SOIL Discuss.,
https://doi.org/10.5194/soil-2019-27-AC1, 2019

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.

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Received and published: 29 July 2019

Anonymous Referee #1

Received and published: 11 June 2019

SOIL Discuss., https://doi.org/10.5194/soil-2019-27

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

General comments

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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.

Authors: Thank you for the comprehensive review. Revisions have been made to bolster references to previous literature, relating our work to previous N2O research.

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

Authors: Both Reviewer#1 and #2 requested that the word 'revisiting be changed. We have given this some thought and can see the reviewers' point; thus we have modified the title to:

"A new look at an old concept: Using 15N2O isotopomers to understand the relationship between soil moisture and N2O production pathways".

Abstract:

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

Authors: The following statement has been added to the revised text (page 1/line 15):

“For each of three soilsâĂŤdiffering in nutrient levels, organic matter and textureâĂŤsoil microcosms were arranged . . . ”

3) 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

Authors: Revised to specify the equation variables for x, FN, and FD. As well, we added the following sentence to explain the potential relevance:

“The presented equations may be helpful for other researchers to estimate N2O source partitioning when soil moisture falls within the transition from nitrification to denitrification”. (added at page 1/line 29)

Introduction:

4) 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

Authors: We have added a sentence acknowledging the use of 15N tracers:

“Indeed, our understanding of the relationship between N2O production and soil moisture has benefited greatly from the use of 15N tracers (Bateman and Baggs, 2005; Stevens and Laughlin, 1997; Groffman et al., 2006).” (added at page 2/line 6)

However, the point we intended to make is that despite the advancements in understanding N2O and soil moisture, the precise relationships remains fairly unclear, especially during the transition. To better convey this message, the text was revised to

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include the following statements:

“However, there remain surprising grey-areas in our understanding of the underlying mechanisms, one such area being the precise relationship between soil moisture and N2O production pathways, especially during the transition from one dominant pathway to another (Bateman and Baggs 2005). (added at page 2/line 8)

and

“While previous research has provided important steps towards better quantifying the relationship using 15N enrichment and acetylene inhibition techniques (Bateman and Baggs 2005), natural abundance 15N techniques may provide superior information by imposing fewer confounding effects on step-wise N transformations.” (added at page 2/line 19)

5) 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.

Authors: We do refer to seminal papers by Toyoda, Ostrom, and Sutka further down this paragraph, but we have now revised the first sentence of the paragraph to acknowledge this body of early work up front.

“. . ..(Van Groenigen et al., 2015). Early work focused on the intramolecular distribution of 15N within the linear N2O molecule (Sutka et al., 2006; Toyoda et al., 2005), investigations of atmospheric or oceanic N2O isotopomers (Popp et al., 2002; Toyoda and Yoshida, 1999; Yoshida and Toyoda, 2000), and soil emitted N2O istopomers (Perez et al., 2001; Yamulki et al., 2001).” (added at page 3/line 3)

6) 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_Lewicka-Szczebak_et_al_2017_-_detailed_description_of_calculation_procedures

Authors: We confirmed that the calculation for the sources of N2O we performed were indeed the same approach as described by Lewicka-Szczebak. We cited the mixing model as described by Deppe et al. 2017, which is parallel to that used by Lewicka-Szczebak et al 2017. We now make reference to both papers that employed this approach (page 5/line 7).

The mapping approach that we employed is that used by Deppe et al. (2017) and Lewicka-Szczebak et al. (2017) has been used before – but based on δ15N SP and δ15N bulk to estimate the fraction of bacterial N2O (Zou et al, 2014). As described by both Deppe et al (2017) and Lewicka-Szczebak et al (2017), they decided to base the mixing model on the relationship between δ15N SP and δ18O values (rather than bulk 15N) for more robust interpretations; accordingly, we followed their recommendations.

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

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.

Authors: As requested, we added an explanation, and acknowledge the underlying assumptions and limitations (see page 5/lines 19–29 of the revised manuscript):

“Rather than relying on average literature-derived endmembers like previous work (Deppe et al., 2017; Lewicka-Szczebak et al., 2017), we used soil-specific endmembers derived from our data to perform the linear mixed model. This is because we measured a wide range of soil WFPS treatments with high frequency between dry and moist conditions for each soil, enabling us to determine the point at which the ðİŻ£15N SP or ðİŻ£18O values either dropped or increased as soil WFPS changed – as precisely as the data permitted. This approach is consistent with earlier recommendations that data is collected at high enough frequencies to capture gradual changes in isotope values as influenced by traditional proxies (i.e., gradual changes in soil WFPS) (Decock and Six, 2013a). However, it must be noted that the underlying assumption is that the soil-specific endmembers are more reflective of transition from nitrification to denitrification in each of the soils tested herein, than general literature-derived endmembers would be for any one soil. Moreover, it is assumed that the endmembers represent N2O fluxes when the sole source was either nitrification or denitrification.” (added at page 5/line 19)

8) 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.

Authors: Revisions have been made to discuss this study in relation to others. We reference the review by Decock and Six (2013a and b), and Lewicka et al (2014):

“Despite similarities among soils in the robust patterns of how SP values are influenced by soil moisture (Fig. 2; Table 2), SP exhibited a significant ($P < 0.0001$) soil ïĆť moisture region interaction. This finding agrees with earlier suggestions that, at finer scales, the 15N2O isotopic signatures and SP values are likely regulated by the active soil microbial community, process rates, soil heterogeneity (Decock and Six, 2013a; Lewicka-Szczebak et al., 2014).” (added at page 8/line 32)

9) 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.

Authors: We have revised the text to address the reviewer’s concerns; transparently identify the limitations of our study; and discuss our study in context to others:

“Previously, the fractionation of SP due to N2O reduction was constrained to a variation of -2‰ to -8‰ (Jinuntuya-Nortman et al., 2008; Lewicka-Szczebak et al., 2014; Well and Flessa, 2009). Ostrom et al. (2007) showed that . . . “ (added at page 9/line 4)

“Reduction slopes for our three soils averaged 0.28, which is similar to the literature-derived average of 0.35 or. 0.33 used by Deppe et al. (2017) and Lewicka-Szczebak et al. (2014), respectively . . . ” (added at page 9/line 13)

“This finding echoes earlier work which suggested that during soil conditions when processes of N2O production and reduction occur simultaneously, the reduction line approach may be limited (Decock and Six, 2013b).” (added at page 10/line 7)

Results and discussion

10) 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

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statistical analysis.

Authors: First, we apologize for a miscommunication regarding N2O fluxes; i.e., we did not measure N2O fluxes; rather, we measured the total amount of N2O produced during the 24-h incubation. This has been made more clear in the revised text (Section 3.1; see response to comment #4 by Reviewer #2).

As for the Reviewer's second point, we are not entirely sure what is being asked for here. To evaluate the influence of soil moisture on N2O production and isotopomers, we analyzed the relationship between WFPS and SP or source fraction during key moisture gradients via linear regressions – see Figure 4 and Table 2. As such, the statistical analysis was approached in two ways: 1) linear regression to characterize N2O isotopic changes as influenced by moisture (see Table 2), and 2) by developing linear models within the transition zone to model the changes in N2O source fraction (Eq 6 & 7), see Fig 4. We believe the way we approached the analyses is best suited for our objectives of this study. To evaluate the influence of soil attributes on N2O and isotopomers, a future study could be designed and carried out to best test numerous different soil types and soil attributes on N2O and isotopomers.

11) 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.

Authors: Thanks for the suggestion. We have adopted this approach and revised the text to reflect the outcome of the analysis:

"Correspondingly, using the mapping model approach, we estimated much larger fractions of N2O were reduced to N2 at 95% WFPS in the Bradwell soil (0.47), compared to the Sutherland or Asquith soils (0.13 to 0.14)." (added at page 8/line 14)

12) 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.

13) 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 interpretation, 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.

Authors: The assumptions, explanations, and limitations are now more clearly described (see authors' response to Comment #7, above).

To check if data interpretation would be influenced by using the soil-specific approach vs the independent endmember/slope approach, isotopomer maps were also calculated using independent literature-derived values (see below Fig). Literature-derived endmembers were set at -2.4 to 34.4 for SPD to SPN, and 11.1 to 43.0 for ðİŻ£18OD to ðİŻ£18ON ; a reduction slope of 0.33 (Lewicka-Szczebak et al., 2017). For our study, using literature-derived endmembers was deemed inappropriate because it overestimated the contribution of denitrification-derived N2O under very dry soil conditions (i.e., 20 to 40% WFPS), to fractions of up to 40% of N2O produced (see figure below) – a result which is in contradiction to common knowledge (Davidson et al. 1991).

In our case, N2O source partitioning using soil-specific endmembers provided an advantage over using independent endmembers because certain endmembers (Bradwell soil) were different from expected/literature-derived values; likely due to real soil biological processes such as microbial communities, the low rate of production, or soil heterogeneity (Decock and Six, 2013a; Lewicka-Szczebak et al., 2014). So, it makes more sense in our case to use soil-specific endmembers (especially because we have the isotopic data over a fine-scale WFPS change, enabling us to pin-point soil-specific endmembers as best we can). We are transparent about the approach, the assumptions, and limitations (see revisions to page 5 which clearly explains that the endmembers are assumed to represent sole nitrification or denitrification). We are open to including the below figure and explanation as a Supplemental material if you deem it necessary, but please note that our objectives were not to compare different endmember approaches. Rather, our goal was to use a reasonable endmember approach to estimate source partitions, and evaluate how soil moisture affects N2O production. See attached Figure.

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

Authors: This section has been revised to reflect our response to the Reviewer's previous comments. In brief, these revisions have to do with placing our results in better context with the published literature. (See tracked changes in accompanying revised manuscript.)

15) 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.

Authors: See response to Comment #8 above in which we added a statement showing indicating that site preference exhibited a significant ($P < 0.0001$) soil ïĆť moisture region interaction. This provides additional support for our decision to use site-specific endmembers to calculate the source fractions attributable to nitrification and denitrification in our modeling. Further, the site-specific end-member approach effectively normalizes the source partitions among soils, enabling data to be pooled for the modeling approach (Fig 4). Refer to discussion under Comment 13.

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

Authors: The text was revised to reference isotope tracer work in response to Comment # 4 above; however, we do not feel that it needs to be repeated here. Our purpose was to determine whether we could use 15N isotopomersâĂŤi.e., natural abundance, not 15N tracersâĂŤto better elucidate the relationship between soil moisture and N2O production pathways. Nevertheless, we have revised the text in this section to read:

“Our results largely support the foundational studies that established the relationship between soil moisture and N2O emissions (Davidson, 1991; Linn and Doran, 1984); however, we provide a method that moves beyond just inferring N2O source pathways towards quantifying the pathway contributions over a range of soil moistureâĂŤand does so without having to add a 15N label.” (underlined text added at page 11/line9)

17) Conclusion Please edit commensurate with previous comments.

Authors: The conclusions have been revised to reflect previous comments.

18) Technical corrections None observed.

Interactive comment on SOIL Discuss., https://doi.org/10.5194/soil-2019-27, 2019.

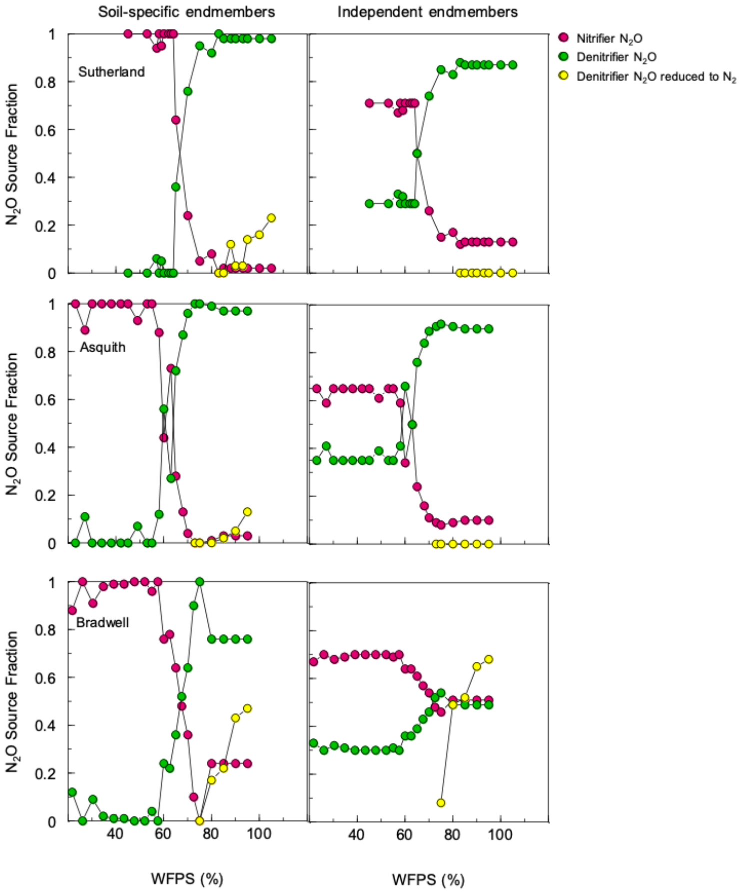

Fig. 1. N2O source fractions based on soil-specific endmember approach (left panels) and independent endmember approach (right panels).

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