

## ***Interactive comment on “Regulation of N<sub>2</sub>O emissions from acid organic soil drained for agriculture: Effects of land use and season” by Arezoo Taghizadeh-Toosi et al.***

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I have copy the response letter below. However, the comments and responses to both reviewers' comments was uploaded in the form of a supplement, in pdf file.

Interactive comment on “Regulation of N<sub>2</sub>O emissions from acid organic soil drained for agriculture: Effects of land use and season” by Arezoo Taghizadeh-Toosi et al. Anonymous Referee #2 Received and published: 21 March 2019

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

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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. Response 16: This is a concise summary of the study. Thank you for the many detailed comments, which we have tried to address below. There was a request from a reviewer of the previous version of the manuscript to provide the detailed account of potential mechanisms of N<sub>2</sub>O production, including the possible role of pyrite. Therefore, we would like to keep it as part of overall rationale of our study.

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

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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. Response 16: Thank you for considering an alternative structure for the paper that would eliminate aspects related to the possible role of iron sulfides for N<sub>2</sub>O formation. The wider study was planned to evaluate this hypothesis, which was first introduced in a previous study published in BGS (Petersen et al., 2012. Annual emissions of CH<sub>4</sub> and N<sub>2</sub>O, and ecosystem respiration, from eight organic soils in Western Denmark managed by agriculture. Biogeosciences 8, 403-422). The present study was intended to provide field observations as reference for controlled manipulation experiments described in a separate submission. Furthermore, the detailed account of potential mechanisms now included meets a request from a reviewer of the previous version of this manuscript. We therefore find that this is important to account for the overall rationale of our work.

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

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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. Response 17: The description of treatment distributions is accurate, but we would like to maintain that sites RG1 and AR1 should be considered as independent fields with individual cropping histories (even if fields were part of the same crop rotation, as explained in Petersen et al 2012). In accordance with this, there were some differences in soil variables (Table 1), and this should not have been the case if this was a nested design, as proposed. While we think that the analysis is valid as conducted, we do not wish to put strong emphasis on land use differences, which were evident even without any statistical support, and we will soften the wording on this contrast throughout the manuscript, as proposed.

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“ 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. Response 18: Please note that this study was preceded by a monitoring study of wider scope (Petersen et al., 2012), where N<sub>2</sub>O emissions were monitored during 14 months in three regions and on three (in one case: two) land uses, which were arable farming, rotational grass and permanent grass. In total 8 site-years were thus available as background for developing the research questions addressed in this new study. The association between seasonal fluctuations in WT and N<sub>2</sub>O emissions was observed in two different regions that were also both characterised by elevated groundwater sulfate. This is why we found it was acceptable to focus resources on spring and autumn periods at a limited number of sites, two of which were already known from the first study, rather than spreading resources across a full year, or across more sites. The reference to this previous study may have been too brief, and we will expand this a little to explain the context.

“ 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. Response 19: We acknowledge the many limitations of a field study such as the one presented here. The ambition to conduct measurements in agroecosystems with management as closely as possible to the practical situation involved various compromises and limitations. We do not wish to overemphasize the results

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presented, and we stand by the statistical analyses conducted, but we will stress the limited data material, and the differences in soil conditions and management. The most interesting result, beside the evidence for different sources of N<sub>2</sub>O in spring and autumn, could be the more qualitative comparison with emission levels as currently estimated for inventories.

“ 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. Response 20: Thank you for the comment. We were deliberately cautious in describing these relationships, since there seems to be much to learn about the mechanisms of N<sub>2</sub>O production and reduction in this system – see also the discussion of pathways in section 4.5. A significant relationship between N<sub>2</sub>O concentrations in the gas probe closest to, but above the WT depth was observed and is reported (Figure 7). However, the distance between probe depth and WT depth would have varied, and in periods with rainfall the WT depth could have fluctuated before a given sampling. For these reasons, we find it is difficult to take the data analysis or discussion much further at this stage. Additional studies could be contemplated, including measurements at higher resolution, and molecular analyses of populations and activities.

“ 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

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emissions or soil concentrations. Response 21: The statistical results for the cumulative (integrated) emissions presented in Table 2 were obtained by calculating specially designed contrasts (linear combinations) of the parameters of the referred model (calculated in such a way that the contrast coincides with the trapezoidal approximation of the integral of the emission over time). Therefore, the generalized linear mixed models referred were indeed used in the text. We will revise this Table to provide additional documentation for these summary results. Specifically, the results for the comparison of fertiliser effect in the autumn will be included. Additional details about the generalized linear mixed model results will be included in the online Supplementary Information.

“ 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. Response 22: We are grateful for the acknowledgement that the relationship between N<sub>2</sub>O in the capillary fringe and N<sub>2</sub>O emissions is an interesting observation. We explained above the limitations of doing a more quantitative analysis and hope for understanding that this was an unexpected result, and that for this reason the sampling strategy was not optimal for addressing in detail the relationship. We will try to link the discussion in section 4.3 more to N<sub>2</sub>O in the capillary fringe, but this may still be a mostly qualitative discussion.

“ 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

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in the discussion section. Response 23: Thanks for this comment. We will revise the Results section keeping this in mind.

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. Response 24: As explained above, in the wider study we did intend to investigate soil pools of iron sulfides, and relationships with N<sub>2</sub>O in the field study, but also recognizing from the beginning that more controlled experiments would be needed for validation of any conclusions. The manipulation experiments constitute a full paper that is now in review. We also find that it is appropriate to report here a preliminary conclusion to the hypothesis presented in the previous BGS paper.

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.

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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).

Response 25: The graphical model results illustrated in Figure 7 do represent the results of a fairly advanced statistical analysis, and p values are now included. This is the quantitative support we have for the discussion of effects of soil properties; seasonal effects were not tested. Please also see Response 48. 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.

Response 26: Thanks for this comment. The present structure was in fact an attempt to highlight plausible mechanisms and interactions, which could potentially account for the observations with respect to soil N<sub>2</sub>O concentrations and emissions. The interpretation offered by the reviewer above was in fact also proposed in the manuscript (Line 541f). Other pieces of evidence, which can help understand the observed differences between land uses and seasons with respect to mineral N, soil N<sub>2</sub>O and N<sub>2</sub>O emissions may be found in the different parts of the discussion, but we acknowledge it this may have been at the expense of

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the larger picture. We would prefer to keep the close links between N<sub>2</sub>O emissions and supporting data, and the links to previous studies. However, we propose to include in section 4.1 a brief introduction to the interpretation that we wish to put forward, and what aspects will be discussed in subsequent sections.

Technical comments:   &Aacute; 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) Response 27: The hypothesis of the manuscript was to focus on wet seasons and management practices. In addition, this manuscript is a resubmitted manuscript, and we would like to keep the same title in order to make it possible for the readers to access to the final revised version later on. Therefore, we considered the reviewer’s comment and will remove the last part of the title which will read: “Regulation of N<sub>2</sub>O emissions from acid organic soil drained for agriculture”.

&Aacute; 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. Response 28: The point here was that N<sub>2</sub>O emissions are more influenced by site management compared to soil C losses.

&Aacute; Line 44: change “, which” to “that” Response 29: This will be done.

&Aacute; Line 64: “The sites” : not sure what sites are being referred to. Could you add more context? Response 30: This will be rephrased to specify that these were the arable sites with extremely high N<sub>2</sub>O emissions in two regions investigated by Petersen et al. (2012): “The two arable sites showing extreme N<sub>2</sub>O emissions in the study of Petersen et al. (2012) had both developed from marine forelands . . .”

&Aacute; Line 120: please add a short explanation for why soil gas data were not presented for unfertilized RG2 during Autumn Response 31: Some probes were damaged during

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handling and removal in connection with field operations at the various sites during spring, and replacements were not available. The measurements at RG2-NF were sacrificed; a note will be added to explain this.

âĀĀ Line 167: was this the fertilized or unfertilized block? Response 32: Intact soil cores to 100 cm depth were obtained from both fertilised and unfertilised subplots, and the analyses represent both fertiliser treatments. See also reponse no. 37.

âĀĀ Line 176: remove “quantitatively” (not sure what it is intended to mean) Response 33: We will remove “quantitatively”.

âĀĀ Line 210-211: Entirely your choice, but perhaps AVS and CRS don’t need to be abbreviated Response 34: We prefer to keep them abbreviated.

âĀĀ Line 197: specify type of filter paper used Response 35: 1.6  $\mu\text{m}$  glass microfibers filter, 691 was used. That information was added to the text.

âĀĀ Line 237: Is the instrument ever checked against a set of standards of varying concentrations? Response 36: Calibration standards (0 to 2000 ppb) were included before and after each sequence run and used for determination of sample concentrations. Also, extra calibration samples were included after every 10 unknown samples to verify signal stability. We believe these are standard procedures and prefer not to spell this out.

âĀĀ Line 339: Indicate whether fertilized or unfertilized blocks were sampled Response 37: Will be rephrased to: “Nitrite-N concentrations were determined in soil profiles from the cores sampled at sites RG1 and AR1 on 23 April and 2 September 2015. Both fertilised and unfertilised subplots were represented, although at site AR1 no fertilisation had taken place at the time of sampling in April. There was variation at depth in the soil, which could not be linked with fertilisation”.

âĀĀ Line 354 change “temporarily” to “temporary” Line 363: change “trends” to “concentrations” Response 38: These changes will be adopted.

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âĀĀ 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”âĀĀam I missing something? Response 39: Please note that the color scale for RG2+F was not correct, and thus concentrations were in general higher at site RG2. When referring to “generally similar”, this should be seen in the context of concentrations of several hundred ppm N<sub>2</sub>O being observed especially at AR sites, but also around DOY150 in RG2+F.

âĀĀ 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). Response 40: Thank you for the comment. We will change the sentence to read: “During autumn, N<sub>2</sub>O concentrations in the soil profile at the RG1 and RG2 sites varied between 0 and 12 ðĪJĜL L-1, with a tendency for highest concentrations at 10-20 cm depth (Figure 5). At site RG1, where both fertilised and unfertilised subplots could be sampled, this was independent of fertilization”.

âĀĀ Line 376: The figures are out of orderâĀĀI think you can swap Figures 4 and 5. Response 41: Figure 4 presents the results of AR fields in spring, and Figure 5 presents the results of RG fields in autumn. We believe the order is correct. Perhaps the confusion is related to the error in contour lines for site RG1-fertilised?

âĀĀ 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 Response 42: The wording of this sentence was unfortunate, as in fact heterogeneity was inferred from N<sub>2</sub>O concentrations. This will be revised. We will also change “significant” to “substantial”.

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â€” Line 384: this is really interpretation, and might be better placed in the discussion. Response 43: Although strictly speaking this is correct, we find that it is helpful to bring up the coincidence between N<sub>2</sub>O accumulation and WT depth in this place, and so we would prefer to keep this statement.

â€” 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. Response 44: The point we made here was that N uptake probably mediated against effects of fertilisation on N<sub>2</sub>O emissions. Unfortunately, we were not able to include manual cuts of the grass before harvest, in order to measure N in harvested biomass.

â€” Line 405: if specific soil variables cannot be identified as causing the differences, perhaps change “soil conditions” to “site differences” Response 45: We will change “soil conditions” to “site characteristics differences”.

â€” 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. Response 46: Thank you for pointing out the complexity of N<sub>2</sub>O-WT relationships in this period. We should in this place have stressed the importance of soil NO<sub>3</sub> availability and referred to Table S2. Also, we will mention that rainfall may induce N<sub>2</sub>O emissions in unsaturated soil layers, when nitrate is present.

â€” Lines 473-4: could be more specific and change “a short period” to “1 to 2 weeks” Response 47: Will be done.

â€” Line 481 and following: Section 4.3 draws a number of conclusions that don’t appear to be supported by any statistical analyses. Response 48: It is true that this

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discussion is based on observations and interpretation of interactions between potential drivers of N<sub>2</sub>O emissions. Please note that soil N<sub>2</sub>O concentrations are equivalent gas phase concentrations, and hence information about soil bulk density and air-filled porosity at the individual gas sampling position would be needed to calculate absolute amounts of N<sub>2</sub>O. With measurements in only one or two blocks per sites, such a discussion is necessarily qualitative, but we believe it may still be useful as basis for development of new research questions or testable hypotheses.

â€” 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? Response 49: It is true that in some plots the accumulation of N<sub>2</sub>O in the soil is not very closely linked to WT depth, but there was a concurrent increase in N<sub>2</sub>O below, and in some cases above, the WT depth. We will modify the sentence to clarify this.

â€” 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. Response 50: We will change the wording to read: “Bacterial nitrification, denitrification, and nitrifier-denitrification are all potential pathways of N<sub>2</sub>O formation (Braker and Conrad, 2011), and the significant relationship with NO<sub>3</sub><sup>-</sup> at AR sites in the autumn (Figure 7) suggested that denitrification in the top soil was the main source in this period”.

â€” Line 544: I'd change “drive” to “regulate”. Response 51: The word “drive” will be changed to “regulate”.

â€” 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. Response 52: The reviewer has a valid point that supplementary data or experiments could probably elim-

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inate some of the pathways discussed here. On the other hand, it is extremely difficult to characterise, let alone quantify, soil conditions at the micro- to mm-scale relevant to microorganisms in the undisturbed soil, and therefore firm conclusions may be difficult to reach. We did not attempt to quantify bulk soil properties in this study, or conduct manipulation experiments. The short summary of related literature was intended as inspiration to the planning of future studies to identify pathways.

Line 544-558: looking at Tables S1 and S2, it seems that there is generally more  $\text{NO}_3^-$  or  $\text{NH}_4^+$  in these soils on April 22 and/or May 13 than there is  $\text{NO}_2^-$  on April 23 (much more if these were the fertilized plots) 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  $\text{NH}_4^+$ ? Response 53: The fact that nitrite accumulated in samples collected in April, but not in September, suggested that there was a difference in the balance between ammonia oxidation and nitrite reduction between the two sampling dates. Soil nitrogen pools are not necessarily uniform, and hence the accumulation of nitrite could be associated with microsites with only a fraction of the total  $\text{NH}_4$  and  $\text{NO}_3$  pools. If indeed detoxification is important in this system, it is conceivable that turnover rates for nitrite would also be high. See also Response no. 55.

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. Response 54: Unfortunately, total soil N concentrations

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were just measured once (Table 1). Concern is raised about the limitations of point measurements as basis for the interpretation of N transformation processes. It may be argued that the soil gas probe measurements of N<sub>2</sub>O represent a more time-integrated measure of N transformations, insofar as the equilibration time is in the order of days (cf. Petersen, 2014; Diffusion probe for gas sampling in undisturbed soil. Eur. J. Soil Sci. 65: 663-671). High concentrations thus indicate a sustained production and not just transient episodes.

â€” Line 550-51: This is partly covered in the note immediately above. I see that NH<sub>4</sub><sup>+</sup> remains at high concentrations, but NO<sub>3</sub><sup>-</sup> does as well, which is why I'm unsure about the suggestion that there is a lack of a mechanism to remove NO<sub>2</sub><sup>-</sup>. â€” Response 55: Peat soil is an extremely heterogeneous environment and may be dominated by dead-end pores (Hoag R.S., Price J.S., 1997. The effects of matrix diffusion on solute transport and retardation in undisturbed peat in laboratory columns. J Contam Hydrol 28:193-205). It is therefore difficult to infer microbial activities from bulk soil concentrations. The graphical model analysis showed relationships between top soil NO<sub>3</sub><sup>-</sup> concentration and N<sub>2</sub>O flux, hence there is some support for the quantitative importance of denitrification. We will include a short discussion on the possible constraints on solute and gas exchange.

â€” Figure 2 caption: indicate whether cores were taken from fertilized or unfertilized blocks. Response 56: As it was mentioned in section 2.4.2 'Soil sampling', soil samples were collected to 1 m depth within 1 m distance from the positions of flux measurements in Block 3 of sites RG1 and AR1. As stated previously, a soil core was collected from both fertilised and unfertilised subplots, but at site AR1 the soil was not fertilised until later in the spring.

â€” 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 dataâ€”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

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surface N<sub>2</sub>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. Response 57: Thank you for these suggestions. We feel that each Figure already has a lot of information, and certainly the presentation of results per block would become more difficult, if both seasons were to be combined into one. In order to keep Figures readable, we would like to maintain the design we have developed.

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. Response 58: In order to make time traceable and consistent throughout the manuscript, we will include DOY in parentheses when month names or season names are used. However, we prefer to keep DOY numbers in x axis.

– 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 N<sub>2</sub>O. Since topsoil nitrate is presented as a significant predictor of N<sub>2</sub>O flux, it could be valuable to be able to compare the data in the figures. Response 59: We would like to keep that information as presented now, in tables of supplementary materials. There is already much information presented in each figure, and adding the mineral N information with standard errors at different depths to those figures would result in reduced readability.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2019-14/bg-2019-14-AC2-supplement.pdf>

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