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Interactive comment on "Revisiting the relationship between soil moisture and N_2O production pathways by measuring $^{15}N_2O$ 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

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

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-Szczeback 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_Lew Szczebak_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-Szczebak 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 d18O and SP at higher soil moisture content as the line representative of N2O reduction. It should be noted, however, that a N2O reduction line is only applicable if N2O reduction was the only process affecting N2O. In the presented experiment, N2O production and reduction likely occurred simultaneously. How simultaneous production and reduction of N2O affects isotope maps is discussed in great detail in Decock and Six. 2013. On the potential of d18O and d15N to assess N2O reduction to N2. 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 N2O fluxes and isotopomer values across the moisture gradient.

In addition, it would be interesting to see the fraction of N2O derived from nitrification, denitrification and N2O reduction for each soil over the moisture gradient, including statistical analysis.

P 7 Line 16-18: I agree that a greater contribution of N2O reduction is a likely explanation for the observed results. The approach by Lewicka-Szczeback would allow the authors to calculate the fraction of N2O reduced to N2 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 N2O 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 N2O reduction to N2. To avoid this confounding factor in data inter-

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 15N in N2O to source partition N2O 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 N2O 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 N2O. 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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