

Interactive comment on “A liquid nitrogen-free preconcentration unit for measurements of ambient N₂O isotopomers by QCLAS” by J. Mohn et al.

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The authors would like to thank Reviewer #1 for his helpful comments and suggestions. These have been addressed individually.

General comments:

1. Comment: The paper presents adaption and testing of an existing preconcentration device (MEDUSA) for isotopic analysis of nitrous oxide at ambient atmospheric mixing ratios. The main advantage of the present approach over existing cryogenic N₂O preconcentration devices is that liquid nitrogen is not required. Quantitative trapping is

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achieved by a commercial chiller combined with a chemical absorbent (HayeSep D). The final goal of the authors is to develop an optical method for position-specific nitrogen isotope analysis in N₂O. The present work is all but a first step to this goal. I would have normally expected that such minor development steps appear as a section of a proper method paper. As such, I am surprised that this work has been published as a stand-alone publication. However, in terms of scientific and technical quality, there are no major flaws with this paper.

Reply: To our knowledge, the continuous site-specific isotopic analysis of N₂O by laser spectroscopy in combination with cryogen-free preconcentration as presented in our paper has not been achieved before and is relevant for many scientists as also mentioned by Reviewer # 3.

We agree that the work presented here is a first step in achieving the ultimate goal of position-specific nitrogen isotope analysis under field conditions; nevertheless this step has addressed several major issues that are by no means of minor importance. It should be recognized that sample preconcentration under field conditions for trace gas isotopic analysis by laser spectroscopy provides special requirements, differing from laboratory setups applied for isotope ratio mass spectrometry (IRMS) or the original “Medusa” designed for concentration measurements of halogenated compounds by gas-chromatography mass-spectrometry. To account for this, the system has been completely redesigned and rebuilt. Moreover, isotope fractionation effects in such devices have not been investigated yet, thus the authors had to develop the adequate methodology and make the corresponding software/hardware adaptations. The spectroscopic implications of preconcentrating ambient air have, to our knowledge, not been considered in any other paper with respect to isotopic ratio measurements. As shown by our work, this might be relevant and can only be studied with considerable experimental and instrumental effort. Being a methodological paper, the authors aim was to present a complete and detailed investigation of this unit, which will present a reference point for follow-up research activities. Based on the results reported here,

namely the evidence for excellent recovery of N₂O, conservation of the N₂O isotope ratios and negligible impact of other atmospheric constituents on the infra-red absorption spectrum, it should be evident that the developed system in combination with a laser spectrometer may be of interest for the research community devoted to measuring the isotope signatures of trace gases, even more so because the system can also be applied for online isotopic analysis of other trace gases with low atmospheric abundance (e.g. CH₄: d¹³C-CH₄, dD-CH₄ and CO: d¹³C-CO, d¹⁸O-CO).

Specific comments:

2. Comment: The "enriched" N₂O (15N/14N 25.4 ‰ enriched vs. "medical" N₂O) has not been described. Also, an independent verification of this value using established techniques (i.e. isotope ratio mass spectrometry) should be included. p. 3107, l. 18: 25.4 ‰ - calibrated how?

Reply: The authors agree to include an absolute calibration of the isotopic composition of the N₂O reference gases applied in the present study. N₂O reference gases were analysed by Sakae Toyoda in the laboratory of Prof. Naohiro Yoshida at the Tokyo Institute of Technology. In detail the following sentences were corrected:

p. 3107, l. 17-19: ...and gravimetrically prepared 90.8 ppm N₂O in synthetic air (Wächter et al., 2008) with a distinct isotopic composition of d¹⁵Na = 25.9 ± 0.4‰ and d¹⁵Nb = 25.2 ± 1.0‰ as analysed by IRMS (Toyoda and Yoshida, 1999) to investigate ...

p. 3109, l. 2-5: ... a N₂O reference gas (90.8 ppm) analysed by IRMS (d¹⁵Na = 25.9 ± 0.4‰ and d¹⁵Nb = 25.2 ± 1.0‰) was diluted ...

p. 3109, l. 16-20: ... to calculate $Dd = d^{15}N_{precon} - d^{15}N_{original}$ (n=4–8). QCLAS calibration was performed using medical grade N₂O (91.1 ppm N₂O, d¹⁵Na = 2.1 ± 0.1‰ and d¹⁵Nb = 2.0 ± 0.4‰) and a gravimetrically prepared enriched gas (90.8 ppm N₂O, d¹⁵Na = 25.9 ± 0.4‰ and d¹⁵Nb = 25.2 ± 1.0‰) both analysed by IRMS

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(Toyoda and Yoshida, 1999).

p. 3112, l. 5-6: All experiments were done with gases that were enriched in d¹⁵Na by 25.9 ± 0.4‰ and d¹⁵Nb by 25.2 ± 1.0‰.

3. Comment: Isotopic fractionation of "medical" and "enriched" N₂O should be tested independently to check whether the preconcentration method suffers from any scale compression.

Reply: The authors agree that scale-compression may affect the analytical results. Therefore, scale compression was considered by calibrating the laser spectrometer applying different reference gases with distinct isotopic composition as mentioned on p. 3108, l. 16-20. The N₂O preconcentration itself might only be subject to fractionation, which was tested and excluded.

Technical corrections:

4. Comment: p. 3100, l. 4: Please replace "isotope ratios" by "relative isotope ratio differences" or "delta values". p. 3107, l. 1: delta values are not ratios

Reply: The authors agree that "isotope ratios" or "isotopomer ratios" for the relative isotope ratio differences d¹⁵Na and d¹⁵Nb are loose terminologies, although widely used in the scientific literature. In the revised manuscript they were replaced by "relative isotope ratio differences" or "delta values" as suggested by Reviewer #1.

5. Comment: p. 3100, l. 18: Replace "greenhouse warming potential" by "radiative forcing among long-lived greenhouse gases".

Reply: In accordance with A. R. Ravishankara et al. (Science 326, 123–125, 2009) the term "greenhouse warming potential" was changed to "... the second largest global warming potential weighted (GWP) emissions of non-CO₂ greenhouse gases".

6. Comment: p. 3100, l. 19: Replace "concentrations" by "mixing ratios".

Reply: Changed

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7. Comment: p. 3100, l. 20: Replace "parts per billion, 10–9 molar" by "parts per billion = 10⁻⁹".

Reply: The authors changed "parts per billion, 10–9 molar" to "parts per billion, 10–9 moles of trace gas per mole of dry air" according to the GAW Report No. 186 (Laurila, T.: 14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, GAW Report No. 186, Helsinki, Finland, 145 pp., 2007).

8. Comment: p. 3100, l. 21: Replace "yr-1" by the international symbol "a-1".

Reply: Changed

9. Comment: p. 3100, l. 21-22: Change to "on a global a scale are microbial production in agricultural and natural soils as well as rivers, estuaries, coastal areas and oceans". Fossil fuel and biomass burning are actually minor sources.

Reply: The authors agree and changed the sentence accordingly.

10. Comment: p. 3100, l. 24: Add "individual" before "sources".

Reply: Changed

11. Comment: p. 3101, l. 12: The value of 7.0 ‰ is too high and was later corrected to 6.5 ‰ (Toyoda S, Yoshida N, Urabe T, Nakayama Y, Suzuki T, Tsuji K, Shibuya K, Aoki S, Nakazawa T, Ishidoya S, Ishijima K, Sugawara S, Machida T, Hashida G, Morimoto S, Honda H (2004) Temporal and latitudinal distributions of stratospheric N₂O isotopomers. *J Geophys Res* 109, D08308, doi:10.1029/2003JD004316) in recognition of interlaboratory comparisons. Kaiser et al. (2003) reported (6.72 ± 0.12) ‰ (Kaiser J, Röckmann T, Brenninkmeijer CAM (2003) Complete and accurate massspectrometric isotope analysis of tropospheric nitrous oxide. *J Geophys Res* 108, 4476, doi:10.1029/2003JD003613). Park et al. (2004) found (6.3 ± 0.3) ‰ (Park S, Atlas EL, Boering KA (2004) Measurements of N₂O isotopologues in the stratosphere: Influence of transport on the apparent enrichment factors and the isotope fluxes to the

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troposphere. *J Geophys Res* 109, D01305, doi:10.1029/2003JD003731). p. 3101, l. 12 & l. 13: Please include errors with these numbers.

Reply: The authors agree that additionally literature should be included and changed the sentence to: The bulk nitrogen isotope ratio ($d_{15}N_{bulk} = (d_{15}Na + d_{15}Nb)/2$) of tropospheric N₂O was found to be enriched by 6.3 ± 0.3 ‰ to 6.72 ± 0.12 ‰ relative to air-N₂ (Yoshida and Toyoda, 2000; Toyoda et al., 2004; Kaiser et al., 2003; Park et al., 2004), with a strong site preference (SP = $d_{15}Na - d_{15}Nb$) of 18.7 ± 2.2 ‰ for the central nitrogen atom (Yoshida and Toyoda, 2000).

12. Comment: p. 3101, l. 17: Values up to 140 ‰ have been reported by Kaiser et al. (2006) (Kaiser J, Engel A, Borchers R, Röckmann T (2006) Probing stratospheric transport and chemistry with new balloon and air-craft observations of the meridional and vertical N₂O isotope distribution. *Atmos Chem Phys* 6, 3535-3556). p. 3101, l. 19: The upper stratospheric N₂O mixing ratio is essentially 0.

Reply: The authors agree and changed the sentence to: In the stratosphere, the abundance of the heavier isotopomers and the SP increases with altitude to values as high as 140 ‰ for $d_{15}N_{bulk}$ (Kaiser et al., 2006) and 100 ‰ for SP (Toyoda et al., 2001), mainly due to isotopic fractionation during UV-induced photolysis and oxidation.

13. Comment: p. 3101, l. 19: Replace "Isotopomer ratios" by "Isotopic signatures". Please note the difference between isotopologues (molecules with different isotopic composition) and isotopomers (molecules with the same isotopic composition, but different arrangement of the isotopes).

Reply: The authors are aware of the IUPAC definitions. To rule out any confusion, the suggestion of the Reviewer was applied throughout the text.

14. Comment: p. 3101, l. 27: There are also optical techniques such as laser spectroscopy (Uehara K, Yamamoto K, Kikugawa T, Yoshida N (2003) Site-selective nitrogen isotopic ratio measurement of nitrous oxide using 2 μm diode lasers. *Spec-*

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trochimica Acta Part A: Molecular and Biomolecular Spectroscopy 59, 957-962) and FTIR techniques (Esler MB, Griffith DWT, Turatti F, Wilson SR, Rahn T, Zhang H (2000) N₂O concentration and flux measurements and complete isotopic analysis by FTIR spectroscopy. Chemosphere: Global Change Science 2, 445-454).

Reply: Studies applying optical techniques for N₂O isotopomer analysis are already presented in the next paragraph on page 3102, l.10-20.

15. Comment: Note that GC-IRMS measurements of N₂O isotopologues do not occur at ambient concentrations, but rely on cryogenic preconcentration and GC separation.

Reply: The authors acknowledge this comment and reformulate p. 3101, l.25-27: In the past the only technique for high precision isotopic analysis was laboratory-based isotope-ratio mass-spectrometry (IRMS) in combination with flask sampling and cryogenic preconcentration.

16. Comment: P. 3101 l. 25 to p. 3102, l. 20: Please reformulate these paragraphs to more accurately reflect what can be and what has been done in terms of IRMS and optical N₂O isotopomer measurements.

Reply: As the presented publication is focused mainly on measurement technology and their specific requirements, a complete and detailed overview is beyond the scope of our manuscript, thus references to some excellent review papers are provided to the reader. Nevertheless we added the following sentence to p. 3101, l. 22: An overview on atmospheric applications of N₂O isotopic analysis can be found in a review publication of Brenninkmeijer et al. (Brenninkmeijer, C.A.M., Janssen, C., Kaiser, J., Rhee, T.S., Assonov, S.S.: Isotope effects in the chemistry of atmospheric trace compounds, Chem. Rev. 103, 5125-5161, doi: 10.1021/cr020644k, 2003).

17. Comment: p. 3104, l. 3: "Redy" should not be hyphenated

Reply: Changed

18. Comment: p. 3104, l. 17 and elsewhere: Please change the "proportional to" sign
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(tilde) to an "approximately equal" sign (two wavy lines arranged like an "equal" sign (=)). The use of the tilde sign to indicate approximation is a bad habit that presumably originates from limitations of typewriters.

Reply: Changed

19. Comment: p. 3104, l. 25 and elsewhere: "sccm" should be written as "cm³ (STP)" and STP (standard temperature and pressure) should be defined because its meaning (temperature and pressure) varies.

Reply: The term "sccm" is a commonly used abbreviation for volumetric flow rate normalized to standard temperature and pressure. Therefore no change was applied.

20. Comment: p. 3108, l. 8: Delete "molar" (amount (of substance) is always measured in mol).

Reply: Changed

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 3099, 2009.