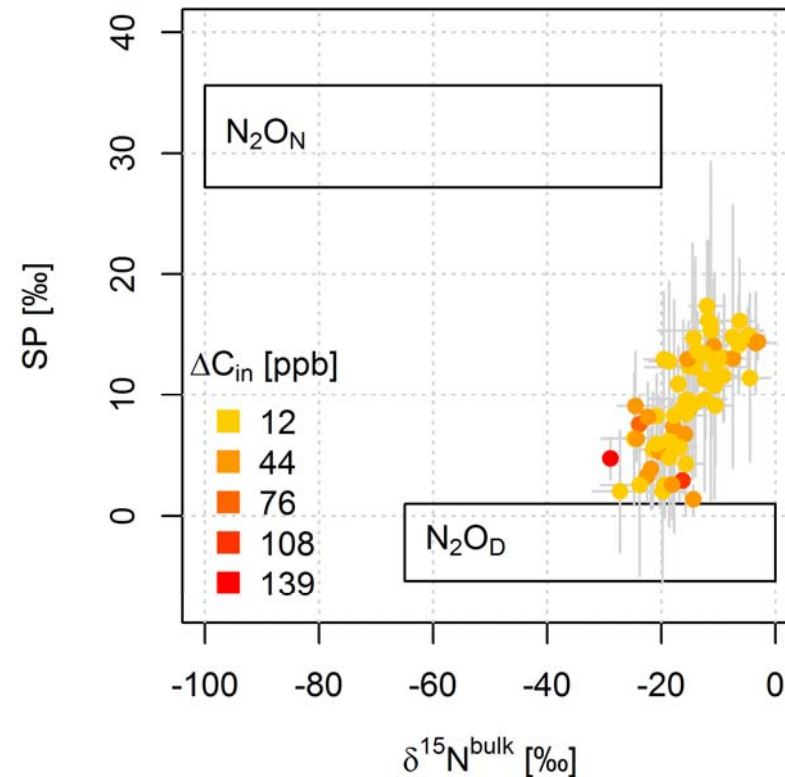
Isotopomer maps (according to Koba et al. 2009)



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Process groups $\text{N}_2\text{O}_\text{N}$ and $\text{N}_2\text{O}_\text{D}$ based on:

Bedard-Haughn et al. (2003), Pörtl et al. (2007), Baggs (2008), Toyoda et al. (2011), Decock and Six (2013)

- high emission rates: denitrification
- enrichment of $\delta^{15}\text{N}^{\text{bulk}}$ and SP indicates N_2O reduction

Conclusions

- simultaneous field measurement of $\delta^{15}\text{N}^\alpha$, $\delta^{15}\text{N}^\beta$ and $\delta^{18}\text{O}$ of N_2O with high reproducibility (0.2, 0.1 and 0.1 ‰)
- during management/rewetting low δ -values and well constrained (denitrification)
- significantly **lower** SP during **wet** phase, **higher** SP during **dry** phases
- isotopomer maps: process dynamics not due to transition of $\text{N}_2\text{O}_\text{D} \rightarrow \text{N}_2\text{O}_\text{N}$; rather due to variable extent of N_2O reduction to N_2
- large (short term) variability probably due to uncertainty, or mismatch between flux and concentration footprint

Thank you for your attention



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Thanks to
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COST-SBF



Controls: whole dataset

- correlations of N₂O isotopic composition highest with

- temperature
- DOC (dissolved organic carbon)

- r² below 30%

- additive models do not increase explanatory power significantly

