Dear editor,
We hereby submit a revision of the paper “Regulation of N₂O emissions from acid organic soil drained for agriculture” (bg-2019-14) by Taghizadeh-Toosi et al. Major revisions were requested, and we are grateful to be granted the extension needed to complete this work.

Perhaps the most critical point raised was the assumptions about land use and site conditions that were necessary to test for these effects. In the revised statistical analyses, individual combinations of site and crop were instead tested separately to avoid such assumptions. Surprisingly, the effects identified in the previous analysis were more or less confirmed, indicating that the relationships were robust.

Review comments were overall constructive and helpful in clarifying many aspects. With the exception of some proposed reorganization of Figures 3-6 we believe that we have acted on all points raised, as specified below in the point by point response. In this light, we hope that it will now be possible to accept the manuscript for final publication.

Kind regards,
Arezoo Taghizadeh-Toosi
Detailed response to reviewer comments (in blue):

I raised several issues in my previous review, and thank the authors for their efforts at addressing them. Overall, I think the discussion is much improved. Unfortunately, I believe my concern regarding the experimental design needs to be further addressed. I do believe that revision is possible, and although it will likely require new statistical analyses, it shouldn’t be overly difficult once the appropriate design is identified.

Below I list four general comments, of which the first two are most important, followed by responses to some of the authors’ responses to my earlier comments, followed by specific comments. Apologies again for the rather verbose review.

Response: We appreciate the reviewer’s critical eye on the data analyses. We have made an effort to meet the different concerns, and in particular assumptions regarding experimental design have been revised, as explained below.

GENERAL COMMENTS

1. One of my main concerns was regarding the robustness of the conclusions that can be drawn from this experimental design (Author response 17). The authors have removed the seasonality analysis, which I appreciate, but I believe that important issues remain. Some of the problem is in the language used to present and discuss results rather than in the underlying science, but science issues remain.

   • This remains a study using only one year of data, though I don’t think this is in itself a problem, it is a limitation. The authors argue in their response 18 that a previous 14-month study (Petersen et al. 2012) should also be considered, and that study does provide context for the results presented here (though note that any results from Petersen et al 2012 that are important for understanding the rationale for this study or for understanding its results should be summarized in this manuscript). However, Petersen 2012 is not part of the analysis, and the current manuscript doesn’t provide any insight into the effects of interannual variability (also it seems that this was perhaps an abnormally warm and wet year). That’s not a problem--I think the authors have done a good job of removing generalizing statements about seasonality from the revised manuscript--but I do think that a statement noting that the analyses of spring and fall are based on data from a single year should be included in the conclusion as part of an acknowledgment of potential limitations of the study.

   Response: There are five references to the study of Petersen et al. 2012 in the Introduction, and we have added additional detail to explain the context:

   “Among sites with arable crops in three regions, two sites had N_2O emissions corresponding to, respectively, 38 and 61 kg N ha^{-1} yr^{-1}; both of these sites showed distinct seasonal patterns with the highest emissions in spring and autumn periods, whereas emissions at the third site were lower (6.4 kg N_2O-N ha^{-1} yr^{-1}) and much less variable. Notably, WT depth at the two sites with seasonal patterns of N_2O emission fluctuated between 10-30 and 10-120 cm depth, whereas WT depth at the third site remained at 90-125 cm depth throughout the 14-month monitoring period.” (l. 53 in cleaned manuscript version)

   Also, we now begin the conclusion by stressing that this is a one-year study:
In this one-year study, N2O emissions were...” (l. 600 in cleaned manuscript version)

- This remains a study that lacks traditional replication of treatments, and I think this issue requires substantial additional revision.

  o The authors argue that RG1 and AR1 should be considered as independent units because they differ in land use history, and were treated as such in Petersen et al. 2012. I’m afraid I’m not convinced—the design is an illustration of the traditional definition of a split plot: two adjacent fields with different treatments (or, as in this case, treatment histories), but a shared geographic location, and thus conditions that have been formed by a history of shared state factors (sensu Hans Jenny). As such they are simply not independent sites. The map in figure 1a, which presents AR1/RG1 as a single site, illustrates the point rather well, and as I understand, sampling positions in the two fields were only 10-20m from one another. One of the clearest issues here is the nearly identical temporal patterns of the water table depth—the kind of shared environmental variable that split plot analyses were created to accommodate. I think it’s fine for the authors to describe patterns at each of the RG and AR locations, but I think the experimental design makes any formal comparison between land uses impossible. If the authors want to examine site differences, I think it would have to done using an n of 3, treating RG1/AR1 as a single site with higher within-site replication, but it would be a good idea to consult a statistician—there may be other options. Because of this issue, I think the graphical analysis may also need to be redone—perhaps organized around sites rather than land uses—if I am correct in my understanding that independence is an underlying assumption (as I mentioned in my previous review, I am not an expert in graphical analysis). In any event, I recommend consulting with a statistician before proceeding with additional revisions.

Response: We acknowledge that site conditions and distribution of treatments represent factors that warrant great caution in data interpretation, and we have indeed acted to meet the concern raised here. Note that the effect on N2O emission of the fertilization treatment was not the same at the four sites; therefore, one of the greatest advantages of using split plot designs (estimating a common effect of the fertilization treatment) vanishes. In the revised analyses we have instead used a single model describing the effect of fertilisation for each site. Therefore, we now report the N2O emissions separately per site (both for the temporal dynamics and the cumulative emissions). We believe that this approach documents the results of our experiment better. The conclusions reached previously still stand, with a few modifications which are described.

  o A related note: the very big site differences between RG2 and AR2 (e.g., in carbon stocks) highlight the rationale for using split plot approaches (such as the one the authors use for their fertilizer treatments): such approaches avoid treatment or land use history differences being confounded with site differences.

Response: See previous comment. In the revised Table 2, results are now presented for each combination of site, crop, fertiliser treatment and season (n=8).

  o The authors also argue that differences between land use was evident without any statistical support, which is a fair argument. I think it’s fine to discuss possible
effects of land use qualitatively, but important to include and clearly highlight the caveat that the study lacks independent replicates for the land use treatments.

Response: We have re-analysed cumulative N2O emissions for individual site-crop combinations by season (see revised Table 2). Results are now expressed as average daily rates, which allowed us to test for differences during spring and autumn, respectively. Furthermore, the temporal dynamics were analysed with a suitable mixed model. Results are now presented and discussed with reference to statistical support where possible, and otherwise wording has been changed to be more qualitative where relevant.

I don’t think these issues mean that the graphical model cannot be applied or provide novel results, but the model needs to be applied using the appropriate experimental design, and can’t treat RG1 and AR1 as independent sites.

Response: As for cumulative N2O emissions, graphical models were reanalysed for individual site-crop combinations by season, see revised Fig. 7 (now split into Figure 7 (spring) and 8 (autumn)). Notably, even without the statistical power of treatment replication, the effects remained largely unchanged with respect to treatment differences.

In Response 17, the authors note that land use was not analyzed statistically. However, the generalized linear mixed model includes land use (“crop”) in the interaction term used as the fixed effect (line 248-249), which is inappropriate given the replication concerns regarding RG1 and AR1.

Response: In the revised analysis, land use treatments were analysed separately.

2. This leads me to the language presenting results. The qualitative results need to be more clearly communicated as such—the way many results are presented here implies that there has been a quantitative statistical analysis conducted. A very simple example is line 328: “Mineral N concentrations were greater at AR1 compared to AR2”. In the scientific literature, such a statement implies a significant statistical difference in mineral N concentrations between the two sites. If a statistical test was conducted, a P value should be included (in general, there should be much more inclusion of p values in the text). If it wasn’t, small changes to the language need to be made that make that clear, e.g., “Mineral N concentrations appeared to be greater at AR1 compared to AR2”. Another small example might be line 334-35: “There was variation at depth in the soil, which could not be explained by fertilization.” The phrase “could not be explained” implies that a statistical test was attempted, but was not significant. If, instead, this is qualitative interpretation of data, it should include more qualifying language, e.g., “There was variation at depth in the, which did not appear to be related to fertilization.”

In fact, there are numerous instances of this kind of presentation of results throughout the manuscript; here are just a few examples (there are many more involving site comparisons, temporal comparisons within sites, fertilizer effects, etc., and all should be addressed): L316: “There were only minor differences. . . between seasons” implies that seasonal differences were tested; can be changed to something like “If there were any differences, they were likely minor. . .”

L 326: “The residence time for mineral N in the soil solution was generally longer at AR compared to the RG sites” implies that site differences were tested; can be changed to
“The residence time for mineral N in the soil solution generally appeared to be longer at AR compared to the RG sites.”

L328: “Mineral N concentrations were greater at AR1 compared to AR2” implies that site differences were tested; can be changed to “It appeared that mineral N concentrations may have been greater at AR1 than AR2”

L 329: “Fertilisation increased NH4+-N and NO3- -N concentrations” implies that differences between fertilized and unfertilized split plots were tested. Can be changed to “It appeared as though NH4+-N and NO3- -N concentrations increased following fertilization”

One quick way around this issue would be to state in the methods section that all interpretations of results are qualitative unless accompanied by a p value, and then to include p values where statistical tests were conducted (in any event, I encourage the authors to include P values for all statements reflecting the results of a statistical test). But a clearer solution would be 1) to test differences statistically if they have not been and include p values, and 2) to change the language describing results to make it qualitative, using words and phrases such as “may,” “appears to,” “might,” etc. to describe apparent patterns that cannot be tested or aren’t important enough to test. I don’t think it’s necessarily a problem to present results qualitatively (though for any results that are important to the central hypotheses being tested, it’s always good to include statistical analyses), but it needs to be very clear when differences were tested and when they were not.

Response: Regrettably, with limited resources we had made the decision to not collect and analyse soil samples at the block level, but instead pool soil samples from each block (by depth interval) for analysis of mineral N. For this reason, we have been unable to formally test effects of fertilisation or temporal dynamics.

We agree with the reviewer that the text should have reflected this more clearly. We have adjusted wording throughout the manuscript and further stress the qualitative nature of the mineral N dynamics with the following sentence:

“Since subsamples were pooled for analysis, only a qualitative description of the effects of treatments and temporal dynamics is possible.” (l. 346 in cleaned manuscript version)

3. I think there could be more detail in the discussion of figures 3-7, which represent a lot of the data presented in this manuscript. Briefly, the text often invokes a relationship between the water table and a) N2O concentrations in the soil or b) N2O fluxes at the surface, but the relationships described in the text are not obvious to me from examining the figures—the spatiotemporal relationship between the water table depth and N2O concentrations seems quite different in different sites and seasons. Additional text walking the reader through the authors’ interpretation of these figures would be helpful. I made related specific comments in my last review, and detail some points below in my response to the authors’ response #46, as well as in specific comments for lines 494, 501, and thereabouts.

Response: In the presentation of results, we gave priority to the comparison of land uses at the four sites, which is why fluxes and subsurface N2O concentrations (and seasons) are presented separately. We have revised the description of these results to better link observations to specific treatments or days, and to better link fluxes with subsurface N2O dynamics.

However, due to the delay in gas exchange through saturated and/or highly tortuous peat soil (a point now stressed in the Discussion l. 489f in cleaned manuscript version), a close relationship between fluxes
and subsurface concentrations can not be expected. We have added a new paragraph to the discussion explaining this (see below).

4. It seems to me that the two conclusions that can be clearly reached from this study are the rejection of the hypothesis that that FeS2 oxidation coupled with NO3- reduction was an important driver of N2O emissions, and the identification of the capillary fringe as an important predictor of surface N2O fluxes. If the authors agree, the conclusion should be revised; as it currently stands, the second of these findings is not discussed at all in the conclusion, and the description of the first conclusion gives the reader the impression that the hypothesized mechanism is possibly and maybe even probably not trivial.

Response: N mineralisation from decomposing peat after WT drawdown was mentioned, but we now specifically refer to the capillary fringe. With respect to FeS2, we have strengthened the wording:

“The hypothesis that NO3- reduction coupled with FeS2 oxidation was an important source of N2O could not be confirmed.” (l. 603 in cleaned manuscript version)

Also, the Discussion now includes a proper reference to the laboratory study confirming this conclusion – this study has now been published (doi.org/10.1080/01490451.2019.1666192).

Minor comment: the response to reviewers letter was sloppy – a number (maybe all?) of the line numbers of revised text referred to in the response to reviewers are incorrect, there are typos in the quoted text revisions (e.g., response 50), and sometimes there’s no indication of what revisions were made or where they can be found in the text (e.g., response 49). I empathize with these kinds of errors, especially after getting a fresh batch of comments from a new reviewer late in the publication process, but anything you can do to make the job of the reviewers easier is appreciated.

Response: An annotated copy with tracked changes was in fact submitted together with the revision, and we specifically referred to in the response letter. The critical comments above therefore appears to be based on a misunderstanding.

Responses to specific author responses
Response 20: I think the authors missed my point here, which was that the manuscript seems to only conduct a qualitative analysis of the relationship between changes in water table depth and changes in surface N2O flux, rather than including a statistical analysis of the relationship between the two variables that could provide quantitative insight into the importance of variation in water table depth for N2O surface fluxes. I agree that the manuscript does provide a graphical analysis showing that capillary fringe N2O is the only significant predictor of N2O surface fluxes at several sites, but being statistically significant and being important are not necessarily the same thing, and the graphical analysis does not include any analysis of the relationship between water table depth per se and N2O. I don’t think that the authors need to do what I am suggesting here for the manuscript to be publishable, but it seems like a missed opportunity.

Response: We did not test possible direct effects of WT depth on N2O flux. However, WT depth was indirectly, in the analysis of N2O flux patterns with graphical models, where N2O concentration above the WT table carried information about WT depth at the time of sampling. As pointed out by the reviewer in a comment to the earlier Response no. 46 (see below), in early autumn the N2O fluxes were greatly
stimulated at a time where WT depth was still low, presumably due to wetting of the upper soil layers in which nitrate had accumulated. This exemplifies that WT depth per se may not be a strong predictor of emissions.

Response 21: Thank you for the response, though part of my concern was not addressed. This concern is largely related to my general comment about the language used to describe results. My concern here had been that there were multiple instances in the manuscript (I cited them in the original comment as including lines 380 and lines 411-412) where temporal variation in surface N2O flux at a site was attributed to fertilizer effects, or where fertilizer effects were excluded as a cause of variation in surface N2O flux. However, the relationship between temporal variability in surface N2O fluxes and fertilizer applications appears not to have been tested statistically.

Response: We have analysed the temporal dynamics of N2O emissions, as well as WT depth. Information about statistical significance has been included where relevant.

Response 25: The authors argue that “The graphical model results (Figure 7) did show increasing N2O emissions with declining, as well as increasing WT depth that depended on soil N status.” I do not think that the graphical analysis included a water table depth variable? A separate point: I also don’t understand what is intended by “increasing WT depth that depended on soil N status” but if the point is that N2O_WT depends on soil N status, that would be an interesting result that deserves more discussion. If instead it’s referring to AR-autumn, where the N2O flux is determined in part by soil N status, then ignore this second comment of mine.

Response: This wording was not too well-considered. In fact the effect of WT depth was indirect, by shifting the position and magnitude of soil volume (in the capillary fringe) with a potential for N2O production. It is true, as stated, that we were thinking about the NO3 accumulation and subsequent wetting of the top soil. No changes made.

Response 39: I’m glad this was caught. I’d encourage the authors to carefully review the script for producing all figures again if they haven’t already.

Response: All Figures were double-checked.

Response 46: I wonder whether this explanation may also hold for DOY 252 and 259: it looks to me as though there are elevated N2O concentrations in surface soils, and no clear connection to the capillary fringe. Wouldn’t that suggest a topsoil source for all of the highest surface fluxes at AR1 during Autumn—a finding supported by the graphical analysis? The text implies that the high WT is responsible for the high emissions for DOY 252 and 259 (“The subsequent decline in N2O emissions at AR sites coincided with WT withdrawal”), but I would think that anoxia in topsoil related to elevated precipitation during this period could be a more likely explanation. The variability in topsoil N2O concentrations looks fairly physically separated from the water table dynamics, and if capillary fringe is not a significant predictor for surface N2O fluxes at this site during autumn, why invoke a relationship between WT withdrawal and surface N2O emission declines?
I have further questions about the interpretation of the subsoil N2O concentration dynamics discussed in my comment on line 494 below.
Response: We largely agree with the interpretation presented above, and the reference to WT dynamics did not imply a causal relationship. We have modified the text to put more emphasis on the wetting of the soil:

“High fluxes were observed on the first day of this monitoring period, DOY 246, at a time where WT depth was still at 40 to 80 cm depth. Instead the high N2O fluxes may have been triggered by saturation of the top soil after 10 and 22 mm rainfall the previous two days. Additional rainfall during the following days then was accompanied by a rise in WT. The subsequent decline in N2O emissions at AR sites coincided with WT draw-down and drainage of the top soil.” (L. 437 in cleaned manuscript version)

Response 54: I think it’s a good move to consider N2O as a time-integrated measure. My previous concern here was very much regarding the limitations of using point measurements of NH4+ and NO3- to infer N transformation rates. I think the framing of the revised discussion addresses my concerns.

Response: Thank you.

Response 56: So the data presented in figure 2 are means (and standard errors) of intact cores containing either fertilized and unfertilized soils in RG1, but for AR1, it’s a mean of intact cores containing only unfertilized soils? I don’t understand the rationale for presenting the data this way (instead of, for example, presenting fertilized and unfertilized soils separately where appropriate). At the very least, the caption should clearly detail this odd fertilization treatment situation.

Response: The management of grassland required that fertilisation took place before we had an opportunity to collect intact soil cores at the remote field site. Subsequent inspection of NO2- results upon sampling one week after fertilisation, however, did not suggest any effect of fertilisation, and this was confirmed by a paired-sample t-test across the six depths. We therefore went ahead and presented soil profiles across both fertiliser treatments.

As recommended, we have revised the Figure caption to describe this procedure.

Response 57: It’s your decision, but there isn’t much fine-scale temporal variation in these figures; I’d think it’s worth graphing up the full year and seeing what it looks like.

Response: Whether seasons or land use treatments should be shown side by side is not an easy decision. However, since grassland sites, and arable sites, are mostly discussed together, we wanted to facilitate a direct comparison with this side by side presentation. Although a case could also be made for other solutions, we have decided not to change the format of Figures 3-6.

Response 59: Again, it’s your decision, but would think it’s worth including in SI as figures as well as data tables—it’s just very difficult to read patterns in a data table. But thank you for including the raw data for researchers who may be interested in using it for their analyses.

Response: Thank you for this suggestion. Given the many variables involved (sites, crops, fertiliser treatments, soil depths and N species), we believe graphic presentations could be either too busy or too disaggregated to have much added value, and therefore we prefer to focus on the Table format.

New specific comments:

Line 23: perhaps define capillary fringe here: “…in the capillary fringe— [definition here]—was.
"(i.e., the soil volume above the water table influenced by tension saturation)" (l. 23 in cleaned manuscript version)

Line 62: it would be helpful to readers if you could provide an explicit definition of capillary fringe here, given how important it is to the manuscript.

Response: text was added (l. 67) to stress that this zone is defined by capillary rise of groundwater, but that it can still be partly unsaturated depending on pore size distribution:

“The capillary fringe of organic soils represents an interface between saturated and unsaturated soil conditions, in which the extent of tension saturation depends on pore size distribution (Gillham, 1984).” (l. 68 in cleaned manuscript version)

Line 105: what ridges? Probably need to provide more agronomic details

Response: It has been specified that these are established around potato rows.

Line 124: Perhaps this should be “method of fertilizer application”? (as N fertilization was noted as an exception in the next sentence)

Response: OK, has been included to clarify this distinction. (l. 131 in cleaned manuscript version)

Line 127: I believe the erroneous NS fertilizer application in RG2 was made on the same date as the second slurry application; if correct I would clarify that fact by starting this sentence with “On the same date as the second slurry . . .” or “Immediately after the second slurry. . . “ If the NS application was made on a different date, indicate the date.

Response: Done.

Line 137: here it would be helpful to explain the choices of spring and fall as emerging from the patterns observed in Petersen 2012, and in the introduction briefly describe those patterns. It could be just 1-2 sentences in the introduction, and an introductory clause to the first sentence here.

Response: The following was added to the Introduction, and is referred to in section 2.4, as requested:

“Among sites with arable crops in three regions, two sites had N2O emissions corresponding to, respectively, 38 and 61 kg N ha-1 yr-1; both of these sites showed distinct seasonal patterns with the highest emissions in spring and autumn periods, whereas emissions at the third site were lower (6.4 kg N2O-N ha-1 yr-1) and much less variable. Notably, WT depth at the two sites with seasonal patterns of N2O emission fluctuated between 10-30 and 10-120 cm depth, whereas WT depth at the third site remained at 90-125 cm depth throughout the 14-month monitoring period.” (l. 53 in cleaned manuscript version)

Line 144: it would give a more complete picture if the dates of these exceptions were enumerated here.

Response: The following was added:
“With a few exceptions (DOY 169 and 265 at site RG1, DOY 132 and 314 at site AR2), each campaign was initiated between 9:00 and 12:00; the order of sites visited in each trip alternated from week to week.” (l. 151 in cleaned manuscript version)

Line 165: revise to “…at -20C until analysis, described in section 2.4.5.”

Response: Done.

Line 170-1: I’m afraid this sentence is hard to follow. It reads as though the diluted soil gas was first transferred to the exetainer, and then from the exetainer to the glass syringe. Perhaps also specify whether exetainers were filled with 10ml gas as they were in the chamber measurements.

Response: Section 2.4.3 has been edited to clarify the procedure. (l. 176 in cleaned manuscript version)

Line 174: As a general rule I’d argue it’s best to explicitly include all applicable methodological detail, rather than referring readers to an additional manuscript (within reason). In this case, my institution does not have a subscription to the European Journal of Soil Science, so my library had to obtain 24-hour access to Petersen 2014 so I could see the dilution calculations; I would include them in the manuscript.

Response: Equation 5 from Petersen 2014 is now shown and explained in section 2.5.

Line 240-245: it would be helpful to specify if/how field temperature and pressure corrections were made to obtain surface flux estimates.

Response: The following sentence was added:

“Nitrous oxide mixing ratios were converted to units of mass per volume using the ideal gas law and values of pressure and air temperature recorded by the weather station.” (l. 257 in cleaned manuscript version)

Line 297: It should be noted here that these characterizations were conducted after the fertilizer treatment of RG1

Response: We did not locate the text referred to above, but we have assumed that it was soil N characterisation. We have added the following sentence:

“At site RG1, fertilisation had taken place one week earlier, but a two-sample t test did not find evidence for an effect on NO3 availability (p = 0.19), and therefore the results from both AR1 and RG1 subplots are presented together.” (l. 355 in cleaned manuscript version)

Line 380: Instead of “independent of fertilization” which suggests a formal analysis, how about “this variation appeared to be broadly similar between fertilized and unfertilized subplots”

Response: OK, paragraph has been revised.

Line 394 and following: this is one of many examples related to my general comment on presenting qualitative results, but the generalized linear mixed model appears to include only time, and not fertilizer, as a factor in the fixed effect, so statements regarding the effects of fertilization should be made qualitatively (e.g., rather than “with no effect of fertilizer
amendment,” use something like “and did not appear to vary in response to fertilization.” Similarly, “no effect of N fertilisation was observed. Hence, the higher emissions were associated with site differences other than fertilization” could be changed to “fertilisation did not appear to influence N2O fluxes. Hence, the higher emissions were likely associated with site differences other than fertilization”). The paragraph starting with line 406 does a good job of qualitatively describing results.

Response: We have revised the text to make sure that results are presented in a qualitative way where necessary.

Line 467: change to “In accordance with this effect of rewetting…” (in general, it’s good to give “this” an object to make it clear what is being referred to)

Response: Done.

Line 490: here and maybe elsewhere there are still instances where time of year are referred to without DOY (here parenthetical DOYs would be particularly helpful since its referring to figures using DOY on the x-axis). In addition, please specify that this accumulation is in the fertilized plots of RG2.

Response: OK, several instances were amended with DOY information.

Line 491: change “significant” to “substantial” if the meaning is “a lot.” Avoid using “significant” except when alluding to the result of a statistical test.

Response: Done.

Line 492: if the contrast is that in RG2 there was only accumulation at certain times and depths but accumulation was everywhere and all the time in the AR sites, change “...accumulation of N2O in the soil” to “...accumulation of N2O across all soil depths throughout the spring” or something similar. Maybe include a reference to Figure 4.

Response: OK, the following wording is now used:

“In contrast, at AR sites N2O consistently accumulated in the soil throughout spring” (l. 536 in cleaned manuscript version)

*Line 494: as was the case with the previous version of the manuscript (see my original comment that elicited the authors’ response 46 and my general comment 3), I’m not sure I see the pattern so clearly. The location of elevated N2O above 40cm in AR2 is attributed to the water table being higher than in AR1, where elevated N2O tends to be in deeper soils, and the authors argue that this points to a capillary fringe source for N2O. But in RG2 the water table is higher than it is in RG1 during the spring, but the N2O distributions are reversed: they are higher at depth in in RG2, where the water table is higher, and higher in shallower soils in RG1, where the water table is lower. The fertilized AR2 also has an inversion of N2O concentrations during spring that seems entirely unrelated to water table depth. In autumn, the N2O at depth declines as the water table depth increases, and the patterns in the two blocks in RG1 seem somewhat opposite of one another even though the water table is just about identical. With so much apparent variation in how N2O concentrations vary with the water table, how do these results all
relate to capillary fringe as the N2O source? What am I missing? I suppose that this comment, in combination with my new response to the authors response 46, suggests an opportunity for the authors to revise and expand their presentation (and perhaps interpretation) of these results. It would be a very satisfying read if the paper spent a little more time on the subtleties in the links the graphical analysis identification of the significant drivers of surface N2O fluxes to the spatiotemporal dynamics presented in figures 3-6 (these are most of the data being presented in the paper, so feel free to give them more attention in the text).

Response: We agree that patterns of soil N2O concentration profiles were complex and not readily aligned with emissions. It is probably important to acknowledge the importance of soil wetness as a barrier towards transport, and we have added a new paragraph to the discussion (section 4.1) to motivate the focus on N2O concentration above the water table, which was a potential site of N2O production:

“A limited number of potential drivers (rainfall, temperature, soil mineral N and soil concentrations of N2O) were monitored to help explain N2O emission dynamics. Soil N2O concentration profiles showed complex patterns where, for example, the highest concentrations were sometimes observed above, and sometimes below the WT depth at both RG (Figure 3) and AR sites (Figure 4). Fertilisation in spring was associated with higher concentrations of N2O below the WT depth at sites RG2 and AR2, which indicated downward transport of fertiliser N, but this was not reflected in elevated N2O emissions. The reason may be that in wet soil the time required to reach a steady state between N2O production and emissions from the soil surface can be significant and increases with distance (Jury et al., 1982). In accordance with this, Clough et al. (1999) observed a delay of 11 days before 15N enriched N2O produced at 80 cm depth was released from the soil surface at a corresponding rate. Since the presence of air-filled porosity is critical for the exchange of gases between soil and the atmosphere (Jury et al., 1982), the soil N2O concentration closest to, but above the WT depth (N2OWT), was taken to represent “subsoil” processes stimulating N2O emissions.” (l. 484 in cleaned manuscript version)

Line 501: I’m not sure why water table dynamics are invoked in the discussion of N2O emissions at AR1, if capillary fringe was not a significant predictor of surface N2O fluxes in the graphical analysis, and, as noted previously (and in my comment on the authors’ response 46), surface fluxes were already elevated before the rise in WT depth? A simpler explanation consistent with the graphical analysis might be that topsoil was the source of surface N2O fluxes in AR1 during autumn, apparently independent of water table depth. If this discussion is intended to be descriptive only of dynamics within the soil (and does not have any relation to surface N2O emissions), that needs to be made clear.

Response: We agree, and we have adjusted the text accordingly, as explained above.

Line 528: It would be helpful to have a definition of “dead-end pores”

Response: These are associated with plant cell remains. This information has been added.

Line 567-559: These are all the kinds of statements that need to be made much more qualitatively in the absence of clear statistical support, and issues with experimental design and strength of statistical support for conclusions need to be highlighted in the conclusion.

Response: The Conclusion section has been rewritten to reflect where statistical support for statement was available, and to reflect better this is our interpretation of the results.

Line 560: remove the comma between “hypothesis” and “that”

Response: Done – and sentence edited.
Line 561: my impression from the results is that NO3- reduction coupled with FeS2 reduction is likely to be a trivial mechanism of N2O production in these soils (a conclusion apparently supported by the related manuscript that has been submitted elsewhere)—this statement makes it sound as though it could be non-trivial.

Response: We agree that this conclusion should be expressed more clearly. Has been rephrased as:

“The hypothesis that NO3- reduction coupled with FeS2 oxidation was an important source of N2O was not confirmed.” (l. 603 in cleaned manuscript version)
Regulation of N$_2$O emissions from acid organic soil drained for agriculture

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Abstract

Organic soils drained for crop production or grazing land are agroecosystems with potentially high, but variable emissions of nitrous oxide (N$_2$O). The present study investigated the regulation of N$_2$O emissions in a raised bog area drained for agriculture, which was classified as potentially acid sulfate soil. Here we hypothesised that pyrite (FeS$_2$) oxidation was a potential driver of N$_2$O emissions through microbially mediated reduction of nitrate (NO$_3$). Two sites with rotational grass, and two sites with a potato crop, were equipped for monitoring of N$_2$O emissions and soil N$_2$O concentrations at 5, 10, 20, 50 and 100 cm depth during weekly field campaigns in spring and autumn 2015. Further data acquisition included temperature, precipitation, soil moisture, water table (WT) depth, and soil NO$_3$ and ammonium (NH$_4$) concentrations. At all sites, the soil was acidic with pH ranging from 4.7 to 5.4. Spring and autumn monitoring periods together represented between 152 and 174 d, with cumulative emissions of 3.6±1.5 kg N$_2$O-N ha$^{-1}$ at sites with rotational grass and 10.2±2.0 kg N$_2$O-N ha$^{-1}$ at sites with a potato crop. Equivalent soil gas phase concentrations of N$_2$O mostly ranged from 10 to around 1415 µL L$^{-1}$ at grassland sites, and up to several hundred µL L$^{-1}$ at potato sites, in accordance with lower soil mineral N concentration availability at grassland sites. Statistical analyses using graphical models showed that soil N$_2$O concentration in the capillary fringe i.e., the soil volume above the water table influenced by tension saturation was the strongest predictor of N$_2$O emissions in spring and, for grassland sites, also in the autumn. For potato sites in autumn, the analysis found there was evidence that NO$_3$ availability in the top soil, together with nitrous oxide concentrations, were the main controls on N$_2$O emissions. Chemical analyses of intact soil cores from 0.1 m depth, collected to 1 m depth at adjacent grassland and potato sites in spring and autumn, showed that the total reduction capacity of the peat soil (assessed by cerium (IV) reduction) was much higher than that represented by FeS$_2$, and the concentrations of total reactive iron (TRFe) were higher than those of FeS$_2$. Based on the statistical graphical models and the tentative estimates of reduction capacities, FeS$_2$ oxidation was found unlikely to be important for N$_2$O emissions. Possible pathways of N$_2$O production in spring and autumn periods, and the potential sources of N, are further discussed.

Key words: Drained peat, potentially acid sulfate soil, rotational grass, potato, nitrous oxide, reactive iron
1 Introduction

Worldwide, 25.5 million ha of organic soils have been drained for agricultural use, mainly as cropland (Tubiello et al., 2016), and this accelerates decomposition of soil organic matter and net carbon (C) and nitrogen (N) mineralisation above the water table (WT) (Schothorst, 1977). Drained organic soils are significant net sources of greenhouse gas (GHG) emissions as carbon dioxide (CO₂) and nitrous oxide (N₂O) (Goldberg et al., 2010; Maljanen et al., 2003). A recent supplement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories on Wetlands (IPCC, 2014) proposed average annual emission factors of 4.3 and 8.2 kg N₂O-N ha⁻¹ yr⁻¹ for temperate grassland on drained organic soil with low and high nutrient status, respectively, and an emission factor of 13 kg N₂O-N ha⁻¹ yr⁻¹ for cropland. For soil C losses, the emission factors proposed for drained organic soils are lower, and they suggested that N released from arable sites in temperate regions may enhance N₂O emissions during a two-year field study on a drained organic soil, whereas the response to N fertilisation was limited, and they suggested that N released by soil organic matter mineralisation was the main source of N₂O. In a study comparing GHG emissions from organic soil with different land uses in three regions of Denmark (in total eight sites), Petersen et al. (2012) also found that site conditions such as WT, pH and precipitation contributed significantly to explain N₂O emission dynamics. Among sites with arable crops in three regions, two sites had N₂O emissions corresponding to, respectively, 38 and 61 kg N ha⁻¹ yr⁻¹; both of these sites showed distinct seasonal patterns with the highest emissions in spring and autumn periods, whereas emissions at the third site were lower (6.4 kg N₂O-N ha⁻¹ yr⁻¹) and much less variable. Notably, WT depth at the two sites with seasonal patterns of N₂O emission fluctuated between 10-30 and 10-120 cm depth, whereas WT depth at the third site remained at 90-125 cm depth throughout the 14-month monitoring period.

In the study by Petersen et al. (2012), extremely high N₂O emissions corresponding to 38 and 61 kg N ha⁻¹ yr⁻¹ were observed from arable sites in two of the three regions investigated. Several processes can lead to N₂O formation in acid organic soil: biotic processes include ammonia (NH₃) oxidation to nitrite (NO₂⁻) by archaea or bacteria (Herrmann et al., 2012; Herold et al., 2012; Stieglmeier et al., 2014), as well as nitrifier denitrification and heterotrophic denitrification by bacteria or fungi (Liu et al., 2014; Maeda et al., 2015; Wrage-Männig et al., 2018). The recently discovered process denitrification by Nitr capreua sp. is also a potential, but probably minor, source of N₂O (Kits et al., 2019; Palomo et al., 2019). Abiotic N₂O production can occur through chemodenitrification (Van Cleemput and Samater, 1996; Jones et al., 2015) or abiotic codenitrification (Spott et al., 2011). The two regions showing extreme N₂O emissions from arable soil had both developed from marine forelands and were categorised as potentially acid sulfate soil, i.e., saturated to poorly drained soil containing pyrite (FeS₂) that, upon oxidation, may lead to acid production in excess of the soil’s
neutralising capacity (Madsen and Jensen, 1988). The capillary fringe of organic soils represents an interface between saturated and unsaturated soil conditions, in which the extent of tension saturation depends on pore size distribution (Gillham, 1984). Previously, it has been speculated that oxidation and reduction of iron sulfides could influence N transformations during periods with changing groundwater level (Petersen et al., 2012).

Drainage promotes oxidation of FeS₂, a process which may be linked to microbially mediated nitrate (NO₃⁻) reduction (Jørgensen et al., 2009; Torrento et al., 2010). The complete reduction of NO₃⁻ to dinitrogen (N₂) can proceed as follows:

\[
30 \text{NO}_3^- + 10 \text{FeS}_2 + 20 \text{H}_2\text{O} \rightarrow 15 \text{N}_2 + 20 \text{SO}_4^{2-} + 10 \text{Fe}(\text{OH})_3 + 10 \text{H}^+ \quad (1)
\]

However, in the capillary fringe residual oxygen (O₂) or, alternatively, the acidification produced by FeS₂ oxidation, could favour incomplete denitrification with accumulation of the intermediate N₂O (Torrento et al., 2010):

\[
30 \text{NO}_3^- + 8 \text{FeS}_2 + 13 \text{H}_2\text{O} \rightarrow 15 \text{N}_2 \text{O} + 16 \text{SO}_4^{2-} + 8 \text{Fe}(\text{OH})_3 + 2 \text{H}^+ \quad (2)
\]

Nitrate reduction via the reaction described in Eq. 2 could potentially have contributed to the very high N₂O emissions reported by Petersen et al. (2012) previously from the two arable sites, where groundwater sulfate concentrations were also consistently high. (Petersen et al., 2012).

Here, we studied four agricultural sites within one of the regions previously investigated by Petersen et al. (2012), i.e., a raised bog area with acid soil conditions. This study included two sites with rotational grass and two sites with a potato crop, and monitoring took place in spring and autumn periods, where high emissions of N₂O occurred in previous studies (Petersen et al., 2012; Kandel et al., 2018). We hypothesised that FeS₂ oxidation coupled with NO₃⁻ reduction was a possible driver of N₂O emissions. It was further hypothesised that N₂O emissions would vary with site conditions affecting denitrification (mineral N availability, rainfall, WT depth and temperature).

2 Materials and methods

2.1 Study sites

The sites investigated in this study were located in Store Vildmose, which is a 5,000 ha raised bog in northern Jutland, Denmark. The area was, until 150 years ago, the largest raised bog in Denmark, and largely unaffected by human activity. The bog overlies a marine plain formed by the last marine transgression; the sea retreated around 8000 BC, and peat later developed in wet parts of the landscape, attaining a maximum depth of 4.5 to 5.3 m in central parts of the bog (Kristensen, 1945). Between 1880 and 2010, the peat has generally subsided by at least 2 m due to drainage for agriculture or peat excavation (Regina et al., 2016), and today the peat depth is mostly 1-2 m, but in some locations even less (Kandel et al., 2018). The peat and underlying sand is acidic and has been categorised as a potentially acid sulfate soil (Madsen and Jensen, 1988). According to Kandel et al. (2018), the peat at 0-25 cm depth in arable soil in this area has a high degree of humification, which corresponds to H8 on the Von Post scale.
Four sites were selected along an east-west transect (Figure 1a). One arable site (AR1) was in a field cropped with second-year potato in 2015, while an adjacent site (RG1) in a neighbouring field had second-year rotational grass; these two sites were also represented in the study of Petersen et al. (2012) as sites N-AR and N-RG, respectively. Land use treatments (i.e., potato and rotational grass) were replicated at sites in other fields, and will be referred to as AR2 and RG2. Site AR2 was located 4.6 km to the west, and site RG2 was located 1.7 km to the east of the paired AR1-RG1 sites (Figure 1a and S1).

2.2 Experimental design

In January 2015, an area of 10 m × 24 m was defined at the location of each site. Sampling positions were georeferenced using a Topcon HiPer SR geopositioning system (Livermore, CA). On 25 February 2015, each site was fenced, and three 10 m × 8 m experimental blocks were defined (Figure 1b). Each site was further divided along its longitudinal axis to establish two 5 m × 24 m fertilisation subplots.

For monitoring of WT depth, piezometer tubes (Rotek A/S, Sdr. Felding, Denmark) were installed to 150 cm depth at the centre of each block. On either side of the piezometers, at 2.7 m distance, collars of white PVC (base area: 55 cm × 55 cm, height: 12 cm [RG] or 24 cm [AR]) were installed to between 5 and 10 cm depth (Figure 1). The higher collars used at AR sites were at level with the ridges established around potato rows during the growth period. The collars, which were fixed to the ground by four 40 cm pegs, had a 4 cm wide flange extending outwards 2 cm from the top to support gas flux chambers. To prevent soil disturbance during gas sampling, platforms (60 cm × 100 cm) of perforated PVC were placed in front of each collar to create a boardwalk. The exact headspace of each collar was determined from 16 individual measurements of distance from the upper rim; this procedure was repeated whenever collars had been removed and reinstalled to accommodate field operations.

Sets of five stainless steel diffusion probes for soil gas sampling at 5, 10, 20, 50 and 100 cm depth were installed vertically within 0.5 m of the flux measurement positions in two blocks (Block 2 and 3) at sites AR1 and RG1, while at sites AR2 and RG2 diffusion probes were installed only in Block 2. The stainless steel probes were constructed as described in detail by Petersen (2014), with a 10 cm diffusion cell having a 3 mm diameter opening at the sampling depth covered by a silicone membrane, which was connected to the soil surface via two 18G steel tubes with Luer Lock fittings (Figure S1).

A HOBO Pendant Temperature Data Logger (Onset Computer Corp., Bourne, MA) was installed at 5 cm depth in Block 2 at each site. A mobile weather station (Kestrel 4500; Nielsen-Kellerman, Boothwyn, PA) was mounted at 170 cm height at site RG1 for hourly recording of air temperature, barometric pressure, wind speed and direction, and relative humidity. Daily precipitation was recorded at <10 km distance from the monitoring sites at a meteorological station, from where data to fill a gap in air temperature were also obtained.

2.3 Management
Management within the fenced experimental sites followed the practices adopted by the respective farmers, e.g., with respect to method of fertiliser application, grass cuts, potato harvest and soil tillage. One exception to this was N fertilisation, which rate, since N fertiliser was only given to one of the two subplots in each block (Figure 1b). Fertilised subplots of the RG1 site received 350 kg ha\(^{-1}\) NS 27-4 fertiliser on 16 April (DOY106), corresponding to 94.5 kg N ha\(^{-1}\). Site RG2 was fertilised with 20-25 Mg ha\(^{-1}\) acidified cattle slurry (pH 6) on 5 May (DOY125), and again on 2 July (DOY183), each time corresponding to 90-110 kg total N ha\(^{-1}\). A few exceptions to this were during autumn using MaT Level2000 data loggers (MadgeTech; Warner, NH, USA). At the RG1 site, the grass was cut in late August, while at the RG2 site the grass was cut in late June and on 9 September (DOY255). Potato harvest at the AR1 site took place in mid-September (DOY 258), with interruptions due to heavy rainfall. At the AR2 site, the potato harvest took place on 23 September (DOY266).

### 2.4 Field campaigns

Based on the patterns of N\(_2\)O emissions observed by Petersen et al. (2012), a monitoring program was conducted during spring from 3 March (DOY063) to 16 June (DOY166), and during autumn from 3 September (DOY243) to 10 November (DOY314). Weekly measurement campaigns were conducted at each of the four sites insofar as field operations permitted. Thus, during spring there were 14, 12, 14 and 15 weekly campaigns at the RG1, AR1, RG2, and AR2 sites, respectively. During autumn there were 10, 10, 7 and 10 weekly campaigns at the RG1, AR1, RG2, and AR2 sites, respectively. Field trips included sampling at two sites, either AR1 + RG1 or AR2 + RG2, and thus all four sites were visited during two field trips on consecutive days. Campaigns included registration of weather conditions and WT depth, soil sampling, soil gas sampling, and N\(_2\)O flux measurements. With a few exceptions (DOY 169 and 265 at site RG1, DOY 132 and 314 at site AR2), each campaign was initiated between 9:00 and 12:00; the order of sites visited in each trip alternated from week to week.

#### 2.4.1 Climatic conditions

Air temperature, relative humidity and barometric pressure were logged at the weather station located at RG1. During field campaigns, the WT depth was first determined in each of the three piezometers using a Model 101 water level meter (Solinst; Georgetown, Canada). At AR1 and AR2, WT depth in Block 3 was further recorded at 30-minute time resolution for a period during autumn using MaT Level2000 data loggers (MadgeTech; Warner, NH, USA). Soil temperatures at 5, 10 and 30 cm depth were measured in each block using a high precision thermometer (GMH3710, Omega Newport, Deckenpfronn, Germany), and in addition continuous measurements of soil temperature at 5 cm depth were collected in block 2 at each site using HOBO Pendant Temperature Data Loggers (Onset Computer Corp., Bourne, MA).
2.4.2 Soil sampling

During all field campaigns, soil samples were collected separately from fertilised and unfertilised subplots by random sampling of six 20 mm-diameter cores to 50 cm depth, (two per block). Each core was split into 0-25 and 25-50 cm depth, and the six subsamples from each depth were pooled. The pooled samples were transported back to the laboratory in a cooling box and stored at -20°C for later analysis of mineral N and gravimetric water content.

On 23 April (DOY113/DOY 113), and again on 2 September (DOY245/DOY 245), undisturbed soil cores (50 mm diameter, 30 cm segments) were collected to 1 m depth within 1 m distance from the positions of flux measurements in Block 3 of sites RG1 and AR1 (cf. Figure 1b). A stainless steel corer (04.15 SA/SB liner sampler, Eijkelkamp, Giesbeek, Netherlands) equipped with a transparent plastic sleeve was used. The steel corer’s lower end was capped with a 4 cm long cutting head, and hence sampling depths were 0 to 30 cm, 34 to 64 cm and 68 to 98 cm. The intact cores were capped and sealed, and transported in a cooling box to the laboratory, where they were stored at -20°C until analysis (see section 2.4.5).

2.4.3 Soil gas sampling

Soil gas samples were collected in 6 mL pre-evacuated Exetainers (Labco Ltd, Lampeter, UK) as described by Petersen (2014) and demonstrated in Figure S2. In brief, the diffusion probes were flushed via the inlet tube with 10 mL N₂ containing 50 μL L⁻¹ ethylene (AGA, Enköping, Sweden) as a tracer, which displaced the gas in the diffusion cell, though with some mixing of sample and flushing gas. A three-way valve, mounted on the outlet tube, was fitted with a 10 mL glass syringe and an Exetainer. The displaced gas was collected in the glass syringe, and from where the glass syringe the 10 mL soil gas sample, now partly diluted by the flushing gas, was transferred to the Exetainer. After gas sampling, the probe was flushed with 2 × 60 mL N₂ to remove ethylene, and the Luer Lock fittings were capped. Samples of the N₂/ethylene gas mixture used for sample displacement were also transferred directly to Exetainers for gas chromatographic analysis (n = 3) as reference for the calculation of dilution factors (Petersen, 2014). Sampling for soil gas was done in parallel with flux measurements, except when equipment had to be removed during periods with field operations. Due to damage of some probes during spring, it was decided to discontinue soil gas sampling in the unfertilised grassland subplot at site RG2-NF, which had by mistake received fertiliser on DOY 183.

2.4.4 Nitrous oxide flux measurements

Gas fluxes were measured with static chambers (60 cm × 60 cm × 40 cm) constructed from 4-mm white PVC, and equipped with a closed-cell rubber gasket (Emka Type 1011-34; Megatrade, Hvidovre, Denmark) as a seal during chamber deployment. Chambers were further equipped with a 12V fan (RS Components, Copenhagen, Denmark) for headspace mixing that was connected to an external battery (Yuasa Battery Inc.; Laureldale, PA), as well as a vent tube with outlet near the ground to minimise effects of wind (Conen and Smith, 1998; Hutchinson and Mosier, 1981). Also, chambers were equipped with an internal temperature sensor (Conrad Electronic SE; Hirschau, Germany), and a butyl rubber septum on top of each chamber for gas sampling. Handles attached to the top were used for straps fixing the
chamber firmly against the collar. Gas samples (10 mL) were taken with a syringe and hypodermic needle immediately after chamber deployment, and then 15, 30, 45 and 60 minutes after closure. Gas samples were transferred to 6 mL Exetainer vials, leaving a 4 mL overpressure.

2.4.5 Soil analyses

Soil samples collected during the weekly campaigns were sieved (6 mm) and subsampled for determination of soil mineral N and gravimetric water content. Approximately 10 g field moist soil was mixed with 40 mL of 1 M potassium chloride (KCl) and shaken for 30 min, and then filtered through 1.6 µm glass microfibre filters. Concentrations of NH$_4^+$ and NO$_2^- + NO_3^-$ in filtered KCl extracts were determined by autoanalyser (Model 3; Bran+Luebbe GmbH, Norderstedt, Germany) using standard colorimetric methods (Keeney and Nelson, 1982). Gravimetric soil water content was determined after drying of soil samples at 80°C for 48 hours.

Additional soil characteristics were determined on the intact soil cores collected in April and September at AR1 and RG1. Five cm sections were subsampled from selected depths and analysed for water content, pH, electrical conductivity (EC), total soil organic C and N, and NO$_2^-$ in soil:water extracts (1:5, w/v) using a modified Griess-Ilosvay method (Keeney and Nelson, 1982). Total organic C and total N were determined in bulk soil samples collected at RG2 and AR2 in the same weeks as sampling of intact cores took place at AR1 and RG1.

The concentration of total reactive Fe (TRFe) at selected depth intervals was determined in the samples from both April and September samplings of intact soil cores. The analysis of TRFe was done using a dithionite-citrate extraction (Carter and Gregorich, 2007; Thamdrup et al., 1994) followed by Fe$^{2+}$ analysis with the colorimetric ferrozine method, which includes hydroxylamine as reducing agent (Viollier et al., 2000). The extraction dissolves free (ferric) Fe oxides (except magnetite, Fe$_3$O$_4$), as well as (ferrous) Fe in FeS, but not FeS$_2$.

The intact soil cores, from the September sampling, were further analysed for acid volatile sulfides (AVS) and chromium reducible sulfur (CRS) as indices of FeS and FeS$_2$, respectively. Quantification of AVS and CRS was based on passive distillation adapted from Ulrich et al. (1997) and Burton et al. (2008). Briefly, 0.5 g soil and a trap with 4 mL alkaline Zn-acetate solution (5%) was placed in 120 mL butyl-stoppered (and crimp-sealed) serum bottles, which were evacuated (1 kPa) and pressurised with N$_2$ (150 kPa) in three cycles to remove O$_2$, eventually leaving the headspace with N$_2$ at atmospheric pressure. Acid volatile sulfide (primarily FeS) was liberated and trapped as ZnS after injection of 12 mL anoxic 2 M HCl followed by sonication (0.5 h) and incubation (24 h) on a rotary shaker (20°C). Using the same approach with replicate soil samples, combined AVS and CRS (primarily elemental S and FeS$_2$) was trapped after injection of 12 mL 1 M Cr$^{3+}$ in 2 M HCl, prepared by reduction of CrCl$_3$ (Roy et al., 2014). Trapped sulfide (ZnS) in the two traps was measured colorimetrically using diamine reagent (Cline, 1969), and CRS was then calculated by difference.
Finally, the total reduction capacity of the peat at depths of 27-30 cm, 61-64 cm and 95-98 cm was determined. In brief, a suspension (soil:solution, 1:25; w/v) of oven dried (105°C) sieved soil (<2 mm) and 25 mM cerium (IV) sulfate reagent, Ce(SO$_4$)$_2$ in 5% sulfuric acid (H$_2$SO$_4$), was shaken horizontally for 24 h at 275 revolutions per minute (rpm). After centrifugation at 2,000 rpm, residual Ce(IV) was measured by end-point titration using a solution of 5 mM FeSO$_4$ in 5% H$_2$SO$_4$. The amount of reduced compounds was calculated and expressed as meq kg$^{-1}$.

2.4.6 Gas analyses

Nitrous oxide concentrations were analysed on an Agilent 7890 gas chromatograph (GC) combined with a CTC CombiPal auto-sampler (Agilent, Nærum, Denmark). The instrument had a 2 m back-flushed pre-column with Hayesep P connected to a 2 m main column with Poropak Q. From the main column, gas entered an electron capture detector (ECD). The carrier was N$_2$ at a flow rate of 45 mL min$^{-1}$, and Ar-CH$_4$ (95%/5%) at 40 mL min$^{-1}$ was used as make-up gas. Temperatures of the injection port, columns and ECD were 80, 80 and 325°C, respectively. Concentrations were quantified with reference to synthetic air and a calibration mixture containing 2013 nL L$^{-1}$ N$_2$O. Soil profile N$_2$O concentrations were frequently at several hundred μL L$^{-1}$; linearity of the EC detector response was ascertained up to 1600 μL L$^{-1}$, but the entire range was not included in analytical runs as a standard practice, and therefore the higher equivalent gas phase concentrations are relatively uncertain.

Ethylene concentrations in soil gas samples and flushing gas were analysed following a separate injection with an extended run time. All GC settings were as described above, except that run time was different, and gas from the main column was directed to a flame ionisation detector supplied with 45 mL min$^{-1}$ H$_2$, 450 mL min$^{-1}$ air, and 20 mL min$^{-1}$ N$_2$; the detector temperature was 200°C.

2.5 Data processing and statistical analyses

Equivalent soil gas phase concentrations of N$_2$O were calculated assuming full equilibrium (Petersen, 2014) according to Eq. 3:

$$c_S = c_m / \left[ 1 - \frac{(V + d_{out})a_F}{(V - d_{in})a_F} \right]$$

where $c_S$ is the concentration of N$_2$O in the diffusion cell and $c_m$ the observed concentration (μL L$^{-1}$); $V$ and $d_{in}$ and $d_{out}$ are the volumes of the diffusion cell, inlet tube and outlet tube, respectively (L); $a_m$ is the concentration of the tracer ethylene in the gas sample analysed (μL L$^{-1}$); and $a_F$ is the concentration of ethylene in the flushing gas (μL L$^{-1}$).

Nitrous oxide mixing ratios were converted to units of mass per volume using the ideal gas law and values of pressure and air temperature recorded by the weather station. Individual N$_2$O fluxes were calculated in R (version 3.2.5, R Core Team, 2016) using the package HMR (Pedersen et al., 2010). This program analyses non-linear concentration-time series with a regression-based extension of the model of Hutchinson and Mosier (1981), and linear concentration-time series by linear regression (Pedersen et al., 2010). Statistical data ($p$ value, 95% confidence limits) are provided by
HMR for both categories of fluxes. The choice to use a linear or non-linear flux model was made based on scatter plots and the statistical output.

The temporal dynamics of \( \text{N}_2\text{O} \) fluxes were analysed by season for individual site-crop combinations using a generalised linear mixed model defined with the identity link function, the gamma distribution (see Jørgensen and Labouriau, 2012; McCullagh and Nelder, 1989), and Gaussian random components. The model contained a fixed effect representing the interaction between crop, fertilisation and sampling day, and random effects representing site and sampling position. The model for daily \( \text{N}_2\text{O} \) emission described above was used to estimate cumulative emissions by integrating the flux curves over time. Treatment effects were then analysed by specially designed linear contrasts as described in detail by Duan et al. (2017), who showed that models with untransformed responses (when using adequate distributions) allow simple statistical inference of the time-integrated \( \text{N}_2\text{O} \) emissions. WT levels at different time points were compared for each site-crop combination by permutation tests (Good, 2005) with 9999 permutations respecting the block structure.

The dependence structure of variables that were potential drivers of \( \text{N}_2\text{O} \) fluxes were studied using a class of multivariate models called “graphical models” (Whittaker, 1990, see also Labouriau et al., 2008a,b; and Lamandé et al., 2011 for applications in soil science). These models represent the dependence of variables using an undirected graph (not to be confounded with the word “graph” used to refer to a plot), which is a mathematical structure composed of vertices, represented by points, and edges connecting pairs of vertices, represented by lines connecting points, according to the convention explained below. In graphical models, the variables of interest are the vertices of the graph (represented as labelled points). Here the variables used were: soil temperature at 5 cm depth (Temp5); soil temperature at 30 cm depth (Temp30); \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) concentrations in the top soil (AmmoniumT and NitrateT); \( \text{N}_2\text{O} \) concentration of the soil gas diffusion probe closest to, but above the WT, i.e., in the capillary fringe (\( \text{N}_2\text{O}_{\text{WT}} \)); and finally, the \( \text{N}_2\text{O} \) flux (\( \text{N}_2\text{O} \)-flux). The dependence structure of these variables was characterised by the conditional covariances between each pair of variables given the other variables. Those conditional covariances were simultaneously estimated using the available data according to a statistical model. The graph representation of the model is constructed by connecting the pairs of vertices (i.e., pairs of variables) by an edge when the conditional correlation of the two corresponding variables, given all the other variables, is different from zero. It is possible to show that two variables directly connected in the graph carry information on each other that is not already contained in the other variables (see Whittaker, 1990, Jørgensen and Labouriau, 2012). Moreover, the absence of an edge connecting two vertices indicates that (even a possible) association between the two corresponding variables can be entirely explained by the other variables. According to the general theory of graphical models, if two groups of variables, say A and B, are separated in the graph by a third group of variables, say C (i.e., every path connecting an element of A with an element of B necessarily contains an element of C), then A and B are conditionally uncorrelated given C (see Lauritzen, 1999). This property, called the separation principle, was used below to draw non-trivial conclusions on the interrelationship between \( \text{N}_2\text{O} \)-flux related variables. The graphical models were inferred by finding the model that minimised the BIC (Bayesian information criterion, i.e., a penalised version of the likelihood function) as implemented in the R package gRapHD (Abreu et al., 2010). This inference procedure yields an optimal representation of the data in the sense that the probability of correct specification of the model, when using this penalisation, tends to one as the
number of observations increases (see Haughton, 1988). The confidence intervals for the conditional correlations were obtained by a non-parametric bootstrap procedure (Davidson and Hinkley, 1997) with 10,000 bootstrap samples. Separate analyses were conducted for each combination of site, crop and season and crop, since different dependency patterns appear in those groups.

3 Results

3.1 Climatic conditions

In 2015, the annual mean air temperature in the area of this study was 8.7°C, and annual precipitation was 920 mm. This was slightly above the ten-year (2009-2018) average temperature of 8.3°C, and well above the ten-year average annual precipitation of 798 mm. During the spring monitoring period, the daily mean air temperature varied between 1 and 15°C, with an increasing trend over the period, and total rainfall was 220 mm. During the autumn monitoring period, the daily mean air temperature declined from 15 to 5°C, and total rainfall was 148 mm; the most intense daily rain events during spring and autumn were 16.9 and 33.2 mm, respectively.

Soil temperature at 5 cm depth showed a clear diurnal pattern (Figure S3), but at all four sites the temperature at the time of chamber deployment was close to the daily mean temperature at this depth. Thus, across the four sites the average deviation ranged from 0.2 to 0.9°C, and the largest deviations on a single day were -2.0 and 2.1°C, respectively.

3.2 Soil characteristics

Several soil characteristics were determined by analyses of intact cores collected in late April (DOY 113) 2015 (Table 1). At all sites the soil was acidic, with pH ranging from 4.7 to 5.4. At the paired sites AR1 and RG1, a weak decline in pH was indicated at 40-50 cm depth. Electrical conductivity at AR1 and RG1 sites ranged from 0.15 to 0.91 mS cm⁻¹, with no obvious trends in the data; the highest value (0.91 mS cm⁻¹) occurred at site AR1 at 93-98 cm in a layer dominated by sand underlying the peat.

The organic matter composition of soil profiles at the four sites varied. Total organic C concentrations at sites AR1 and RG1 were 34-43% in the upper 0-40 cm, but then dropped to only 0.3-0.6% at c. 1 m depth in the sand. The peat was amorphous and well-decomposed at 0-20 cm depth, while the underlying peat was dominated by contained intact plant debris. At site RG2, the process of peat degradation was evident even at 0-50 cm depth, where TOC concentrations only just met the requirements for being defined as an organic soil; the organic C content was below 20 and 10% at 0-25 and 25-50 cm depth, respectively. Site AR2 was characterised by a uniform peat layer (33-38% organic C) at 0-50 cm depth. Across all sites, the C:N ratios ranged between 14 and 26 in the organic soil layers.
Two iron sulfide fractions, as well as total reactive iron, were quantified. Acid volatile sulfide ranged from 1.7 to 4.9 μg S g⁻¹ soil across the four sites and showed no clear relationship with soil depth. This was also the case for CRS, which ranged from 24 to 155 μg S g⁻¹ dry weight soil. Total reactive Fe (TRFe) concentrations in soil profiles from sites AR1 and RG1 ranged from 1.19 to 4.99 mg g⁻¹ dry weight soil at 0-50 cm depth, and hence concentrations of reactive Fe were up to 1500 times higher than concentrations of Fe in AVS (assuming this was FeS), and 25-120 times higher than Fe in CRS (assuming this was FeS). At sites AR1 and RG1, TRFe declined below 20 cm depth and was close to zero in the sand below the peat layer (Table 1). The highest concentrations of TRFe at sites RG1 (Figure 2b) and AR1 (Figure 2d) occurred at 20 cm depth on 23 April, (DOY 113). At site AR1, a sink for TRFe at 40-60 cm depth was indicated. This was, disregarding Depth 6 (93-98 cm), the concentration of TRFe at Depth 5 (47.5-52.5 cm) was significantly lower than concentrations at more shallow depths (p < 0.05). Differences in TRFe concentration were only minor observed at site RG1, and any differences in the distribution of TRFe between seasons were probably also minor (not tested). There was a strong correlation between TRFe and TOC across all sites (r = 0.88, n = 16).

The total reduction capacity was determined by a wet oxidation procedure using Ce(SO₄)₂. At both AR1 and RG1, the total reductive capacity of the peat at 27-30 cm depth was outside the range of the analytical method at >11,500 meq kg⁻¹. The reduction capacity dropped to around 1000 meq kg⁻¹ at 60 to 65 cm depth with a declining organic matter content, and to ≤100 meq kg⁻¹ in the sandy layer at 100-109 cm depth.

### 3.3 Soil mineral N dynamics

Soil concentrations of NH₄⁺ and NO₃⁻ at 0-25 and 25-50 cm depth were determined in connection with field campaigns (Tables S1-S4). Since subsamples were pooled for analysis, only a qualitative description of the effects of treatments and temporal dynamics is possible. The residence time for mineral N in the soil solution was generally appeared to be longer at AR compared to RG sites. At AR sites, there was an accumulation of mineral N (Table S2, S4) at both depth intervals during May, that also occurred before N fertilisation. Mineral N concentrations were apparently greater at AR1 compared to AR2, and at site AR2 only NO₃⁻ accumulated. Fertilisation increased following fertilisation, NH₄⁺-N and NO₃⁻-N concentrations were 100-200 μg g⁻¹ dry weight soil at all sites except RG2 (Table S3), where acidified cattle slurry was applied. Accumulation of NO₃⁻-Nitrate accumulated at all sites in the weeks after fertilisation was observed at all sites, and also there was evidence for some transport to 25-50 cm depth.

Nitrite-N concentrations were determined in soil profiles from the cores sampled at sites RG1 and AR1 on 23 April (DOY 113) and 2 September (DOY 245) 2015. Both fertilised and unfertilised subplots were represented, although at site AR1 the RG1 fertilisation had not yet taken place at the time of sampling in April. There was variation at depth in the soil, which could not be explained by fertilisation, one week earlier, but a two-sample t test did not find evidence for an effect on NO₃⁻ availability (p = 0.19), and therefore the results from both AR1 and RG1 subplots are presented together. In April, the average concentration of NO₃⁻-N at both sites was highest (c. 10 μg g⁻¹ dry weight soil) around 40 cm depth and declined towards the surface and deeper layers (Figure 2a,c). However, due to heterogeneity of soil profiles, the differences between depths were not significant (p = 0.22 for RG1 and p = 0.06 for AR1). A decline in NO₃⁻
-N concentration was indicated at 50 cm depth at site AR1 relative to site RG1, and also, where a depletion of TRFe was indicated. However, there was also a lower concentration of particleless organic matter (cf. TOC in Table 1), which may account for this difference. In September, NO₂-N concentrations were <1 μg g⁻¹ dry weight soil at both sites, while the much higher concentrations of TRFe were comparable to those in April.

3.4 Groundwater table dynamics

Across the four sites, WT changes ranged from 60 to 100 cm. During spring, WT depth at sites RG1 and AR1 varied between 17 and 81 cm, with a steady decline until the end of April (DOY170), and by DOY 119 the WT depth was significantly (all p values < 0.05) below that of all previous samplings except DOY112 (Figures 3 and 4). Then followed by a period with fluctuations (frequent rainfall, where WT fluctuated (no significant changes) around 60-80 cm depth due to frequent rainfall (Figures 3 and 4)). During the first half of September (DOY24 - DOY259), rainfall caused the WT to rise from 80 to 40 cm depth (p < 0.05; Figures 5 and 6). On two occasions (DOY24 - DOY248 and 260) the WT depth rose to 20 cm depth and only gradually declined during the following days (data not shown). From mid-September (DOY258) the WT rose followed by a period with a gradual WT decline until early November (DOY308), whereupon the WT showed an increasing trend from 90 to 45 cm depth during a week with intense rainfall. At site RG2, (Figure 3) the WT initially declined (p < 0.05) and then remained mostly at 50-60 cm depth during spring, with a temporary rise to 30 cm depth from June (DOY129; see Figure 3) DOY139; p < 0.05. In the autumn, sampling campaigns could not be initiated until DOY260 due to harvest, were resumed on DOY 245. By this time, the WT was close to the surface following intense rainfall, but then declined (p < 0.05) to 80-100 cm in the sandy subsoil (Figure 5). The WT depth at site AR2 was consistently declined initially (p < 0.01) and then fluctuated between 45 and 60 cm depth during spring except for a transient increase (p = 0.05) to 35 cm depth in early June (Figure 4). During autumn, the WT rose (p = 0.05) to the soil surface in September (DOY260), and then gradually withdrew (p = 0.05) until early November (DOY307) when rainfall caused a 40 cm increase (Figure 6), as also observed at sites RG1 and AR1.

3.5 Soil N₂O concentration profiles

The distribution and temporal dynamics of N₂O in the soil profiles showed important contrasts between grassland and arable sites. Equivalent gas phase concentrations of N₂O in passive diffusion samplers were determined concurrently with gas sampling, and results are presented as contour plots (Figures 3-6; data in Table S5). Concentrations in many cases varied by several orders of magnitude between sites and sampling days, and between depths within individual profiles, and therefore a logarithmic grey scale was used to show internal gradients. The gaps in Figures 3-6 indicate periods, where diffusion probes could not be installed or were temporarily removed due to field operations.

Under the rotational grass at site RG1, soil N₂O concentrations during spring were mostly between 0.1 and 3 μL L⁻¹ (Figure 3). A higher concentration (15 μL L⁻¹) was observed at 40-80 cm depth in the fertilised subplot around DOY139-DOY139, but only at the lower position (Block 3) of the field plot. At site RG2, the concentrations of N₂O in the soil during spring were generally similar to those of RG1, although there were more values in the 1-10 μL L⁻¹ concentration range in the unfertilised plot (Figure 3, Table S5). However, on 3 June (DOY154-DOY154) a significant
increase in much higher N\textsubscript{2}O concentration occurred in the fertilised part of the plot with a maximum of 560 μL L\textsuperscript{-1} at 100 cm depth (i.e., well below the WT). Soil N\textsubscript{2}O concentrations in the unfertilised plot were also increased around this time, but only to a maximum of 15 μL L\textsuperscript{-1} and mainly near the soil surface.

The arable site AR1, with sampling positions located in a different field, but only 10-20 m from those of site RG1, showed apparently very different soil N\textsubscript{2}O concentration dynamics during spring (Figure 4). There was a consistent accumulation of N\textsubscript{2}O at 50 and 100 cm depth where seasonal concentrations averaged 340 and 424 μL L\textsuperscript{-1}, respectively. In contrast, at 5, 10 and 20 cm depth the average N\textsubscript{2}O concentrations were 10-30 μL L\textsuperscript{-1}, and there was no clear response to fertilisation on DOY 111-114 in terms of soil N\textsubscript{2}O accumulation. The soil N\textsubscript{2}O concentrations suggested that there was considerable within-site heterogeneity in soil conditions, as the highest concentrations were often observed in the unfertilised subplot. Between DOY 73 and DOY 100, the maximum concentrations of N\textsubscript{2}O peaked at nearly 1500 μL L\textsuperscript{-1} were recorded at 50 cm depth and were 2.1 fold higher than on DOY 99, and a similar concentration at 100 cm depth on DOY 112, both in the unfertilised subplot. At site AR2, the highest soil N\textsubscript{2}O concentrations during early spring were consistently observed at 20 cm depth, but there seemed to gradually decline to reach the background level of 0.3 μL L\textsuperscript{-1} in mid-May (around DOY 113). In the unfertilised field plot subplot, the N\textsubscript{2}O concentration decreased to reach 272 μL L\textsuperscript{-1} at 20 cm depth in early September and 272 μL L\textsuperscript{-1} following rainfall, and with WT increasing 35 cm depth. With fertilisation, soil N\textsubscript{2}O concentrations were even higher at 10 cm depth and reached nearly 400 μL L\textsuperscript{-1} in mid-June. The observed accumulation of N\textsubscript{2}O near the soil surface was accompanied by increasing N\textsubscript{2}O emissions during this period (Figure 4).

During autumn, N\textsubscript{2}O concentrations in the soil profile at the RG1 and RG2 sites varied between 0 and 12 μL L\textsuperscript{-1}, with a tendency for higher concentrations at 10-20 cm depth (Figure 5). At site RG1, where both fertilised and unfertilised subplots could be sampled, this was apparently independent of fertilisation.

September was characterised by heavy rainfall (114 mm in total), and at site AR1 a substantial rise in the WT from 80 to 40 cm depth was observed (Figure 6). Soil N\textsubscript{2}O concentrations showed a concurrent pattern, with maxima at 10 and 100 cm depth through to DOY 226/DOY 266 (end of September), and after this time soil N\textsubscript{2}O accumulation rapidly declined concurrently with WT and drawdown. Nitrous oxide concentrations equivalent to several hundred μL L\textsuperscript{-1} were measured even at 5 cm depth during this period. During late autumn, the N\textsubscript{2}O concentration at 0-50 cm depth varied between 0 and 20 μL L\textsuperscript{-1}, whereas at 100 cm depth it remained high at 100-850 μL L\textsuperscript{-1}. At site AR2, the groundwater level was higher than at AR1 and came close to the soil surface by mid-September (DOY 260). Soil N\textsubscript{2}O accumulated in both fertilised and unfertilised subplots following saturation of the soil, again with the highest concentrations apparently occurred at 20 cm depth. A secondary increase was observed near the soil surface at the last sampling on DOY 231/DOY 314 in November, in response to a period with rainfall and a rapid WT rise.

### 3.6 Nitrous oxide emissions

The weekly sampling campaigns during spring and autumn showed that with few exceptions N\textsubscript{2}O emissions, expressed as average daily rates, were significantly higher at AR1 compared to grassland sites independent of season and fertiliser N application. At site RG1, N\textsubscript{2}O emissions during (Table 2). One exception was
Interestingly, at Graphical models were used to study the dependence structure among selected soil variables and N\textsubscript{2}O fluxes. At site AR2, where a peak in N\textsubscript{2}O emissions occurred as indicated \((p = 0.06)\) on DOY 154-DOY 155, and the flux was still elevated at the next two samplings—(Figure 3). This high flux coincided with the accumulation of N\textsubscript{2}O in the soil profile described above, and it was the only time that an effect of fertilisation was observed. The grass in the fertilised subplot showed a clear visual response to fertilisation, which indicated that fertiliser N was effectively taken up by the sward.

At site AR1, the N\textsubscript{2}O fluxes were generally much higher than at grassland sites during spring (Figure 4). Fluxes during early spring reached 2000-6000 µg N\textsubscript{2}O m\textsuperscript{-2} h\textsuperscript{-1} and were higher than in late spring where, as for site RG1 (Figure 4). Since there was no effect of N fertilisation was observed. Hence, (cf. Table 2), the higher emissions were associated with differences, probably derived from soil N pools and caused by factors other than fertilisation.

The potato field at site AR2 showed a different pattern, with N\textsubscript{2}O fluxes remaining low during early spring, and for several weeks after fertilisation. The highest emissions occurred, independently of fertilisation, an increasing trend (not significant) was observed in June following a wet-rising wet WT, which was at 35 cm depth on DOY 154.

In the autumn, N\textsubscript{2}O fluxes from site RG1 were consistently low (Figure 5). The first sampling at site RG2 was on DOY 259-DOY 269 in mid-September, where a high flux of 3000 µg N\textsubscript{2}O m\textsuperscript{-2} h\textsuperscript{-1} was seen, which dropped to near zero within 1-2 weeks. Nitrous oxide emissions at site AR1 were high during September at 4000-10,000 µg N\textsubscript{2}O m\textsuperscript{-2} h\textsuperscript{-1} independent of across the two N fertilisation treatments (Table S2), and subsequently declined \((p < 0.05)\) to near zero (Figure 6). High fluxes were observed on the first sampling day of this monitoring period, DOY 246, while DOY 246, at a time where WT depth was still at 40 to 80 cm depth. However, this trend was not observed. Instead, the high N\textsubscript{2}O fluxes may have been triggered by saturation of the top soil after 10 and 22 mm rainfall on the previous two days. Rainfall. Additional rainfall during the following days then was accompanied by a rise in WT. The subsequent decline in N\textsubscript{2}O emissions at AR sites coincided with WT withdrawal and drainage of the top soil.

Cumulative N\textsubscript{2}O emissions were calculated for the 99-105 day monitoring period in spring, and for as well as the 47-69 d period in the autumn. Daily rates were surprisingly consistent in the two periods (Table 2a), and therefore the following refers to cumulative emissions across both periods. At RG sites, the average N\textsubscript{2}O flux from site RG1, the total emission was 4 kg N\textsubscript{2}O-N ha\textsuperscript{-1} independent of fertilisation, whereas at RG2 the fertilised grassland was significantly higher than from unfertilised grass (7.3 vs. 2 kg N\textsubscript{2}O-N ha\textsuperscript{-1} during spring, respectively. At AR sites with potato, there was no significant effect of N fertilisation, instead the cumulative N\textsubscript{2}O emissions at AR2 were 18-20 kg N\textsubscript{2}O-N ha\textsuperscript{-1} but much higher than from RG sites. In the autumn, the average cumulative emissions at the RG and AR sites were 7 and 15 kg N\textsubscript{2}O-N ha\textsuperscript{-1}, respectively, at site AR1.

3.7 Interrelationships between driving variables of N\textsubscript{2}O production

Graphical models were used to study the dependence structure among selected soil variables and N\textsubscript{2}O fluxes. Interestingly, at both RG sites, especially in both spring (Figure 7a) and autumn (Figure 7b), and at AR sites in spring (Figure 7c), there was a high degree of correlation between N\textsubscript{2}O fluxes and rainfall, which is consistent with theoretical considerations.
The only exception to this pattern was if disregarding the two variables NitrateT, a characteristic of the organic soil, and Temp5, which showed no direct link to any other variable (Figure 7c,d). The only relationship with respect to N\textsubscript{2}O flux that could not be explained by indirect correlations between the other variables was the variable NitrateT recorded in spring (Figure 7c,d). Where NitrateT separated N\textsubscript{2}O flux from the other variables in the graph, this indicates a separation principle (an instance of the general theory of graphical models, see section 2.5) according to the separation principle (an instance of the general theory of graphical models, see section 2.5) that information about the variable NitrateT rendered the other variables uninformative with respect to N\textsubscript{2}O flux. For example, in the analysis of AR sites (AR1 in spring (Figure 7c,d)), the variables N\textsubscript{2}O flux and Temp5 were not directly connected, and therefore any correlation between Temp5 and N\textsubscript{2}O flux could be completely explained by other variables.

4 Discussion

This study investigated seasonal dynamics of N\textsubscript{2}O emissions and soil conditions in an area, which has been designated as a hotspot for N\textsubscript{2}O emissions (Leppelt et al., 2014). Spring and autumn monitoring periods together covered between 152 and 174 d, and cumulative N\textsubscript{2}O emissions during these periods were in total 2.4 ± 0.5 kg N\textsubscript{2}O-N ha\textsuperscript{-1} for rotational grass and 11 ± 1.3 kg N\textsubscript{2}O-N ha\textsuperscript{-1} for arable sites with a potato crop. These numbers, representing 5-6 month periods, thus confirmed previous results (Petersen et al., 2012) that annual N\textsubscript{2}O emissions from organic soil in this area are comparable to (RG), or clearly above (AR), the IPCC emission factors for drained organic soil of 8 and 13 kg N\textsubscript{2}O-N ha\textsuperscript{-1} yr\textsuperscript{-1} for nutrient rich grassland and cropland, respectively (IPCC, 2014). The area has been characterised as potentially acid sulfate soil (Madsen and Jensen, 1988), and a previous study showed ground water sulfate concentrations in excess of 100 mg L\textsuperscript{-1} (Petersen et al., 2012). We therefore hypothesised that N\textsubscript{2}O emission coupled with FeS\textsubscript{2} oxidation could be a pathway of N\textsubscript{2}O formation in this acid organic soil.

Pyrite, measured as CRS, was quantified at selected depths (Table 1) and the soil bulk density of the peat was assumed between 0.15 and 0.3 g cm\textsuperscript{-3} (data not shown), and the total amount of CRS at 0 to 50 cm depth could therefore be estimated to 200-350 mmol FeS\textsubscript{2} m\textsuperscript{-3}. The N\textsubscript{2}O emissions observed during spring and autumn monitoring periods constituted up to 145 mmol N m\textsuperscript{-2} in total (site AR1), and it is thus theoretically possible that the process described by Eq. 2 contributed to emissions of N\textsubscript{2}O. However, the FeS\textsubscript{2} concentration (0.24 ± 2.4 mmol kg\textsuperscript{-1}) represented a minor part of the total reduction capacity (>11,500 meq kg\textsuperscript{-1} at 27-30 cm depth). Also, the concentration of total reactive Fe was 25-120 times higher than that of FeS\textsubscript{2} (though less in terms of reduction equivalents). Reducing agent is therefore likely that reducing agents other than FeS\textsubscript{2} were therefore likely
4.1 Environmental drivers of N$_2$O emissions

A limited number of potential drivers (rainfall, temperature, soil mineral N and soil concentrations of N$_2$O) were monitored to help explain N$_2$O emission dynamics. Soil N$_2$O concentration profiles showed complex patterns where, for example, the highest concentrations were sometimes observed above, and sometimes below the WT depth at both RG (Figure 3) and AR sites (Figure 4). Fertilisation in spring was associated with higher concentrations of N$_2$O below the WT depth at sites RG2 and AR2, which indicated downward transport of fertiliser N, but this was not reflected in elevated N$_2$O emissions. The reason may be that in wet soil the time required to reach a steady state between N$_2$O production and emissions from the soil surface can be significant and increases with distance (Jury et al., 1982). In accordance with this, Clough et al. (1999) observed a delay of 11 days before N$_2$O emissions were considered. Among the factors considered, the graphical models for individual site-crop combinations consistently identified N$_2$O concentration in the capillary fringe as the strongest predictor of N$_2$O emissions from both grassland and arable soils in spring (Figure 7a-d), and from grassland soils in autumn (Figure 8a-b). The implication is that N$_2$O concentrations at depth in the soil, and not in the top soil, were the main source of N$_2$O escaping to the atmosphere in these cases. In accordance with this, there was no immediate apparent effect of N fertilisation on emissions of N$_2$O independent of emissions at RG2 after the application of land acidified cattle slurry as a notable exception. Other studies also found a limited response to fertilisation (Maljanen et al., 2003; Regina et al., 2004), although Regina et al. (2004) later observed a peak in N$_2$O emissions after rainfall. Goldberg et al. (2010) reported that N$_2$O emissions from a minerotrophic fen were produced at 30-50 cm depth, in accordance with the observations presented here, where the highest concentrations of N$_2$O were mostly observed at 20 or 50 cm depth (Table S5).

Peat decomposing in the capillary fringe during WT drawdown could have been the source of N for N$_2$O production. It is well established that N$_2$O emissions from organic soil may be enhanced by drainage (Martikainen et al., 1993; Taft et al., 2017), and the response will appear within days, as shown by Aerts and Ludwig (1997) in an incubation study with an oscillating WT. A stimulation of N$_2$O emissions by WT drawdown was also observed by Goldberg et al. (2010) when simulating drought under field conditions, although a pulse of N$_2$O also occurred after rewetting in the study. In accordance with this, rising WT and/or increasing soil wetness in effect of rewetting, rain events during late spring and early autumn consistently enhanced N$_2$O emissions at all sites in the present study. This was not necessarily a result of WT changes. Despite 32 mm rainfall on DOY 244 and 245, the WT depth at site AR was still at 40 to 80 cm, and could not account for the very high DOY 246 (Figure 6), but N$_2$O emissions observed on DOY 246 (Figure 6) were high. Well-degraded peat will release as little as 10% of its water to drainage
(Rezanezhad et al., 2016, p. 4), and it is therefore likely that the rainwater was absorbed by peat above the WT and created conditions suitable for denitrification, close to the soil surface, which explains the significant correlation between N₂O emissions and NO⁻ (Figure 8c).

The increase in N₂O emissions during WT cycles reported by Aerts and Ludwig (1997) was observed only with eutrophic peat, whereas a mesotrophic peat showed no effect of WT dynamics on N₂O emissions, which were consistently low. A similar interaction between nutrient status and WT depth was observed in field studies comparing N₂O emissions from minerotrophic and ombrotrophic boreal peatlands (Martikainen et al., 1993; Regina et al., 1996). In the present study, soil NH₄⁺-N and NO₃⁻-N concentrations at site RG1 increased to 133 and 120 µg g⁻¹ dry weight soil upon fertilisation, respectively, but largely returned to the background level of around 5 and 10 µg g⁻¹ dry weight soil, respectively, within a week (Table S1). In contrast, at site AR1 there was significant substantial accumulation of NH₄⁺-N and NO₃⁻-N even before fertilisation on DOY 141, and soil mineral N remained high for several weeks (Table S2). This accumulation of soil mineral N around the time of potato crop establishment could have stimulated N₂O emissions in the arable soil. Grasslands on organic soil generally show lower emissions of N₂O compared to arable organic soil (Eickenscheidt et al., 2015), presumably because plants compete successfully with microorganisms for available N. Schothorst (1977) estimated peat decomposition indirectly from the N-content in herbage yield of grassland and concluded that the soil supplied 96 kg N ha⁻¹ when the drainage depth was 25 cm, but 160 and 224 kg N ha⁻¹ with the drainage depth at 70 and 80 cm, respectively. Hence, plant uptake of N mineralised from soil organic matter above the WT likely contributed to the much lower N₂O emissions from rotational grass in this study.

Nitrous oxide concentration profiles provided indirect information about soil mineral N dynamics. At RG sites, soil N₂O concentrations during spring were generally low and thus did not provide clear evidence for microbial N transformations, which supports the conclusion above that plant uptake was a main sink for the N released during peat decomposition. At site RG2, one exception was the accumulation of N₂O around 10 cm depth observed in late May (Figure 3), which could have been caused by leaching of mineral N from the acidified cattle slurry following extensive rain. In contrast, at AR sites there was significant accumulation of N₂O accumulated in the soil throughout spring irrespective of fertilisation, at site AR1 the highest concentrations occurred at 50 cm depth, while at site AR2 with a higher groundwater table the highest concentrations were at 20 cm depth, in accordance with the higher groundwater table. These observations indicated that N₂O gas produced in the capillary fringe consistent with peat decomposition was a source of mineral N, and a likely source of N₂O above, and possibly also below the saturated zone (see next section). Following N fertilisation, the accumulation of N₂O in the soil profile was mostly associated with precipitation and rising WT.

In the autumn, the graphical models identified NO₃⁻ in the top soil (site AR1 only) and soil temperature at 30 cm depth as significant predictors of N₂O emissions at arable sites (Figure 7). The accumulation of NO₃⁻ was much greater at site AR1 compared to AR2, suggesting differences in N mineralisation potential, possibly because AR1 had better drainage of the top soil (e.g., WT at 80 vs. 40 cm depth on DOY 246; Figure 6). It is not clear if the source of N was decomposing potato crop residues or accelerated peat decomposition following soil disturbance at harvest, or both. Rainfall most likely triggered denitrification by rapidly increasing WT depth and soil water-filled pore space and raising WT depth, thereby impeding the supply of N₂O to much of the soil profile (Barton et al., 2008). This
interpretation is supported by increasing N2O concentrations below, as well as above the WT depth depending on site and block, and in fertilised as well as unfertilised subplots (Figure 6). In an annual study, conducted in other parts of the Store Vildmose bog, Kandel et al. (2018) also measured high emissions of N2O from a potato crop, i.e., around 2000 µg N2O m⁻² h⁻¹ in October 2014 and 6000 µg N2O m⁻² h⁻¹ in June 2015, which coincided with NO3⁻ accumulation and rainfall. Precipitation was also high during September 2015, and the rapid rise in WT towards the soil surface resulted in a marked decline in NO3⁻. Nitrite was accompanied by accumulation of N2O in the top soil at all sites. However, N2O concentrations reached only around 10 µL L⁻¹ at RG sites, as opposed to several hundred µL L⁻¹ at AR sites, confirming that soil mineral N availability was a limiting factor for N2O emissions.

4.2 Pathways of N2O emissions

Bacterial nitrification, denitrification, and nitrifier-denitrification are all potential-potentially significant pathways of N2O formation (Braker and Conrad, 2011). The significant relationship correlation with NO3⁻ in the top soil at AR sites (site AR1 in the autumn (Figure 2c)) suggested that denitrification activity in the top soil controlled N2O emissions during this period. This was different in early spring, where mostly soil mineral N concentrations were low, and N2O accumulated near the WT depth. Here, ammonia oxidation activity may therefore have controlled limited N2O emissions either directly, or indirectly via production of NO2⁻ or NO3⁻. Ammonia oxidising bacteria (AOB) are scarce in acid peat despite the presence of nitrite oxidising bacteria (NOB) (Regina et al., 1996), and some studies indicate that ammonia oxidising archaea (AOA) predominate in both abundance and activity (Herrmann et al., 2012; Stopnišek et al., 2010). Stieglmeier et al. (2014) isolated an AOA from soil emitted N2O at a rate corresponding to 0.09% of the NO3⁻ produced independent of O2 availability, but it is not known if this organism is present in acid organic soil, and at this time an indirect control of denitrification activity seems more plausible.

Stopnišek et al. (2010) found that AOA activity was not stimulated by an external source of NH₄⁺ and concluded that the activity was associated with N released from decomposing soil organic matter. Well-decomposed peat is dominated by dead-end pores associated with plant cell remains, which are characterised by a slow exchange of solutes with active pore volumes (Hoag and Price, 1997), hence ammonia oxidation in confined spaces could be important in organic soil. The anaerobic conditions of saturated peat may have been a limiting factor for limited N mineralisation and a consequence ammonia oxidation activity during early spring, a constraint which was alleviated as the WT declined and oxygen entered deeper soil layers. Nitrite had accumulated at 70-50 cm depth in late April at both RG1 and AR1 sites (Figure 2), which was consistent with peat decomposition and ammonia oxidation following WT drawdown. Total concentrations of NH₄⁺ and NO3⁻ at 25-50 cm depth were significant (Tables S1 and S2), but well-decomposed peat is dominated by dead-end pores (Hoag and Price, 1997), and it is likely that ammonia oxidation to a large extent took place in such pores having a slow exchange of solutes with active pore volumes. The accumulation of NO3⁻ suggested there was an imbalance between ammonia oxidation and nitrite oxidation activity, O2 entered deeper soil layers. Estop-Aragonés et al. (2012) found that oxic-anoxic interfaces in peat soil were located above the WT depth, and hence the capillary fringe in this study may have been still partly anoxic, which can explain the correlation between N2O emissions and N2O emissions in graphical models. In late April (DOY 113), NO2⁻ had accumulated at 20-50 cm depth at both RG1 and AR1 sites (Figure 2), suggesting that there was an imbalance between ammonia oxidation and nitrite oxidation activity. Oxygen affinity differs between nitrifiers, with AOA>AOB>NOB (Yin et al., 2018), and
...have caused the accumulation of NO$_2^-$. In acid soil, this would result in product inhibition by HNO$_3$ if there were no mechanism to remove NO$_2^-$. This would be especially true for AR sites, where mineral N accumulation was three to four times higher compared to RG sites (Tables S3-S6). Nitrifier-denitrification is a mechanism by which ammonia oxidisers can avoid HNO$_3$ accumulation, and this process leads to N$_2$O formation (Braker and Conrad, 2011). Another potential sink for NO$_2^-$ is chemodenitrification, an abiotic reaction in which NO$_2^-$ reacts with Fe$^{3+}$ to produce N$_2$O (Jones et al., 2015):

$$4\text{Fe}^{2+} + 2\text{NO}_2^- + 5\text{H}_2\text{O} \rightarrow 4\text{FeOOH} + \text{N}_2\text{O} + 6\text{H}^+ \quad (\text{24})$$

where in Eq. 24 Fe(OH)$_3$ is shown as anhydrous FeOOH. A possible depletion of TRFe was indicated at 50 cm depth at site AR1, which coincided with a similar depletion pattern for NO$_2^-$ (Figure 2). Nitrifier-denitrification and chemodenitrification are both sinks for NO$_2^-$, and therefore both pathways are potential sources of the N$_2$O emissions observed during early spring.

The observation at AR sites there was often considerable accumulation of N$_2$O below the WT, which suggests there was also an anaerobic pathway of N$_2$O formation. The fact that TRFe concentrations were much higher than those of AVS or CRS (Table 1) makes it relevant to consider alternative reactions involving iron oxides/hydroxides, which have a potential to produce N$_2$O. One such recently described pathway is Feammox, a process whereby ammonia oxidation coupled with ferric iron reduction can produce NO$_2^-$ below pH 6.5 (Yang et al., 2012):

$$6\text{Fe(OH)}_3 + 10\text{H}^+ + \text{NH}_4^+ \rightarrow 6\text{Fe}^{2+} + 16\text{H}_2\text{O} + \text{N}_2\text{O}_2^- \quad (\text{45})$$

Nitrate can also be produced under these conditions (Yang et al., 2012; Guan et al., 2018):

$$8\text{Fe(OH)}_3 + 14\text{H}^+ + \text{NH}_4^+ \rightarrow 8\text{Fe}^{2+} + 21\text{H}_2\text{O} + \text{N}_2\text{O}_2^- \quad (\text{56})$$

A shuttle of Fe$^{3+}$ between Feammox and chemodenitrification (Eq. 25 and Eq. 4) could explain the accumulation of N$_2$O under anoxic conditions in the saturated zone, presumably with the availability of NH$^+_4$ from peat mineralisation and denitrification (Eq. 5) as a limiting factor. The confirmation of pathways will require more detailed investigations that should include molecular analyses targeting microbial communities in the soil profile.

5 Conclusion

Nitrous oxide In this one-year study, N$_2$O emissions were consistently higher from arable sites compared to rotational grass. This was independent of fertilisation. There were strong seasonal dynamics in N$_2$O emissions, and instead N$_2$O emissions could be associated with soil N mineralisation, rainfall patterns and temperature. We hypothesised we present evidence that different pathways were involved. Concentrations of pyrite were low compared to the total reduction capacity of the peat, and Fe was predominantly in forms other than pyrite. While the hypothesis that N$_2$O was produced by NO$_2^-$ reduction coupled with Fe$^{2+}$ oxidation, could not be dismissed, it is likely that other processes were more important. There were strong seasonal dynamics in N$_2$O source of N$_2$O could therefore not be confirmed. Nitrous oxide emissions and evidence that different pathways were involved. We propose...
that oxidation of N mineralised from decomposing peat after WT drawdown in spring were independent of fertilisation, since there was mostly no effect of mineral N in the top soil. The significant effect of N\textsubscript{2}O concentration in the capillary fringe indicated that emissions during spring, and for grassland during the autumn, were associated with soil N mineralisation in this environment, as modified by rainfall patterns and WT dynamics. We propose that chemodenitrification (or nitrifier-denitrification) of NO\textsubscript{2} produced in the capillary fringe is a main source of N\textsubscript{2}O in acid organic soil during spring, whereas in the autumn, where NO\textsubscript{3} accumulated in arable soil after harvest, N\textsubscript{2}O emissions were associated with rising WT and heterotrophic denitrification as this can be a main pathway, in arable soil as a result of NO\textsubscript{3} accumulation. Mitigating N\textsubscript{2}O emissions from acid organic soil is challenged by the complexity of underlying processes. However, reducing mineral N accumulation by ensuring a vegetation cover outside the main cropping season, and stabilising the WT depth by effective drainage, are potential mitigation strategies.

Author contributions. ATT, LEL, TJ and SOP designed the study. ATT, LEL, VE and SOP carried out sampling and analyses. ATT, RL and SOP were responsible for data analyses. ATT and SOP prepared the manuscript with contributions from all co-authors.

Acknowledgements. This study received financial support from the Danish Research Council for the project “Sources of N\textsubscript{2}O in arable organic soil as revealed by N\textsubscript{2}O isotopomers” (DFF – 4005-00448). We would like to thank the dedicated staff involved in field campaigns, including Bodil Stensgaard, Søren Erik Nissen, Sandhya Karki, Karin Dyrberg, Holger Bak and Stig T. Rasmussen. We would also like to acknowledge the support of three farmers hosting the field sites: Poul-Erik Birkbak, Rasmus Christensen and Jørn Christiansen.

References


Table 1. Selected characteristics of soil profiles at the four monitoring sites with rotational grass (RG1, RG2) and potato crop (AR1, AR2). All analyses were done in triplicate; results shown represent mean and standard error of two soil profiles for which a complete data set was available. Soils for analyses were collected in late April (DOY 113) except for AVS and CRS (early September). Abbreviations: EC, electrical conductivity; TOC, soil organic carbon; TRFe, total reactive iron; AVS, acid volatile sulfide; CRS, chromium reducible sulfur.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>pH</th>
<th>EC (g 100 g⁻¹)</th>
<th>TOC (g 100 g⁻¹)</th>
<th>Total N</th>
<th>C:N ratio</th>
<th>TRFe (mg Fe g⁻¹)</th>
<th>AVS (μg S g⁻¹)</th>
<th>CRS (μg S g⁻¹)</th>
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<tr>
<td><strong>RG1</strong></td>
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</tr>
<tr>
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<td>5.1</td>
<td>0.26 (0.10)</td>
<td>37.4 (0.2)</td>
<td>1.75 (0.00)</td>
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<td>2.51 (0.86)</td>
<td>155 (62)</td>
</tr>
<tr>
<td>Depth 2</td>
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<tr>
<td>7.5-12.5</td>
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<td>21.3</td>
<td>4.03 (0.44)</td>
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<td></td>
</tr>
<tr>
<td>17.5-22.5</td>
<td>5.3</td>
<td>0.37 (0.18)</td>
<td>39.7 (0.3)</td>
<td>1.80 (0.04)</td>
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<td>4.14 (0.32)</td>
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<td>Depth 4</td>
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<td>43.1 (2.7)</td>
<td>1.85 (0.03)</td>
<td>23.3</td>
<td>3.04 (0.26)</td>
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</tr>
<tr>
<td>Depth 5</td>
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<td>1.47 (0.64)</td>
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<td>2.50 (0.55)</td>
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</tr>
<tr>
<td>0-25</td>
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<td>1.71 (0.00)</td>
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</tr>
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</tr>
<tr>
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<td>3.78 (0.14)</td>
<td>1.65 (0.02)</td>
<td>45 (8)</td>
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ND – Not determined due to TOC and total N concentrations being at the limit of detection.
NA - Not analysed.

Taghizadeh-Toosi et al. (2019) presented slightly different AVS and CRS results for AR1 representing all the six profiles collected at this site.
Table 2. Cumulative Daily emissions of N₂O (\(\text{N}_2\text{O} \text{ ha}^{-1} \text{ d}^{-1}\)) during the monitoring periods in spring (99–105 days) and autumn (47–69 days) monitoring period.

Estimation for each season was performed using the trapezoidal approximation of the integral of the emission curve. Numbers in parentheses indicate 95% confidence intervals, and significant differences, (at 5% significance level), corrected for multiple testing by the single-step method, are indicated by asterisks. RG, rotational grass; AR, arable crop (potato); F, fertilised; NF, unfertilised.

<table>
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<td>DOY</td>
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<td>Cumulative</td>
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<tr>
<td></td>
<td>63-</td>
<td>N₂O-N ha⁻¹ d⁻¹</td>
<td>20-25</td>
</tr>
<tr>
<td></td>
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<td>AR1</td>
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<tr>
<td>DOY</td>
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<td>20-25</td>
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<td>167</td>
<td>a</td>
<td>a</td>
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<tr>
<td>AR2</td>
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<tr>
<td>DOY</td>
<td>63-</td>
<td>1622-2122</td>
<td>251-313</td>
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<td></td>
<td>167</td>
<td>a</td>
<td>a</td>
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</table>

*The monitoring periods (spring and autumn) were: DOY63-162 and DOY252-314 (RG1); DOY64-169 and DOY260-307 (RG2); DOY63-162 and DOY246-308 (AR1); DOY64-169 and DOY245-314 (AR2).† F, fertilised; NF, not fertilised.
Figure captions

Figure 1. A. Location of sites AR1 and RG1 (both at 57°13’59.7"N, 9°50’40.3E), RG2 (57°13’55.9”N, 9°52’20.2E) and AR2 (57°13’7.6”N, 9°46’26.9E). B. Experimental design at each of the four sites, with three blocks centered around piezometers (●) and two subplots, one of which received N fertiliser at the rate of the surrounding field. Six collars for gas flux measurements ($S$1-S6) were distributed as indicated, and sets of 5 diffusion probes for soil gas sampling were installed near collars in selected positions (see text).

Figure 2. Nitrite-N (a, c) and total reactive iron, TRFe (b, d), in undisturbed soil cores were collected at sites RG1 and AR1 on 23 April (DOY113; white symbols) and 2 September (DOY245; grey symbols). Results shown are mean and standard error ($n = 2$). At site RG1 fertilisation had taken place one week earlier, but a two-sample $t$ test did not find evidence for any effect on NO$_x$ availability ($p = 0.19$). The dotted lines indicate WT level on the two sampling dates.

Figure 3. The top panel shows rainfall, air temperature and management (F – fertilisation) at sites RG1 (left panels) and RG2 (right panels) during spring, 3 March (DOY63) to 16 June (DOY169). The middle section shows N$_2$O fluxes (black circles; mean ± standard error, $n = 3$) and contour plots of soil N$_2$O concentrations in fertilised subplots, and the lower section the corresponding results for unfertilised subplots. A logarithmic grey scale was used in order to show trends within both RG and AR treatments, and between depths. Soil gas sampling positions are indicated in the contour plots; numbers shown are N$_2$O concentrations ($\mu$L L$^{-1}$). Green lines show the WT depth (which varied slightly between blocks). B2 and B3 refer to block number of diffusion probe positions.

Figure 4. The top panel shows rainfall, air temperature and management (T – tillage; F – fertilisation) at sites AR1 (left panels) and AR2 (right panels) during spring, 3 March (DOY63) to 16 June (DOY169). The middle section shows N$_2$O fluxes (black circles; mean ± standard error, $n = 3$) and contour plots of soil N$_2$O concentrations in fertilised subplots, and the lower section the corresponding results for unfertilised subplots. A logarithmic grey scale was used in order to show trends within both RG and AR treatments, and between depths. Soil gas sampling positions are indicated in the contour plots; numbers shown are N$_2$O concentrations ($\mu$L L$^{-1}$). Gaps are indicated where soil gas sampling probes were installed late, or removed due to field operations. Green lines show the WT depth (which varied slightly between blocks). B2 and B3 refer to block number of diffusion probe positions.

Figure 5. The top panel shows rainfall, air temperature and management (H - harvest) at sites RG1 (left panels) and RG2 (right panels) during autumn, 3 September (DOY245) to 10 November (DOY314). The middle section shows N$_2$O fluxes (black circles; mean ± standard error, $n = 3$) and contour plots of soil N$_2$O concentrations in fertilised subplots, and the lower section the corresponding results for unfertilised subplots. A logarithmic grey scale was used in order to show trends within both RG and AR treatments, and between depths. Soil gas sampling positions are indicated in the contour plots; numbers shown are N$_2$O concentrations ($\mu$L L$^{-1}$); the probes were absent in the unfertilised subplot after harvest. Green lines show the WT depth (which varied slightly between blocks). B2 and B3 refer to block number of diffusion probe positions.
Figure 6. The top panel shows rainfall, air temperature and management (H - harvest) at sites AR1 (left panels) and AR2 (right panels) during autumn, 3 September (DOY 245) to 10 November (DOY 314). The middle section shows N$_2$O fluxes (black circles; mean ± standard error, n = 3) and contour plots of soil N$_2$O concentrations in fertilised subplots, and the lower section the corresponding results for unfertilised subplots. A logarithmic grey scale was used in order to show trends within both RG and AR treatments, and between depths. Soil gas sampling positions are indicated in the contour plots; numbers shown are N$_2$O concentrations (µL L$^{-1}$). Green lines show the WT depth (which varied slightly between blocks). B2 and B3 refer to block number of diffusion probe positions.

Figure 7. Using Results of a graphical model, a statistical analysis was conducted for each site crop combination of crop (RG, AR) and season (spring, autumn). a. RG, spring; b. RG, autumn; c. AR, spring; and d. AR, autumn. A. RG1-Spring; B. RG2-Spring; C. AR1-Spring; and D. AR2-Spring. The edges (“lines”) connecting vertices (“points”) indicate significant relationships conditional correlation between explanatory variables and the response variable (N$_2$O flux). Statistical results for direct effects on N$_2$O flux are: [1] 2.32 (0.12 - 9.11), p = 0.01367; [2] 0.2413 (0.06 - 3.05), p = 0.0344; [3] 0.78 (0.41 - 2.47), p = 0.0007; [4] 1.84 (0.78 - 9.00), p = 0.008; and [5] 2.15 (1.40 - 9.99), p = 0.002. Key to variables: AmmoniumT: NH$_4^+$ at 0 - 25 cm depth; NitrateT: NO$_3^-$ at 0 - 25 cm depth; N$_2$O WT: equivalent soil gas phase concentration closest to, but above the water table depth; Temp5: soil temperature at 5 cm depth; Temp30: soil temperature at 30 cm depth.

Figure 8. Results of a graphical model for each site crop combination in the autumn. A. RG1-Autumn; B. RG2-Autumn; C. AR1-Autumn; and D. AR2-Autumn. The edges (“lines”) connecting vertices (“points”) indicate significant conditional correlation between the variables given the other variables. Statistical results for effects on N$_2$O flux are: [1] 0.27 (0.19 - 0.38), p = 0.002; [2] 0.16 (0.007 - 0.28), p = 0.049; [3] 0.19 (0.09 - 0.28, p = 0.021); [4] 0.15 (0.06 - 0.21, p = 0.032); and [5] 0.29 (0.17 - 0.35, p = 0.005). Key to variables: AmmoniumT: NH$_4^+$ at 0 - 25 cm depth; NitrateT: NO$_3^-$ at 0 - 25 cm depth; N$_2$O WT: equivalent soil gas phase concentration closest to, but above the water table depth; Temp5: soil temperature at 5 cm depth; Temp30: soil temperature at 30 cm depth.
Figure 1
Figure 2.
Figure 32.
Figure 3
Figure 4

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AR2: 71 d varedi mangler (21 cm)
Figure 5
Figure 6
Figure 7

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Figure 8