

Interactive comment on “Early season N₂O emissions under variable water management in rice systems: source-partitioning emissions using isotopocule signatures along a depth profile” by Elizabeth Verhoeven et al.

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Review of Verhoeven et al. Biogeosciences By Nathaniel E. Ostrom and Jenie Gil Lugo, Michigan State University

This is an impressive manuscript directed toward using natural abundance isotope ratios to evaluate the production and reduction of nitrous oxide in rice agroecosystems in response to water management practices. The manuscript is extremely thorough in terms of its sampling design and extent of measurements but also in the thoroughness

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with which the authors review the literature and logic with which they present their arguments. There are relatively few manuscripts that take this care; particularly in the early stages of the submission process. The presentation of both open and closed models is innovative and the explanations of the models are quite clear. We commend the authors for their efforts. There are three significant areas in this manuscript that need to be addressed and a number of minor issues that we list below. First, we appreciate the authors' use of the term “isotopocule” to more accurately describe the bulk and site dependent isotopic composition of nitrous oxide but, regrettably, their use of this term is incorrect (see Ostrom and Ostrom, 2017). Isotopocule is a contraction of “isotopic molecule” and this term refers specifically to the 12 distinct isotopic molecules that result when the two isotopes of nitrogen and 3 isotopes of oxygen are combined in every imaginable way. Thus it is incorrect to use isotopocules to describe isotope ratios. Isotopomer refers to the two isotopocules of nitrous oxide that have the same mass but differ in the location of ¹⁵N. Isotopologues is not a very useful term as it implies differences in both mass and isotopic composition. Given this, perhaps it would be best to simply use “isotope ratios” to describe both bulk and site specific isotopic information. Secondly, we are concerned with the use of constant values for the kinetic isotope effects (KIE) associated with nitrous oxide reduction in their models. The literature cited in the paper clearly demonstrates that the KIE associated with nitrous reduction is variable and yet the authors chose a single value of 6.6 per mil in their models. Further, the Jinuntuya-Nortman et al (2008) demonstrate that the KIE decreases with increasing water filled pore space. Third, we are concerned with the use of ranges in $\delta^{18}\text{O}$ of nitrous oxide associated with various sources of nitrous oxide to describe microbial origins. While SP is considered a conservative tracer of the origins of nitrous oxide it is widely know that bulk $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values are not conservative. Thus while ranges of values can be compiled from the literature it is uncertain how well these values represent what can be expected in the natural environment. It is known that $\delta^{18}\text{O}$ values in nitrous oxide can be altered by exchange with water and, indeed, the authors estimate that 100% of the O in nitrous oxide has exchanged with water.

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Given this high degree of exchange, how reasonable is it to use constant isotope values to infer microbial origins? We don't believe that any of these concerns should result in rejection or major restructuring of the manuscript. Rather, we would like to see the authors acknowledge these concerns and discuss what the implications of variation in KIE's and source isotope values would have on their model results.

Page 4, line 1-2: Abiotic production of N₂O can occur by many pathways and it seems the values cited here reflect production from hydroxylamine. We recently reported SP values of 16 per mil for N₂O production from NO (Stanton et al., 2018, *Geobiology* (DOI :10.1111/gbi.12311)).

Page 7, line 10: What are the minimum concentrations required to obtain accurate isotope values for nitrate and ammonium?

Page 9, line 29-32. As mentioned above, this is a good representation of the literature $\delta^{18}\text{O}$ values but given concerns about water exchange can we realistically expect these values to apply to field studies?

Page 10, line 5: It would seem this slope is determined from a single pair of values when a wide range of values for the KIE associated with nitrous oxide reduction can be found in the literature. What is the impact of variation in the slope on the outcomes of this model?

Page 13, line 22: "In the WS treatments, high N₂O emitted fluxes were also associated with lower $\delta^{15}\text{N}$ signatures". This statement is not entirely accurate. In WS-AWD two peaks of N₂O were observed (Figure 3), firsts on June 17, with high $\delta^{15}\text{N}$ signatures (~20‰ and the second on June 23 with lower $\delta^{15}\text{N}$ signatures (~40‰, both peaks showing similar N₂O flux.

Page 18, lines 18-19: The use of "high" net isotope effects can be misleading because the NIE's are negative. A value of -6, for example, is higher than -16 but reflects a lower degree of isotopic discrimination. Perhaps use "greater degree of isotopic

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discrimination" or a similar phrase.

Page 18, line 20: The use of a single value to describe the net isotope effect for reduction of nitrous oxide is not very accurate as it is well known that this value varies. Jinuntuya-Nortman et al. (2008) demonstrated that water filled pore space is inversely related to the net isotope effect and at high values of water filled pore space this value approaches zero. Given that this environment is frequently characterized by high and variable water filled pore space how realistic is it to use a single value? What would be the impact on the model outcomes of allowing this value to vary over the range of literature values reported?

Page 19, Line 25: Authors postulates that high SP values relative to $\delta^{18}\text{O}$ or $\delta^{15}\text{N}$ observed in N₂O pore air from WS treatments, could be explained by greater contributions from abiotic hydroxylamine decomposition. However, in order to produce enough N₂O from abiotic hydroxylamine decomposition, to switch or enriched SP values significantly, it wouldnt require high NH₄⁺ concentrations (Rubasinghege et al., 2011; Heil et al., 2015)? In this study, the NH₄⁺ concentrations were very low during the sampling period.

Page 21, line 13: The finding that oxygen exchange is 100% is very concerning. Doesn't 100% exchange compromise the use of $\delta^{18}\text{O}$ to partition sources of nitrous oxide?

Figure 4: Is there a reason why the reduction and mixing lines are plotted in A but not on the figures in B?

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