

The authors evaluate subsoil concentrations and emissions of nitrous oxide (N<sub>2</sub>O) and related soil variables at sites in a raised bog in Denmark which had been identified as having high potential N<sub>2</sub>O emissions. They conduct measurements over spring and fall, 2015, in four sites (two of which are immediately adjacent to one another): two cropped with potato and two with grasses; each site was also split into fertilized and unfertilized treatments. Using graphical analysis, they determine that in most sites, the concentration of N<sub>2</sub>O at the capillary fringe was the driver of emissions, though in one season/site combination, N<sub>2</sub>O emissions were related to sub-surface soil temperature and nitrate concentration. The relationship between water table depth and N<sub>2</sub>O appeared to vary by site and by season, but included a declining water table depth triggering N<sub>2</sub>O emissions in spring, and rising water table depth triggering N<sub>2</sub>O emissions in autumn. Pyrite was largely excluded as making an important contribution to N<sub>2</sub>O production or emission, and a range of possible mechanisms of N<sub>2</sub>O production were discussed. Lower emissions from grassland plots were attributed to greater plant uptake of soil N. Annual fluxes were comparable to or higher than IPCC Tier I emission factors for drained organic soils.

**General comments:**

This is my first reading of the manuscript. This is an impressive field study with a lot of interesting data, and the importance of N<sub>2</sub>O concentrations in the capillary fringe for N<sub>2</sub>O emissions is a nice result, as is the finding that pyrite and iron monosulfide are unimportant, and the confirmation of high emissions from these soils. However, I have a number of concerns regarding the experimental design, support for some of the conclusions presented, and organization of the manuscript. The manuscript and discussion in particular could benefit from substantial revision after some contemplation of what the core advances of the study are. There seem to be three main aspects of the study (in no particular order): 1. Understanding the mechanism of N<sub>2</sub>O production, with a particular examination of the potential roles of pyrite and iron monosulfide. 2. Understanding the variables related to surface N<sub>2</sub>O fluxes. 3. Understanding the relationship between water table and soil N<sub>2</sub>O concentrations (and N<sub>2</sub>O flux). These different aspects are part of a single system, and ideally the paper will weave these aspects together into a single coherent story of the patterns and mechanisms behind N<sub>2</sub>O dynamics and its drivers. As noted below, I think it may make sense to refocus this manuscript around results related to items 2 and 3, for three reasons: a) it may help to clarify this study, b) results apparently highly relevant to item 1 have been kept for a second manuscript, and c) this study wasn't designed to be a comprehensive investigation of the specific mechanism of N<sub>2</sub>O production in these soils.

Based on the first referee's review, it sounds as though this may be a revised version of an earlier manuscript; if so, sorry to be bringing new concerns at this stage of the publication process, and apologies for the long comments. Note: I don't have expertise in graphical analysis or in the specific technique used to measure subsurface N<sub>2</sub>O concentrations.

Specific comments:

■ Experimental design:

- The experimental design is unusual, with elements of different types of partly nested designs. Essentially, the first arable potato site (AR1) and first rotational grass site (RG1) are part of what traditionally would be called a split-split-plot design, but RG2 and AR2 are in a split-plot design. What this means is that the role of site in the analysis—there are effectively three sites—varies in its relationship with the treatments. AR1 and RG2 are nested within site, but RG2 and AR2 are not. Additionally, the lack of nesting of AR2 and RG2 within site raises additional issues, since RG2 has such a big difference in organic C content, so treatment is confounded with site in the RG2/AR2 pairing (in addition to the different fertilizer types used). Although differences between the potato and grass treatments are discussed in the results, and the title suggests that these and seasonal differences are the focus of the manuscript, I don't see any methodological description of the analysis that could allow one to compare RG and AR treatments. I'm not strictly sure how it would be done, but I also don't have a problem with softening the wording of the conclusions that can be drawn about the differences between RG and AR treatments—it does look like there may well be treatment differences there, I'm just not sure that with this design that it's possible to establish that statistically. So I think it needs to be made clear that if a strict statistical comparison was not conducted, the conclusions drawn aren't statistically supported (and any related concluding statements should be softened). And if a statistical comparison was conducted, details on how the nesting within site of RG1 and AR1 but not AR2 and RG2 was handled would be helpful. There is also no replication of bog—the results can't technically be generalized beyond the Store Vildmose raised bog. This is not a problem, and the authors don't attempt to extrapolate beyond the Store Vildmose, but it is a limitation that should be explicitly acknowledged. None of these issues should affect the finding that the capillary fringe is often/typically the primary determinant of the magnitude of N<sub>2</sub>O flux.
- I am always concerned about field studies the present just one year of data, as it does limit insights into the degree to which patterns observed provide generalizable insights. The manuscript title suggests that comparisons of seasons is one of the central findings of the study, but since only one year of data are included, it is impossible to rigorously compare seasonal differences, as there is no replication of season. There are a lot of varying results in this study, which only strengthen this issue. I don't think these issues affect the finding on the frequent importance of capillary fringe N<sub>2</sub>O concentrations for surface emissions, though.
- In the end, these issues might make the conclusions of this study fairly descriptive with respect to the specific questions of the effects of season and land use on N<sub>2</sub>O emissions and subsurface dynamics. That doesn't mean that these specific results aren't valuable, just that the nature and limitations of the conclusions that can be drawn from the study on these specific questions need

to be made very clear in the manuscript. Rethinking what the central finding or findings of the manuscript are may be helpful.

- The data on the changes in the water table and subsoil concentrations of N<sub>2</sub>O are great. But the conclusions drawn in section 4.3 could be more compellingly supported (there does not appear to be any quantitative analysis of the relationship) and discussed. Looking at the figures, in some cases N<sub>2</sub>O concentrations are enhanced above the water table, in other cases, below the water table, and an overall relationship is not immediately obvious. The importance of the capillary fringe concentrations for surface emissions makes this discussion of particular interest, and worth spending some text to guide the reader through your interpretation.
- The manuscript often reports whether there was an effect of fertilization (e.g., line 380, lines 404-405, 412-413, and others) or appears to test fertilizer vs site effects (e.g., line 405), and the methods detail how generalized linear mixed models were used to analyze the temporal dynamics of N<sub>2</sub>O. However, I don't see any reporting of the statistical results of this model or its application to the impact of fertilization on N<sub>2</sub>O emissions or soil concentrations.
- A follow-on point is the very nice finding that N<sub>2</sub>O at the capillary fringe generally controlled N<sub>2</sub>O emissions, rather than any variables in the topsoil. But this result raises the question of what controls variation in N<sub>2</sub>O concentration at the capillary fringe. This question seems to be of first order importance in this system, but is not addressed quantitatively in the manuscript. It might help tighten the manuscript if the discussion in section 4.3 is tied more explicitly to N<sub>2</sub>O concentrations in the capillary fringe.
- A general comment: In presenting results, it could be helpful to start each section with a general description of the main results or patterns found instead of starting with detailed information for individual blocks; that detailed information can be presented later, to support the general patterns or describe deviations from those patterns. Anything you can do to guide readers through the results is great! In addition, the authors occasionally slip interpretation into the results section that would be more appropriate in the discussion section.
- One of the main questions addressed in this manuscript is that of the importance of FeS<sub>2</sub> oxidation for N<sub>2</sub>O production. Line 530-531 invokes a separate but presumably related manuscript that presents results showing that FeS<sub>2</sub> oxidation is unimportant in this peat soil. It is difficult to say without knowing what the focus of that manuscript is, but my hunch is that it may make more sense to include the FeS<sub>2</sub> results from this field study in the separate manuscript (presumably focused on mechanisms of N<sub>2</sub>O production in these soils), since we are effectively only getting half the story here. Something to consider, anyway. In the end, this manuscript doesn't provide much in the way of firm insights into the mechanisms of N<sub>2</sub>O production—that's not an inherent problem, it's just not something this study was designed to do—so one idea would be to cut out that part of this manuscript, and make the focus entirely on quantification of fluxes, the nice soil N<sub>2</sub>O & water table data (and capillary fringe finding), and environmental drivers more generally. It would be easy enough then to include a paragraph on mechanisms of N<sub>2</sub>O production that cites the other manuscript. Also, just to note, many journals require any related manuscripts that have been submitted

elsewhere to be included as part of a manuscript submission, so would be a good idea to check the policy of the journal in question when you submit the separate manuscript.

- The manuscript argues that the water table depth was related to surface N<sub>2</sub>O emissions (e.g., section 4.1), but that this relationship varied by site and by season, and speculates that soil properties modified the water table depth/N<sub>2</sub>O relationship. However, there doesn't seem to be any statistical/quantitative analysis to support a water table depth/N<sub>2</sub>O relationship or how other soil properties modify that relationship (and as noted above, it's not possible to statistically evaluate seasonal differences).
- section 4.1 is largely a re-statement of results; much of the actual discussion about the water table/N<sub>2</sub>O relationship is sprinkled throughout subsequent sections. A restructuring of the discussion might make the results easier to digest, with one section focused on discussing the capillary fringe result and one focused on understanding the water table/N<sub>2</sub>O relationship. Some discussion about why the patterns are so variable could be valuable, including some explanation of why water table increases stimulate N<sub>2</sub>O production at all sites in the autumn (and contrast with the results of other studies, e.g. Maljanen et al. 2003, which saw no effect of rising water table on N<sub>2</sub>O emission). One possible straw man interpretation could be that in the early spring (or late spring in the case of AR2), N<sub>2</sub>O production is limited by NH<sub>4</sub><sup>+</sup> (and/or NO<sub>2</sub><sup>-</sup>/NO<sub>3</sub><sup>-</sup>) availability, which in turn is constrained by the availability of O<sub>2</sub>. The decline of the water table may release the O<sub>2</sub> constraint. In the autumn, in contrast, it is possible that aerobic conditions limit N<sub>2</sub>O production, and a rising water table or precipitation leads to higher N<sub>2</sub>O emissions. If indeed the case, why a possible seasonal shift from substrate to O<sub>2</sub> limitation happens would be interesting to understand.

#### **Technical comments:**

**Line 1: I would change the title to reflect the focus of the revised manuscript (in addition, as noted above, it seemed to me that neither seasonal nor land use differences were able to be rigorously tested, and so it would be better to exclude phrases like "effects of land use and season" from the title)**

**Line 45: You can check my math, but it seems to me that the global warming potential is still uniformly larger for C than for N<sub>2</sub>O here. I don't think it is necessary to make the case that N<sub>2</sub>O fluxes are more important than carbon fluxes, just that the N<sub>2</sub>O fluxes are large.**

**Line 44: change ", which" to "that"**

**Line 64: "The sites" : not sure what sites are being referred to. Could you add more context?**

**~Line 120: please add a short explanation for why soil gas data were not presented for unfertilized RG2 during Autumn**

**Line 167: was this the fertilized or unfertilized block?**

**Line 176: remove "quantitatively" (not sure what it is intended to mean)**

**Line 210-211: Entirely your choice, but perhaps AVS and CRS don't need to be abbreviated**

**Line 197: specify type of filter paper used**

**Line 237: Is the instrument ever checked against a set of standards of varying concentrations?**

**Line 339: Indicate whether fertilized or unfertilized blocks were sampled**

Line 354 change “temporarily” to “temporary”

Line 363: change “trends” to “concentrations”

Line 370: Figure 3 seems to suggest that the N<sub>2</sub>O concentrations in the top 40cm of soil look to be 1-2 orders of magnitude higher in the fertilized RG1 than fertilized RG2. And unfertilized RG2 looks to be 1-2 orders of magnitude higher than unfertilized RG1 between 60 and 100cm depth for most of the spring. Yet they are described as “generally similar.” I wouldn’t have thought that would be considered “generally similar”—am I missing something?

Line 375-6: Since there are apparently no soil gas data from unfertilized plots in RG2 during autumn, this statement is too strongly worded (even independent of questions of whether the effect of fertilization was tested).

Line 376: The figures are out of order—I think you can swap Figures 4 and 5.

Line 380: could you be specific about what soil conditions showed significant within-site heterogeneity? Also, use “substantial” instead of “significant” if this heterogeneity wasn’t tested, and if it was, consider providing P values

Line 384: this is really interpretation, and might be better placed in the discussion.

Line 400: were any measurements made of N in harvested biomass? It could certainly help support the story that differences in uptake could alter N<sub>2</sub>O emissions from different plots.

Line 405: if specific soil variables cannot be identified as causing the differences, perhaps change “soil conditions” to “site differences”

Line 411-12: I’m not sure I see this pattern clearly: emissions are already high when the water table is at 80, and in the fertilized plots of AR1, emissions are 1/3 as large on DOY 259 than DOY 252, even though the water table is at its peak on DOY 259. There’s also no apparent effect of the increase in water table starting on DOY 307, and emissions look quite elevated on DOY 246, which may be before the increase in water table began. A quantitative analysis would be helpful.

Lines 473-4: could be more specific and change “a short period” to “1 to 2 weeks”

Line 481 and following: Section 4.3 draws a number of conclusions that don’t appear to be supported by any statistical analyses.

Line 516-517: I’m not sure I see this rapid increase in N<sub>2</sub>O around the water table depth in all the blocks in figure 6?

Lines 533-534: I think it might be better to say that “denitrification in topsoil was the main source. . .” since there is no explanation of how the N<sub>2</sub>O in the capillary fringe is produced.

Line 544: I’d change “drive” to “regulate”.

Line 532 and following: this is interesting discussion, but if there are supplementary data that could support application of the ideas to this study (e.g., water filled pore space, acetylene reduction experiments, etc), it would strengthen it considerably. If the manuscript in preparation on FeS<sub>2</sub> oxidation includes any detailed examinations of these questions, it may be better to limit the speculation here.

Line 544-558: looking at Tables S1 and S2, it seems that there is generally more NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup> in these soils on April 22 and/or May 13 than there is NO<sub>2</sub><sup>-</sup> on April 23 (much more if these were the fertilized plots—I could not see any indication of whether the undisturbed core was from fertilized or unfertilized plots). If correct, that suggests that perhaps there is not an imbalance between ammonia oxidation and nitrite oxidation? Perhaps all nitrifier

populations are temporarily saturated by the increase in available  $\text{NH}_4^+$ ? The discussion in Lines 486-489 also seems to suggest that denitrification was cranking along pretty well in the AR sites. And perhaps there's reason to be cautious about inferring processes from snapshots of concentrations, whether a single depth profile or weekly measurements of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Presumably, high concentrations could indicate anything from slow loss rates of each compound (whatever the pathway may be), or could reflect rapid N mineralization rates. If, by chance, total N concentrations were measured at each sampling date, calculations of net mineralization and net nitrification might be able to provide additional insight into whether and where reactive N might be accumulating.

Line 550-51: This is partly covered in the note immediately above. I see that  $\text{NH}_4^+$  remains at high concentrations, but  $\text{NO}_3^-$  does as well, which is why I'm unsure about the suggestion that there is a lack of a mechanism to remove  $\text{NO}_2^-$ .

Figure 2 caption: indicate whether cores were taken from fertilized or unfertilized blocks.

Figures 3 through 7: I think it might be easier to evaluate these data if the entire year of data are presented in a single plot, rather than separating spring and fall data—I don't think it would make it any more difficult to read the data. An axis break could be included between DOY 167 and DOY 246. You could also explore presenting surface  $\text{N}_2\text{O}$  flux in a log scale—there may be a variation that would be visible on a log scale that is difficult to discern on the current linear scale because of the dates with very high fluxes.

The manuscript text switches freely between using DOY, month, and terms like “early spring” to describe time, which makes it challenging for the reader to compare the text and figures. Sometimes the DOY is included parenthetically when month names are used, which is great, but this practice should be extended throughout the text. Alternatively, the x axis labels could be changed to month names and days.

Tables S1 through S4 would be much easier to read in figure form (possibly in a single figure), though I appreciate the inclusion of the summary data here. Actually, why not explore adding these data as a second y axis in figures 3-6, sharing the panels used for  $\text{N}_2\text{O}$ . Since topsoil nitrate is presented as a significant predictor of  $\text{N}_2\text{O}$  flux, it could be valuable to be able to compare the data in the figures.