

Interactive comment on “Revisiting the relationship between soil moisture and N₂O production pathways by measuring ¹⁵N₂O isotopomers” by Kate A. Congreves et al.

Anonymous Referee #1

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Revisiting the relationship between soil moisture and N₂O production pathways by measuring ¹⁵N₂O isotopomers

General comments

The authors present a very nice and high quality dataset of N₂O isotopomers from soil incubated over a gradient of moisture content. The study, however, has some major shortcomings in relating the dataset to the state of the art in N₂O research. I encourage the authors to elaborate in 3 areas: 1) Latest approaches to interpret N₂O isotopomer data 2) Consultation of literature on the effect of soil moisture on sources of N₂O based

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on isotope tracer work 3) Literature on factors controlling N₂O reduction With a more in depth analysis of the data and discussion of the results in relation to current literature, I believe this study can become a valuable and much appreciated contribution to the discipline.

The reviewer has no intentions of promoting or favoring own or colleagues' work in the comments. The cited literature is intended as a resource and starting point for a more in-depth literature search.

Specific comments

Title:

P 1 The word 'revisiting' in the title implies to me that our understanding was wrong, but the isotopomers confirm what we already knew.

Abstract:

P 1 Line 14: the authors mention 'three soils'. I suggest adding a sentence explaining the difference between the three soils

P 1 Line 24: I assume x is soil moisture in this equation. Please specify and explain to the reader the potential relevance or importance of these equations

Introduction:

P 2 Lines 3-4 and Lines 8-13: There are several studies that investigated the effect of soil moisture on mechanisms underlying N₂O emissions using ¹⁵N tracers. A few examples: - Stevens et al. 1997. Measuring the contributions of nitrification and denitrification to the flux of nitrous oxide from soil. *Soil Biology and Biochemistry* 29: 139-151 - Bateman and Baggs 2005. Contributions of nitrification and denitrification to N₂O emissions from soils at different water-filled pore space. *Biology and Fertility of Soils* 41: 379-388

P 2 Line 19: Early studies on the use of isotopomers appeared in the early years 2000

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by Ostrom et al., Well et al., and Toyoda et al. Please cite key early studies on the use of N₂O isotopomers to source partition N₂O.

Materials and methods: P 4 Line 25 – P 5 Line 20: A number of studies have been published on how to interpret N₂O isotopomer data. Lewicka-Szczepack published an elegant method for calculating N₂O from nitrification, denitrification and the fraction of N₂O reduced to N₂ based on SP and d¹⁸O of N₂O. Details on the calculation approach can be found here. I recommend that the authors revise their calculation of the sources of N₂O based on more recently published approaches. https://www.researchgate.net/publication/328135133_Mapping_approach_model_after_Lewicka-Szczepack_et_al_2017_-_detailed_description_of_calculation_procedures

The approach used by the authors has some major limitations, outlined below.

1) The authors use soil-specific end-members in their isotope mass balance, based on data from their experiment. While it cannot be excluded that isotope values characteristic of nitrification and denitrification are to some extent soil-dependent, the authors' approach relies on the assumption that at low moisture content, nitrification was the sole source of N₂O, while denitrification was assumed to be the sole source of N₂O at one of the medium range moisture contents. There is no independent measurement of the contribution of nitrification, denitrification and N₂O reduction to N₂. Limitations and assumptions of their approach need to be clearly stated.

Whether end-members are likely soil-dependent was discussed in a literature review by Decock and Six 2013. How reliable is the intramolecular distribution of ¹⁵N in N₂O to source partition N₂O emitted from soil? *Soil Biology and Biochemistry* 65: 114-127. Empirical studies since have further tested the effect of soil on end members, for example, Lewicka-Szczepack et al. 2014. Experimental determinations of isotopic fractionation factors associated with N₂O production and reduction during denitrification in soils. *Geochimica et Cosmochimica Acta* 134:55–73. The results of the presented study should be discussed in relation to other studies published on this topic.

2) The authors use the relationship between $\delta^{18}\text{O}$ and SP at higher soil moisture content as the line representative of N_2O reduction. It should be noted, however, that a N_2O reduction line is only applicable if N_2O reduction was the only process affecting N_2O . In the presented experiment, N_2O production and reduction likely occurred simultaneously. How simultaneous production and reduction of N_2O affects isotope maps is discussed in great detail in Decock and Six. 2013. On the potential of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ to assess N_2O reduction to N_2 . European journal of soil science 64:610-620.

Results and discussion

P 6 Figure 2: It would be useful to see results of a statistical analysis on the effect of soil on N_2O fluxes and isotopomer values across the moisture gradient.

In addition, it would be interesting to see the fraction of N_2O derived from nitrification, denitrification and N_2O reduction for each soil over the moisture gradient, including statistical analysis.

P 7 Line 16-18: I agree that a greater contribution of N_2O reduction is a likely explanation for the observed results. The approach by Lewicka-Szczeback would allow the authors to calculate the fraction of N_2O reduced to N_2 based on the isotopomer data.

P 7 Line 22: A lot of literature has been published on factors controlling complete denitrification. See for example - Butterbach-Bahl et al. 2013. Nitrous oxide emissions from soil: How well do we understand the processes and their controls? Phil. Trans. R. Soc. B 2013 368, 20130122, - Groffman et al. 2006. Methods for measuring denitrification: Diverse approaches to a difficult problem. Ecological Applications 16:2091–2122 - and references therein.

P 7 Line 29-32: It is very likely that multiple processes underlying N_2O emissions acted simultaneously to cause a higher than expected SP value. It needs to be very clear from the discussion that there was no independent measurement of nitrification, denitrification and N_2O reduction to N_2 . To avoid this confounding factor in data inter-

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pretation, I strongly recommend the authors to use end-members from the literature for data-interpretation. Various studies have reviewed and summarized data for such end-members, for example: - Decock and Six 2013. How reliable is the intramolecular distribution of ^{15}N in N_2O to source partition N_2O emitted from soil? *Soil Biology and Biochemistry* 65: 114-127; - Ostrom and Ostrom 2017. Mining the isotopic complexity of nitrous oxide: a review of challenges and opportunities. *Biogeochemistry* 132:359–372; - Denk et al. 2017. The nitrogen cycle: A review of isotope effects and isotope modeling approaches. *Soil Biology and Biochemistry* 105:121-137.

P8 Line 1 – P 9 Line 9: Here and elsewhere, please edit based on previous comments.

P 9 Line 10-27: This is an interesting analysis. I am interested to see models relating soil moisture to sources of N_2O based on updated source calculations in line with the most recent literature. Based on the raw isotope data, I suspect a significant moisture by soil interaction with respect to sources of N_2O . Statistical tests for such an interaction should be shown. Such an interaction may also have implications for the modeling approach in section 3.4 of this paper.

P 9 Line 27-28: Please refer to isotope tracer work, as suggested earlier.

Conclusion

Please edit commensurate with previous comments.

Technical corrections

None observed.

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