

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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Authors response to reviewer 1: We appreciate the detailed and constructive comments of reviewer 1. We feel that this review has picked up on many issues we struggled with in presenting this data. Our initial and consistent objective was to use the isotopic data as a tool to conclude more about how the management practices affect processes. However, we simply were unable to collect sufficient, season long data in all three treatments to make more robust comparative agronomic conclusions as relates to N₂O and N₂ emissions. We feel strongly though that the data collected provides

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valuable insight into detailed process changes under the different water managements and provides a solid and unique dataset to help push forward the interpretation and use of natural abundance isotope methods. Additionally, as you mention later, we do not have baseline, pre-growing season emissions to show these treatments were similar before the season. Rather, our goal was to collect as much data prior to the first in-season fertilization as possible with the aim of analyzing in detail the response to N fertilization between the treatments, as it turns out, the data collected pre-fertilization was often more interesting. It was not possible to install our equipment prior to 2 days before seeding. In fact the treatments likely did NOT have the same basal emissions because this was the 5th year for each of the treatments under alternative water management. In the first three years these treatments were managed slightly differently, as described in (Miniotti et al., 2016; Peyron et al., 2016). In 2015 and 2016 the WS-AWD water management was adjusted and applied as described in this paper and in (Verhoeven et al., 2018). The DS-AWD was managed as dry-seed + flooding (essentially, delayed permanent flood) for the first 4 years and then adjusted to DS-AWD in for the 2016 year (current publication). Text in the materials and methods has been added to emphasize the paddy history. We have also added a sentence in the conclusions reminding readers of this. *note, significant changes have been made to the manuscript, the page and line numbers referenced below refer to the revised version without any of the track changes visible. Detailed individual responses: 1. One of the objectives is to “semi-quantitatively assess N₂O and N₂ losses among rice water management treatments”. Though this objective is set at prominent position, there is hardly information in form of tables or figures. One would expect such information in view of the objectives.

This is a valid point. We have made a minor change to the phrase referenced above by replacing ‘losses’ with ‘loss rates’ to avoid implying that we determined cumulative losses. Indeed, at the onset of this work our aim was to comprehensively compare N₂O and N₂ losses among the different water treatments. In reality we were unable to obtain high enough fluxes or concentrations of N₂O throughout the growing season and across treatments to make isotope measurements at many time points. We realized

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this in the previous year during a separate, lead up study, therefore in the experiment and dataset presented here we decided it was more valuable to concentrate our efforts and resources on the beginning of the growing season when N₂O was higher. Given this we do not feel comfortable to extrapolate our results to growing season emissions. We feel that Fig. 1 and Fig. 6 do quantitatively present N₂O emissions for the three treatments during the measurement campaign. We elected not to present a graphic of N₂ emissions in the main paper because we felt the data was too patchy for the WS treatments (often the N₂O emissions were too low for accurate isotope measurements). In this respect, our method failed. In the original manuscript, we included a graphic of these emissions in the Supplementary material, Fig. S13 C and D. It is labeled 'N₂O reduction' rather than N₂ production, because it was a calculated N₂ production based on N₂O reduction from our modeling. We are open to other ideas of graphing or presenting this data, we were just trying not to over-interpret our data and to be transparent about what the data is.

2. In view of N losses, Crop yields would be very interesting as well. It would probably be wise to add such data in view of objective b

The following data has been included in the text at the beginning of the results section, P12L126

Treatment Yield (t/ha) LSD DS-AWD 6.6 b WS-FLD 8.9 a WS-AWD 8.2 a

The effect of lower N demand in the DS-AWD is also now mentioned on P18L16 and P25L14

3. The core of the study clearly is the comparison of open and closed system calculations, and their plausibility. The manuscript stops short of clearly presenting and comparing the results of the associated calculations in form of a figure. Such a figure would help the reader to understand why some scenarios were excluded. In addition, the exclusion of open system dynamics could be presented in more detail

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We politely disagree that the core of this manuscript was the comparison of open and closed system calculations. We feel that in an uncontrolled environment and using in-situ measurements it is very likely that a mixture of open and closed system dynamics existed. Indeed, we chose to statistically analyze and discuss only the mean of the two dynamics in our discussion (P23L2). We have added the following text to our materials and methods as well, to emphasize this, P10L1

“In reality, the heterogeneity in microbial microhabitat within the soil most likely results in a mixture of closed versus open system dynamics. Therefore, final data interpretations were made for the average findings across open versus closed systems dynamics. “

Further more, Figure 5 does present the results of open and closed system modeling and the mean is indicated by a purple line. Our data shows that open system modeling consistently led to lower rN₂O (= higher reduction) and lower denitrification contributions than closed system (Fig. 5). Likely, some days and/or treatments were more dominated by one scenario or another, but we cannot say. Therefore, to maintain equality between the treatments, we took the average of the two dynamics.

There may be some confusion between open and closed system models and then scenario 1 and 2. These are different, both scenarios were applied to open and closed system models, originally resulting in 4 possible rN₂O values. In scenario 1 we assume that N₂O produced by denitrification processes is produced and reduced and then mixed with that of un-reduced N₂O. In scenario 2, we assume that un-reduced N₂O from both end member pools is mixed and then reduced. We found few plausible solutions for scenario 2 (Fig. S3 and Table S2) so decided to eliminate this scenario to simplify the discussion.

4. The supporting information is frequently used in the manuscript, which is ok, but in view of the complex calculations described in section 2.7, I suggest that an example data point is used to show the calculation procedure, and why a sum of squares of 500

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was considered meaningful. Authors: A detailed protocol for the calculation of closed system values can be found on ResearchGate (DOI: 10.13140/RG.2.2.17478.52804). An example of our open system calculations is now given in a supplementary Excel worksheet. Both of these materials are now referenced in the text on P10L24 and P12L8, respectively.

Examining our values and their distribution, we chose a sum of squares of 500 as a reasonable value, over which solutions tended to be very implausible, i.e. orders of magnitude out the range of other results for at least one value. Our search for model solutions was set to minimize the sum of squares between our modeled and observed values, therefore it stands to reason that high sum of square values are associated with less robust model values. At the time, we felt that evaluating results based on sum of squares for the model as a whole rather an outlier analysis of individual values (i.e. for rN_2O , denitrification contribution, etc.) was both more just and simpler. In retrospect, a more standard method of outlier elimination may have been a better choice. However, we strongly feel that this would not have resulted in a different outcome. Between 2.6 – 7.3% of values had a sum of squares over 500 (below). Over all the sub datasets, 3.4% of values had a sum of square > 500.

5. The authors present calculated Net isotope effects, however the authors are not clear with regard to their assumptions (open/closed system), and the calculation applied violates some basic assumptions of Rayleigh distillation (details below). Though the authors attempt to provide information why the calculated values do not agree with literature isotope effects, the approach is constructed and in my opinion does not bring the manuscript any further. I suggest considering to skip this section.

Authors: We have corrected our terminology and now refer to our calculated fractionation factors as, $\Delta^{15}N_x$. We fell that retaining these calculations is valid and important. There is a large body of literature reporting isotope effects, net or otherwise under controlled conditions and also from field studies. We believe it is important to present and contextualize our data for comparison to past work. We agree that this method has

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limitations and flaws, indeed one of our goals was to try and push forward the development of new methods that do not rely on 15N values in substrates. We have changed our notation to η , which is more consistent with the literature for net isotope effects. We have also added the following text to the materials and methods, P9L23.

“The calculation of $\Delta^{15}\text{N}_x$ can be compared to the net isotope effects for nitrification and denitrification derived N_2O , as found in the literature. In reality the processes in equations 1 and 2 entail a series of sequential reactions each of which has a unique isotope effect ($\epsilon_{\text{N}_2\text{O},1}$, $\epsilon_{\text{N}_2\text{O},2}$, $\epsilon_{\text{N}_2\text{O},3}$, ...). It is not possible to measure the isotope values of many of the intermediaries in these reactions series, particularly in in-situ field settings, therefore we report the $\Delta^{15}\text{N}_x$. For the calculation of $\Delta^{15}\text{N}_x$ we assume open system dynamics because all measurements were in-situ where substrates, products and intermediaries could be replenished by other processes.”

6. Nutrient concentrations are quite variable. I suggest adding nutrient concentrations and measured fluxes for an appropriate time interval prior to experiment start to show the comparability of the treatments. Please also add seeding dates and all fertilizer applications to the figures 2,3,5 and 6.

Authors: See general comments as well. Unfortunately we do not have data for the time period prior to seeding because we were unable to install equipment until all field preparation and leveling was complete. The data collected during the first 3 weeks of the study, prior to the fertilization, were intended to be our background for understanding treatment response to the fertilization. We have added information to the materials and methods describing the field history. P4L31-33, P5L1-4.

Abstract P1L18: please add emissions after N_2O Authors: We did not make this amendment because as the sentence is worded, we are referring to both emitted and pore air N_2O . We have moved the position of the () so that it does not break up the sentence in an awkward place, and we hope the sentence is now more clear.

The sentence now reads: “In a field experiment with three water management treat-

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ments, we measured N₂O isotopocule signatures of emitted and pore air N₂O ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and site preference, SP) over the course of six weeks in the early rice growing season. “

L24: please add and in front of “fungal denitrification” Authors: Completed.

Introduction P2L9: I suggest changing from “biological” to “microbial source processes”. Authors: Good suggestion, done.

L25: please check the comma after while. Authors: The comma has been removed.

P4L4: the “which serves to enrich” construction of the sentence sounds odd to me. What about “The reduction of N₂O to N₂ enriches the pool of remaining N₂O that is measured in ¹⁵N and ¹⁸O and, thus changes $\delta^{15}\text{N}$ -N₂O, $\delta^{18}\text{O}$ -N₂O and SP. Authors: This sentence revision has been adopted.

L9 onwards: This segment on calculation approaches leaves the reader a little confused. Will there be calculations in the manuscript? Why this segment? Please add an explanatory sentence, or consider skipping this segment. It is also not necessarily true that closed system calculations lead to higher substrate enrichment. This depends very much on the amount of reacted substrate.

Authors: We have eliminated these two sentences on open versus closed system calculation approaches.

In general, I am missing some background information: Rice is one of the dominant crops in the world, consumes a tremendous amount of water, even in water-scarce regions, and flooded rice production also contributes greatly to the global methane budget. Saving methane may be counterbalanced by N₂O emissions

Authors: This is a good point. We have flipped the order of our second and third paragraphs as well as re-arranging some of this now second paragraph, see P2L14-29. We hope this now better addresses the general background. If needed, we are happy to add more.

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Materials and Methods P5L26: why did the DS treatment receive less fertilizer than the WS treatments? At first glance, this does not make a lot of sense. Please clarify.

Authors: The three treatments received the same amount of total N per season, 160 kg N/ha. However, N was split applied in three applications designed to maximize NUE based on farm management experience. Our experiment was set up within a larger agronomic trial, which was managed under 'best management practices' for each respective water regime. It is known that rice plant development and growth will be slower under dry seeding, therefore the two WS treatments received N rates of 60, 60 and 40 kg N/ha at fertilizations 1,2 and 3 while the DS treatment received a lower initial rate and then higher subsequent rates: 40, 70 and 50 kg N/ha at fertilizations 1,2 and 3. Fertilization 1 and 2 were covered in the measurement campaign included in this manuscript. We fully acknowledge that this can lead to difficulty in directly comparing the treatments at a given timepoint. On the other hand, it makes the data much more realistic and arguably more comparable as N rate was timed to coarsely align with plant demand so as to minimize the residual N in the soil. This data is given in table 1. We have added a line to this table with the July 14th fertilization and have also added the following sentences to the methods for clarification.

P5L26. "A total of 160 kg N ha⁻¹ as urea was applied to all treatments, with one pre-plant application on May 16th and two in-season applications on June 21st and July 14th (Table 1). Following best management practices for the three water management practices, a smaller pre-plant urea application was applied in the DS-AWD treatment, followed by a larger application in this treatment at the second and third fertilization. In the DS-AWD treatment, urea was applied at 40, 70 and 50 kg N ha⁻¹, while these rates were 60, 60 and 40 kg N ha⁻¹ for the WS treatments at fertilization 1, 2 and 3, respectively."

P6L15: do I understand correctly that the precision of the GC was +/- 12ppb / 24 ppb? This would be a quite low precision, however for the fluxes it may be less severe. Chamber height controls the sensitivity of the chamber so that I suggest giving also a

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detection limit at, for instance, 0.6 ppm maximum headspace concentration. Authors: We do scale our GC detection limit based on the concentration in the sample. The samples in our exetainers are drawn directly from the chamber headspace and are assumed to represent chamber headspace at the moment of sampling. Using 10 reps of at least 5 varied concentration standards we created a regression curve of concentration vs stdev and use this to determine the detection limit for a given concentration. The high and low points on this curve are 300ppb (stdev =12 ppb) and 1000ppb (stdev = 24 ppb) and we chose to give these as examples in the text, P6L15. When calculating fluxes, we determined fluxes to be below detection if the change over time was less than the stdev associated with the highest concentration of the 4 measurements. Essentially $T4 - T1 > \text{stdev of } T4$. We have added a clarifying sentence to this effect on P6L20. P9L11-14: I am not sure if I understand this correctly: is $15\text{N-N}_2\text{O}$ in this case the isotopic composition in soil water, or in emitted soil air? Please clarify. I suppose, the authors use $15\text{N-N}_2\text{O}$ in pore water. I don't agree with the authors that this calculation is valid, for the following reasons:

Authors: Neither, the $15\text{N-N}_2\text{O}$ used in the calculation of net isotope effects was pore air N_2O taken at the three depths, the 15N-NO_3^- and 15N-NH_4^+ were analyzed in pore water samples taken at the same depths. Sampling for pore air and pore water occurred within 5 hrs of each other on the same day. We have tried to clarify this in the materials and methods P9L19.

1) $15\text{N-N}_2\text{O}$ is not necessarily formed from exactly the location of which the nitrate originates, and may have formed from $\text{no}_3^- / \text{nh}_4^+$ as well.

Authors: We agree, we feel that this is discussed in section 4.2, P19L1

2) the reaction coordinate is unknown, i.e., there is no knowledge on how much of the nitrate / nh_4^+ has been transformed. The equation is only valid, if the n_2o has formed in an infinitesimal time after consumption of the substrate.

Authors: We have modified our terminology and now refer to this value $\Delta 15\text{N}_x$. Further,

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we assume open system dynamics for these reactions because refreshing of substrate or consumption of product at any point in time cannot be excluded.

3) there are other possible intermediates in these conversions, all of which obscure this calculation. This needs to be clarified in detail.

Authors: See earlier response and amendment to materials and methods.

P9L19: I am not sure what “Additionally” means in this context. I would assume that for both open and closed systems, two possible scenarios were considered. To clarify this I suggest: “For both the open and closed modeling methods, two possible scenarios were considered. . .”

Authors: This is good suggestion and this phrasing has been adopted.

P9L25-32: This segment is unclear to me. I guess it is most straightforward to tell my understanding of it, and you clarify in the text: there are 5 publications reporting d18O-N2O for a pure culture experiment during which exclusively N2O was produced, which gives you a good estimate for d18O-N2Oden. You want to add the value measured by Lewicka 2017 to this database (reason remains unclear, I can only encourage mentioning the really careful experiments by Lewicka 2017 as reason to extend the database). However, Lewicka 2017 was corrected for 18O-H2O. Maybe I am right in this assumptions. It became more clear to me after having a look an Figure 1. If so, I suggest you mention Figure 1 in line 22-23, and add 18O-N2Oden, 18O-N2Onit, and the corresponding SP values to figure 1, with an extra tick mark at the corresponding axis, and have the label in the plot region close to the axis. The whole approach may become more clear then. I also suggest not starting with the special case of the 18O-values corrected for water 18O, but start with the general explanation and then describe the detail.

Authors: We have made the suggested changes to Fig. 1. We have re-arranged and re-written this section and hope that it is now more clear. The section now reads.

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“A schematic of our closed system approach is given in Fig. 1. For both open and closed methods, two possible scenarios were considered as described by (Lewicka-Szczebak et al., 2017); scenario 1 (sc1), where N₂O is produced and reduced by denitrifiers before mixing with N₂O derived from nitrification or scenario two (sc2) where N₂O is produced from both processes, mixed, and then reduced. In both models, N₂O is originally produced from two possible endmembers; denitrification/nitrifier-denitrification (denoted by subscript den) and nitrification/fungal denitrification (denoted by subscript nit). Our SP endmember values (SP_{den} and SP_{nit}) and N₂O reduction fractionation factors ($\epsilon^{18}\text{O}_{\text{red}}$ and ϵ^{SPred}) were taken directly from Lewicka-Szczebak et al. (2017) (Table 2). For $\delta^{18}\text{O-N}_2\text{O}(x)$ endmember values we could not directly use the values reported in Lewicka-Szczebak et al. (2017) because these were reported relative to $\delta^{18}\text{O-H}_2\text{O}$ (as $\delta^{18}\text{O-N}_2\text{O}(\text{N}_2\text{O}/\text{H}_2\text{O})$) and we did not measure the isotope signature of water in our study. Therefore, $\delta^{18}\text{O-N}_2\text{O}_{\text{nit}}$ was re-calculated using the original mean values ($\delta^{18}\text{O-N}_2\text{O}$ as opposed to $\delta^{18}\text{O}(\text{N}_2\text{O}/\text{H}_2\text{O})$) of the six studies referenced by (Lewicka-Szczebak et al., 2017), this yielded a mean of 36.5‰ (Sutka et al., 2006; Sutka et al., 2008; Frame and Casciotti, 2010; Heil et al., 2014; Rohe et al., 2014; Maeda et al., 2015). For $\delta^{18}\text{O-N}_2\text{O}_{\text{den}}$ we adjusted the value used in Lewicka-Szczebak et al. (2017) by an estimate of $\delta^{18}\text{O-H}_2\text{O}$ of water for our site rather than re-calculate from the four studies originally referenced by Lewicka-Szczebak et al. (2017) (Sutka et al., 2006; Frame and Casciotti, 2010; Lewicka-Szczebak et al., 2014; Lewicka-Szczebak et al., 2016). We used a $\delta^{18}\text{O-H}_2\text{O}$ value of -8.3‰ as reported by Rapti-Caputo and Martinelli (2009) for an uncontained aquifer of the Po River delta. We chose to do this because some of the mean values used by Lewicka-Szczebak et al. (2017) were themselves calculated from data originally reported. Our intention was to keep endmember values as consistent as possible between this study and Lewicka-Szczebak et al. (2017). ”

In view of the following text, I don't understand why the orange sc2-line does not cross

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the sample. For my understanding, this is not correct. Please clarify.

Authors: You are absolutely correct, thanks! The sample point has been moved up to pass through both intercepts.

Results P13L20: from figure 3, this pattern is not obvious for ^{15}N - N_2O . Please clarify.

Authors: The sentence has been removed.

P15L2: Nutrient concentrations are quite different for the treatments. Please add an appropriate time period prior to experiment start to show that initial nutrient concentrations were equal.

Authors: Please see previous comments.

P15L28: see comments above on net isotope effects.

Authors: Please see earlier comment.

Discussion P18L3-4: The sentence starts with while, it seems like the sentence has not been finished correctly.

Authors: Well noted. The sentence has been revised to read, "In contrast, saturated conditions favoring complete denitrification certainly prevailed in the WS treatments at times" P18L2

P19L11: it is unclear what you mean with a stronger trajectory towards N_2O reduction.

Authors: The sentence has been revised to read: "In both $\text{SP} \times \delta^{18}\text{O}$ and $\text{SP} \times \delta^{15}\text{N}$ plots our sample values mostly fell between the mixing and reduction lines predicted by either isotopic relationship (Fig. 4) and somewhat surprisingly showed stronger enrichment, indicative of greater N_2O reduction in the DS-AWD treatment relative to the WS treatments." P20L7

P19L22: not clear if the denitrifying microsites are assumed to be more abundant in WS treatments? Please clarify.

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Authors: The sentence has been revised to read: “More NO₃⁻ was available for denitrification in the DS-AWD treatment, thus for greater enrichment of this pool to occur we propose that more NO₃⁻ was trapped in denitrifying microsites as the soil dried or O₂ was consumed.” P20L18

P19L24: How can abiotic N₂O formation explain the high SP values greater than 30 in WS-FLD, i.e., the scatter? As you point out, this pathway is associated with SP of 35.

Authors: This is a valid point. We can only really speculate on these high values. It is plausible that N₂O produced by abiotic or fungal denitrifiers was further reduced, enriching the SP value somewhat more. However, we would expect to see enrichment of ¹⁸O as well, which wasn't always the case. We believe in part, there is just more error in the WS treatments because we were much more often close to the concentration detection limit of our IRMS, most of the values falling above SP 40 per mil were emitted N₂O. We have revised the sentence in question. P20L23

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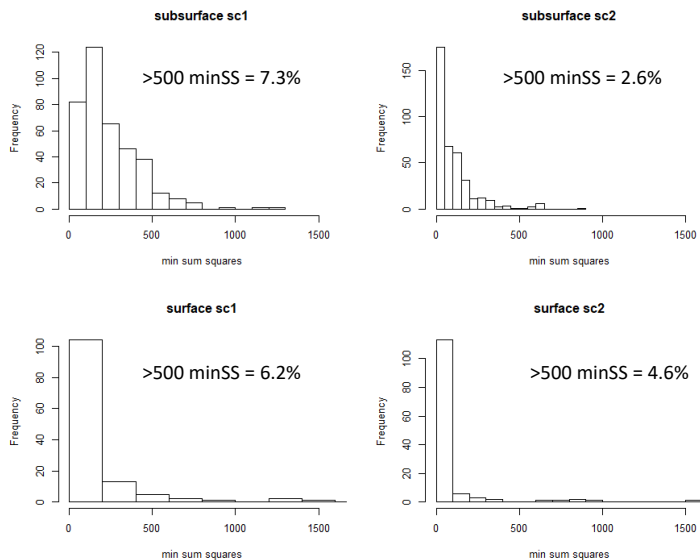


Fig. 1.

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