Dear Editor,

We particularly thank the reviewer and the editor for the attention paid to the quality of language and took care to correct the mistakes highlighted. The answers to the several questions raised by the reviewer are detailed below. In complement to these points, the manuscript has also been corrected for the "supplementary fig. and table" that now read Fig. SX and Table SX.

We believe this study is of great concern of the community. With the help of the Editorial team and the Reviewers, the community would benefit more from this study.

Sincerely,

Laura Sereni, on the behalf of all the co-authors.

RC1

Does the paper address relevant scientific questions within the scope of BG?
R1 Yes, the topic is highly relevant to BG, encompassing physical, chemical, and biological processes as they impact nitrogen transformations in soil and subsequent emissions.
Does the paper present novel concepts, ideas, tools, or data?
R1 Yes, to my knowledge, the combined focus on impacts of copper on nitrogen transformations and integration of those impacts into an existing biogeochemical model is novel.
Response: Thank you.

Are substantial conclusions reached?
R1 Unsure. I am not entirely clear on what the authors' conclusions are, so I would request clarification of the conclusion section.
Response:In accordance with this remark, we focused the conclusions the main points raised in this study, that are the ability of the DNDC-Cu version we proposed to reproduced soils nitrates stocks for contaminated samples and the different descreased in N-species emissions for Cu concentration increase depending on the previous moisture.

Are the scientific methods and assumptions valid and clearly outlined?
R1 The overall approach is valid. It is difficult to integrate experimental and modeling work, and this work does that well.
My most serious concern with the approach is that the bioassays investigating the effect of copper on nitrification were only conducted on soil that was not previously contaminated with copper. As microbial communities are quite adaptive, one could reasonably expect that there would be different results if the experiments were conducted on soil with a history of copper contamination. Indeed, there may already be studies on that topic; if so they would be relevant to incorporate. The question then becomes which situation is most relevant globally – short-term effects upon introduction of copper (such as the 3 days of exposure tested here), or longer-term consequences of contamination. Given the authors' focus on improving predictive capability of continental models under climate change, I'd expect longer-term effects would be more relevant.
It would also be helpful to provide more justification for the selected soil type and the copper concentrations used here. Consideration of bioavailable copper would also seem appropriate and might allow for conclusions that are more generalizable to other soils.

Response:> Indeed, you're right, and we agree that there would be different results if the experiments were conducted on soil with a history of copper contamination. The importance of progressive vs. abrupt contamination in ecotoxicological effect is actually debated. Indeed, some authors found that thresholds values for field contaminated soils are around 3 times largest than for spiked soils (Smolders et al., 2008) while others found no effect of aged contamination on bacterial structure, bacterial respiration or nitrification (Oorts et al., 2006; Brandt et al., 2010). These references and discussion upon history contamination have been added lines

83-86 to better justify our experimental setup (“It is not straightforward to assess that abrupt contamination can lead to distinct effects on microbial structure of functions than progressive contamination”).We actually focused on this scenario as an example on double (climatic and contamination) stress. Also, we hypothesized that first moisture stress will differentially select microbial communities implicated in the nitrification/denitrification processes thus underlying the combined effects of these two stresses on soil functions. Furthermore, this kind of model might be used to assess the short term effect of pesticides or fertilizer application and in this case there is no Cu ageing.

In our study we choose to follow the effect of two successive stresses of moisture and contamination on nitrification potential. In this context, we needed some control not contaminated with copper. However, finding experimental sites where the only changing factor is copper contamination is very difficult. Moreover, copper contamination in the field is almost always associated to other contaminations. To avoid these discrepancies, we decided to contaminate ourselves the soil by spiking a non-contaminated soil. This is a classical method to study copper contamination effects (Oorts et al., 2006; van Gestel, 2012).

Considering your remark about bioavailable copper, You are right, and Cu contents in solution were actually measured. But when writing the manuscript we found that these values did not help us for additional arguments. However you are right, it is legitimate to ask the question of the balance of copper in solution. Thus, according to your remark, we added a supplementary Table with these values that is now introduced lines 147-148. Also, survey that might be used for modelling are much often provided in term of total Cu rather than of Cu in solution.

Are the results sufficient to support the interpretations and conclusions?

(See comment on conclusions above)

R1: The experimental results seem not to be considered as leading to any conclusions. For the sentences in the conclusion about N2O, and the last sentence of the abstract, I do not find sufficient support in this paper. N2O was not measured here, and DNDC has difficulty predicting the proportion of N2O from denitrification (e.g. https://doi.org/10.1016/j.scitotenv.2018.07.364), so it seems quite speculative to make these conclusions based only on results from a model that was only calibrated and validated with respect to nitrate. I have similar concerns about conclusions about the abundance of denitrifying bacteria, particularly since they are typically facultative and thus may not directly correspond to the concentration of nitrate. Modeling is not my core expertise, as is probably evident from my comments. However, to conclude that a new model performs better, I would typically want to see it compared to calibrated versions of existing models.

Response: Thanks for your remark. We acknowledge that the measurement of NO_3 only is a limitation of our study, this is why we noticed at the previous lines 410-412 that this study did not allows us to determine if the double stress rather affect nitrification or denitrification (“However, the experiments performed here did not allow us to determine if the soil Cu contamination rather affects nitrifying bacteria (e.g. decrease in nitrifying activity and in NO_3-N production) or denitrifying bacteria (e.g. increase in denitrifying activities and NO_3-N consumption)”).Following your remark, we now underlined this difficulty in DNDC to reproduce N_2O emissions in lines 414-417 that now reads: ‘”Also, our modeling approach of N_2O-N, N_2-N and NOx-N production in the contaminated context could have been more constrained with measurement of denitrification rate to assess the effect of Cu on proportion of production and consumption of N-NO_3.. Also, the 4.3 paragraph (previously 4.2) deals with the difficulty in upscaling for modelisation of bio-physical processes. However, the calibration of the model for an absolute estimation of N_2O/NOX was not the purpose of our work as we aimed at estimating the relative effect of the double stress on N_2O/NOX emissions. Indeed, all the Figures showed emissions rates in function of Cu concentration. Nevertheless, to underline these aspects, we decided to include in the new version of the manuscript, the Supplementary Fig. 1 (now introduced lines 313-314) showing the difference between modeled and measured N-NO_3 concentrations for the initial DNDC version and for our DNDC-Cu version, for each Cu concentrations.

Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?

R1: I have several questions about how the experiments were conducted. No replication is mentioned in 2.2, but data from replicates is given in Table 1. In addition to having these be consistent, I'm wondering if the samples were from replicate microcosms or from replicate samples taken from the same microcosm. How was sampling conducted? In particular, were microcosm soils mixed before sampling for measurements and bioassays? I'm not clear about how the drying was done, or how long it took for microcosms to reach the drought/dry state. What temperature was used for the microcosm incubation? How long was the microcosm incubation? Section 2.2 says 45 days, but other places refer to one month and five weeks. This also relates to another question – were the drought and dry-rewetting treatments at a dry or wet state for their final week of incubation before the bioassays? When was NH4+ added to the bioassays, and at what concentration? I'm not clear on how much liquid was in the bioassays, not sure how to interpret soil solution 1:12. Does this mean that the approximately 5 g of soil was mixed with 60 mL of liquid? Did you account for the moisture differences, or simply take 5 g wet weight from the relevant microcosm? Line 124 and 130 contradict. Line 285 gives yet a third description. On the modeling side, I have an even greater level of confusion. In the abstract it states that DNDC was used, with modifications to account for soil copper effects. Yet in the methods it states both DNDC and a model by Zaehle and Friend … which are two different models … and later it states that the model was written in R, which suggests that DNDC was not used at all. Given this fundamental confusion, I have not done a detailed review of section 2.3. It would be helpful to have more clarity on which equations are taken directly from previous models and which have been modified in this work.

Response Thank for notice some imprecision on the experiment's description. The initial incubation procedure is describe in the first paragraph in 2.2 (now l.110 to 1209) while the second now (l. 121 to 145) describes the bio-assay. In line 121 we now mention that the bio-assay was made in triplicate, using 3 replicates taken from one microcosm per initial incubation treatment. For clarity, the number of dry and wet periods have been clarified l.116, so that on the 5 weeks initial incubation period the DR treatment ended by a near-saturation period. Also, we added more information about the amount of water used for bioassay, the soil solution ratio and the sub-sampling of microcosms with different initial incubation (now l. 123-127). The 5g mentioned refers to the fresh weight at the moment of sampling while for the bio-assay we took only 3.5 g (corresponding to 3g in a dry-weight basis) of each moisture treatment then added water. This is also added in the new version of the manuscript at line 124-125.Considering the NH_4^+ for the bioassays it was added at the beginning of the bioassay in a large excess (3mM). This precision has been added l. 127.

Considering the model, we used a simplified version of the DNDC of Changsheng Li et al. (1992) that have been adapted by Zaehle & Friend (2010b). This simplified version was written in fortran and to facilitate the manipulation, we rewrote it in R. Also, equations came directly from the DNDC model with a modification of the k value and the Cu effects equations (Eqs.13, 28-31) have been added. We hope that now l.225 is clearer with the specification introduced ("We wrote the model adapted from Zaehle & Friend, (2010) in R…").

Do the authors give proper credit to related work and clearly indicate their own new/original contribution?

There is a wide body of literature on the effects of copper on soil microbial communities, which is not really incorporated here. Also many studies looking at the effect of moisture on N cycling in soil. These omissions make it difficult to make a clear argument for the novel contribution here.

Response! Done. We added 8 references ((Butterbach-Bahl et al., 2013; Galloway et al., 2008, Baath et al. 1989, Schimel, 2018; Stark and Firestone, 1995, Borken and Matzner, 2009; Fierer et al., 2003; Guo et al., 2014) ,2 being review articles to better assess the effects of copper on the soil microbial communities, and of moisture on the N cycling respectively at l.45, 46, 50,56. Also, considering your previous remark on Cu ageing, we added references at lines 82-84 that provide controversial results about the importance of Cu ageing in ecotoxicological studies and that reads ("It is not straightforward to assess that abrupt contamination leads to distinct effects on bacterial structure of functions than progressive contamination (Brandt et al., 2010; Oorts et al., 2006; Smolders et al., 2009).")

Does the title clearly reflect the contents of the paper?

R1: In my opinion, the title is not representative of the paper, promising much more than is delivered. It examines copper, not a wide range of soil contaminants. Similarly, the focus is on N2O, not the full array of greenhouse gases. There may be similar issues with the modeling description, but that is harder to evaluate given my confusion with the methods.

Response: Done. Considering that the title might indeed be too promising we proposed a new title: "To what extend can soil moisture and soil Cu contamination stresses affect nitrous species emissions? An attempt of estimation through calibration a nitrification/denitrification model" to better highlight the focus on Cu contamination and on N GHG emissions.

Does the abstract provide a concise and complete summary?

R1: The abstract is well-organized and covers the expected content. Clarity could be improved, in particular around where the double stress came into the experiments. (see also language comments below)

Response: Done. Also, considering your following remarks, we rephrased both the abstract and the material and methods parts in some points to better clarify what correspond to the initial incubation and what was the bio-assay. The abstract can now reads ("For that, initial incubation of soils were performed at different soil moistures in order to mimic expected rainfall patterns during the next decades and in particular drought and excess of water. Then, Cu was added to asses using a bio-assay effect of this double stress on soil nitrate production " l. 25-27 while the material and methods part is clearly separated in two paragraph starting respectively by "For the 5 weeks' initial incubation" L.110 and by "At the end of the initial incubation period," l.121

Is the overall presentation well structured and clear?

R1: Organization of the intro and methods was straightforward. I found the results very difficult to follow. It would be helpful to me if the experimental measurements were presented before the explanation of how they were incorporated into the model. Or, if those are not considered part of your results, then frame the whole paper as a modeling paper rather than an experimental and modeling paper. Similarly with the discussion –there is currently very little, if any, discussion of the experimental results.

> Response: Done. Following your remarks, we re-organized the results and discussion section to better separate the ecological implications in terms of NO_3/NH_4 ratio and on N species emissions (lines 331-362). The description in term of relative variations was also enlighten with deletion of some sentences (previously lines 317-321, 322-323 and 338-341). Furthermore, we modified the order of paragraphs in the discussion section (4.2 and 4.3, actual lines 406-459) to follow the same order in the results and in the discussion.

Is the language fluent and precise?

R1: The language is at times not fluent or precise, but the intent is generally clear. Highlighting some early examples:
Title Extend should be extent
Abstract: prospect I think should be predict
Abstract: nitrate production modulation
Intro lines 70, 75
Another area of confusion for me is the word preincubation. From the figure I understand that this is referring to the initial incubation at different moisture levels, but in the abstract this period was referred to as an incubation, and in section 2.2 as an incubation and as microcosms. It would be helpful to be consistent about how you name this part of the experiment.

Response: Thank you for noticed the mistakes and inappropriate words that have been corrected. We also emphasized that the initial incubation refers to the 5 weeks under various moisture treatments while the bio-assays refers to the 3 days with Cu gradient in the materials section (lines 109-111).

Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?

R1: No major concerns here. In my experience, the "N" would follow the compound name, e.g. N2O-N.

We were more used to the abbreviation with "N" at the beginning of the words, but considering your remark it seems that both are employed. Also, for convenience we modified to wrote with "N" at the end of the word.

Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?
R1: I found the discussion difficult to follow. You might consider organizing it around your conclusions. Please use different symbols/line types as well as different colors in the figures. This is a fairly easy change that will make them more accessible for color blind readers and for those who still print in black and white.

Response: According to your remarks, we combined line type to color type for Figures. However, we choose to conserve the current color in the supplementary, especially colors that are helpful to represent error associated with model.
Concerning your remark about discussion, we reordered the paragraph to follow the conclusions. Also, we rephrased some parts, like the description of the preincubations effect on PNA sensitivity to Cu stress (l.392-402); or the limitations of DNDC in N_2O estimations (l 492-494).

Are the number and quality of references appropriate?
R1 : The paper is generally well-supported by references. Some specific comments on references: I would have liked to see more recent references included in the first paragraph (lines 44 and 50). Although it is an excellent work I don't find Jones et al 2014 a good support for the sentence in lines 46-47. The reference list is inconsistent in format and several references are lacking information such as page number or doi. See also comment on related work above.

Response: Following your comment, we changed the Jones reference for Butterbach-Bahl et al. 2013 and Galloway et al. 2008, references and added several references as mentioned for the commentary above. Moreover, reference list has been completed with page numerotation and doi.

Is the amount and quality of supplementary material appropriate?
R1 :Yes. I appreciate that the authors have posted so much data.

Response : Thank you.

RC2

General comments

R2: This paper describes a dual lab experiment and modeling study looking at how increasing copper in the soil interacts with soil moisture to nitrate production and related fluxes. This is an interesting topic and the "modex" (model-experiment) approach is promising. I applaud the authors for making their analytical code and data available for review—thanks. The text is generally well written although there are many minor English issues that occasionally make things unclear.

Unfortunately, there are many unclear and/or weak spots in the current manuscript. Some of the experimental conditions and assumptions are unclear; the introduction makes some questionable assertions; the Cu experiment is very short, while environmental contamination tends to be much longer, making it unclear how relevant the results are (this point is also noted by the other reviewer); many of the figures and model assessment should be re-thought or clarified. I agree with the other reviewer that the discussion is unfocused and difficult to follow, and the authors' final conclusions are unclear.

In summary, there are many points of interest here, but the current manuscript needs extensive revisions and should then be re-reviewed.

R2 : Specific comments

1. **Line 19: "assess" the effect? Also should be "extent" in the title**
2. **32: in general R2 is not sufficient for assessing model performance, as it doesn't say anything about bias (but I see lines 288-289, which are better, thanks)**
3. **53: "biogeochemical models"?**
4. **68: Lado 2008 is about European soils — a very different thing that global soils, which is the scale of ESMs**

Response: Thank you for your remarks. We corrected the vocabulary mistakes in the text. Considering the Lado reference, we first cited this reference because the JRC constructed very precise databases of European soil heavy metals concentration that may be easily used by ESMs. However, considering your remark, we added a worldwide reference with the FAO report on soil pollution state.

5. R2 is there a control (no Cu addition)? Unclear

Response: Indeed, we had a control treatment. To gain clarity, we now have written in the text at lines l.133 the explanation of the existence of a control with only 12 $mgCu.kg^{-1}$ corresponding to the geochemical background that's now reads: "final soil [Cu] of 62, 112, 262, 512, 762, 1012 and 2012 mg Cu.kg $soil^{-1}$ and control with 12 mgCu.kg $soil^{-1}$."

6. R2: 235:Please specify versions of all R packages used, in addition to the R version. Also, maybe time to update the latter!

Response: The version for gap (v.1.2.2) have been specified l.239 and this of R version was precised l.254

7. R2: 280: what is the timestep of the DNDC version used?

Response: The time step of the DNDC version used was 30 min. We now specify it at line 223.

8. R2 285: were data randomly separated into parameterization and validation datasets? This is a crucial and unclear point

Response: Unfortunately, we didn't have enough data to separate the dataset between parametrization and calibration sets. This is now clearly written at line 235 and 243 with "The dose-response curves of PNA during the bioassay to Cu gradient were plotted and tested with linear, quadratic or cubic functions as fitting models" and "The fits between the model and the data of soil nitrate concentration during the bioassays"

9. R2 288-289: would be good to test and report whether these slope values are significantly different from 1.0, and whether the intercept is different from zero

Response: Considering your remarks, we added the uncertainties around slopes 1:1 in their descriptions lines 308,309,312,313 (slopes significantly different from 1:1).

10. R2: 449-465: most of this is simply restating the results and should be removed

Response: We simplified the conclusions considering this remark and remove experiments description (previously l. 452-455) and NH_4 emissions description (previously l. 459) As we found important to resume the main results in conclusion, we however kept few sentences at lines (previously 449-453, 454-456, 459-474).

11. R2: Figure 2: is the x axis logarithmic? It makes reading and interpreting the graphs difficult

Response For all graphs, we plotted the x-axis in log representation as the gradient of Cu was much closer in the small Cu values. The two figures below represent the nitrous emissions (first figure) and soil nitrate concentration (Fig Rep 2) without (left panel) and with (right panel) log representations. If you prefer the representation without, we can modify all Figures.

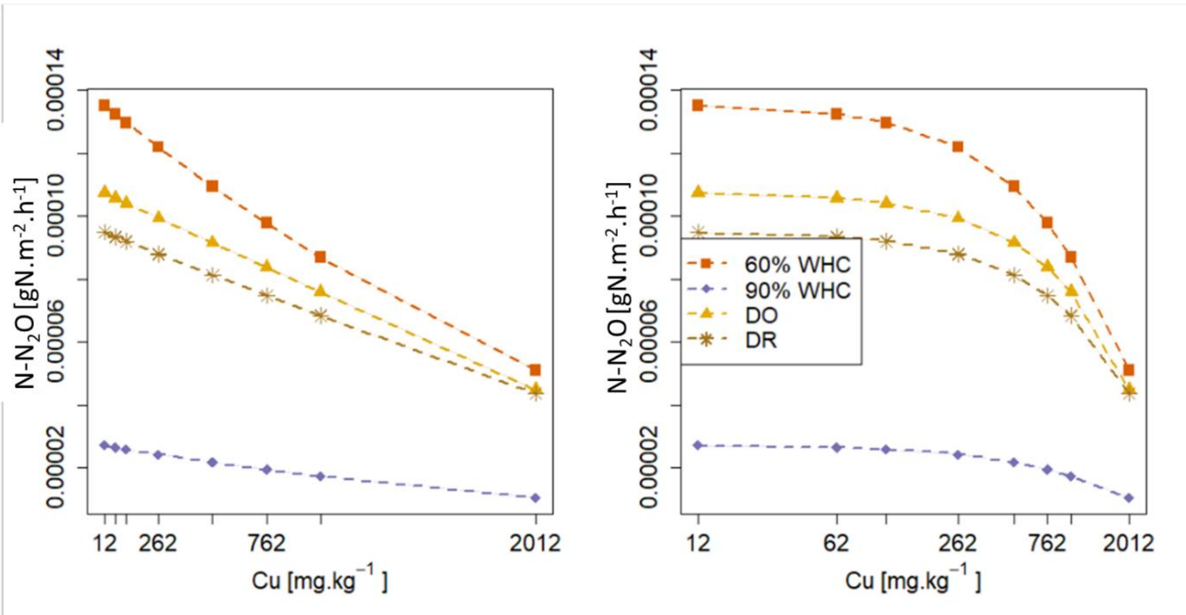

Fig. Rep 1: Modeled soil nitrate concentrations as a function of Cu concentrations without (left) x-axis log representation and with (right panel) x-axis log representation

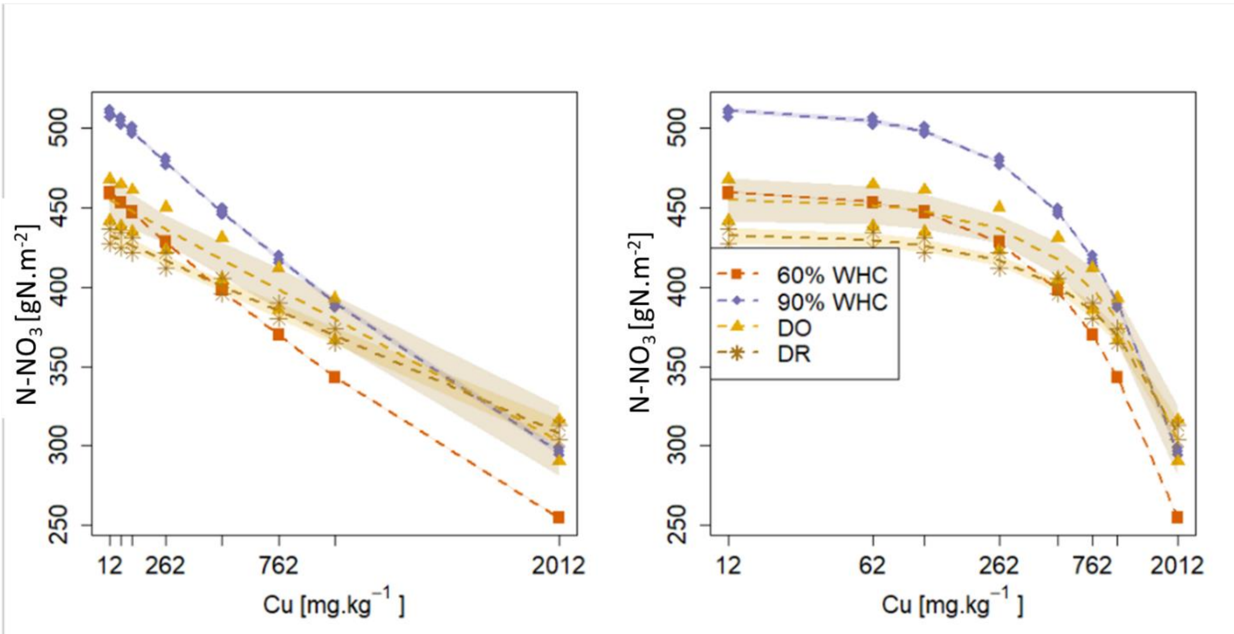

Fig. Rep 2: Modeled soil nitrate concentrations as a function of Cu concentrations without (left) x-axis log representation and with (right panel) x-axis log representation

12. R2 : Figure 3: please show 1:1 lines

Response: The 1:1 lines were already represented but was added to the legend. This now reads: "**Fig 3**: Comparison of modeled against measured soil [nitrate] incubated in different moisture with 1:1 line"