

## ***Interactive comment on “Site selective real-time measurements of atmospheric N<sub>2</sub>O isotopomers by laser spectroscopy” by J. Mohn et al.***

### **Anonymous Referee #4**

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The authors combined and extended previous work on air sample preparation and stable isotope analysis of ambient N<sub>2</sub>O, and benchmarked their setup with reference measurements (standards, IRMS) and a brief field experiment on a grassland site under normal (autumn) conditions and fertilizer application.

The manuscript is well written with enough technical detail to understand the differences and modifications that resulted in improved performance compared to previous work on N<sub>2</sub>O preconcentration setups and laser spectroscopy analysis of N<sub>2</sub>O isotopomers by the same authors. The performance of the setup is impressive, and the presented results demonstrate it can be used to identify distinct isotopic signals in the field. Nevertheless, I ask the authors to consider the following comments:

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1. 'liquid nitrogen-free', 'HayeSep D trap'; operating a field setup without liquid nitrogen is truly an advantage, but defining what is used (instead of what is not) would be more helpful in text (p816l12) and abstract. For instance, 'sorption-based' instead of 'liquid nitrogen-free'. In addition, please describe 'HayeSep D', with the product and manufacturer details in parenthesis. For instance, a 'porous polymer sorption trap (HayeSep D, ....)'.
2. 'real-time'; The 'real-time' aspect of the approach, as mentioned in title and text (e.g., abstract, p816l10, p825l15), may be misleading when using an alternating sample collection and sample analysis stage. The approach predetermines discontinuous sampling and may give the impression it results in true time-series of the mixing ratios of N<sub>2</sub>O isotopomers, whereas Fig. 2 shows the intermittency of the automated schedule. Also, similar laser spectroscopy instruments are used for measurements at much shorter integration times that more closely relate to the time scales of the processes involved in exchange near the surface. In summary, I would argue that 'real-time' should be reserved for a measurement setup that would not need pre-concentration. 'In-situ' would be more appropriate terminology.
3. A discussion is missing on how the presented setup is expected to perform in summer when a different temperature regime influences sampling & analysis, and N<sub>2</sub>O exchange processes are expected to be different. As the trap temperature is raised to 10 degrees, this would require cooling on a hot day? Information of the environmental conditions during the experiment (temperature) would be helpful. This may also lead to a positive argument, as the system was able to detect significant diel cycles in a presumably cool part of the season.
4. It would be useful to know if the problematic laser driver was replaced with a unit of the same make and model, or not (p821l15).
5. Details of the fertilizer experiment are given in the Results & Discussion section

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- on p822115 and the caption of Fig. 3, but not in the Methods section.
6. The automation schedule is presented ‘as is’ without further discussion on how this could be changed or improved upon, or relaxed to increase number of samples. Could the std I-1 be measured in shorter intervals such as used around 200 min and after 400 min. And what would be the resulting performance if samples and standards are integrated over shorter intervals? The data abundance of a QCLAS would easily allow such an analysis, for example by averaging fractions of the data in the scheduled stages shown in Fig 2. In addition, from Fig 2 it seems that longer time periods are used for the measurement of std-I-1 than for measurement of preconcentrated air (e.g. in the first 190 min). Is that correct? If so, why? If this is determined by the trapping time, please discuss if this can be reduced too, for instance by higher flow rates or otherwise.
  7. The Keeling plot approach is only briefly introduced. As a two end-member mixing model (following Keeling, 1958/1961) it relies on a number of assumptions. I wonder if the assumption of a stable background signal for  $N_2O$  is violated over the course of the day, for instance due to differences in conditions for day-time and night-time. Are the processes involved in production and exchange of  $N_2O$  and any isotopic signals (bulk, SP) continuous processes and is there a stable background signal? Please add convincing arguments why the ‘Keeling-plot’ approach can be used for 24 hour integration of  $N_2O$  data. Without consideration or discussion it may give the reader the impression that the used approach is sound, even if it is only applied to demonstrate the performance of the setup in relation to the natural and (fertilizer) treatment induced variability. With the above in mind, please review lines such as "After fertilizer application the isotopic source signatures are better constrained because of a larger diurnal change in  $N_2O$  mixing ratios".

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Minor comments:

8. p820l21: A definition is given for  $\delta^{15}\text{N}_{\text{bulk}}$  as the the weighted average of two site-specific abundances (p815l3). Were the IRMS reference values for  $\delta^{15}\text{N}_{\text{bulk}}$  also computed from the measured site-specific values or determined separately?
9. please clarify acronyms used in figures in the figure captions and use acronyms consistently (CH or Switzerland, versus or vs.).
10. Fig 4. Axis label 'Nr. of bins'. Is this 'Number per bin'?
11. p819l8: (... , Varian, ???) Located where?
12. Title mentions 'site selective', the text 'site-specific'. Please choose.

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