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Biogeosciences
Discussions

Interactive comment on "Impact of reactive surfaces on the abiotic reaction between nitrite and ferrous iron and associated nitrogen and oxygen isotope dynamics" *by* Anna-Neva Visser et al.

Anna-Neva Visser et al.

a.visser@unibas.ch

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First, we would like to thank the reviewer for his/her valuable inputs and comments on our manuscript. We have to admit that the outliers in the N2O data are indeed real outliers due to a "concentration/linearity effect" during the measurement in which overly large peak areas in the raw data biased the results. After a thorough check of the raw data, these few data points were removed and the graphs were re-drawn. We contend the data now presented are valid and accurate. We apologize for the mistake.

L98: "hold the potential to disentangle abiotic and biotic NO2- reduction " - this cannot be concluded from the previous sentences, which say that for both biotic and abiotic processes we deal with significant isotope effect

Reply: We will rephrase that part.

L184: "flushed before for 5 hrs with 5.0 He" - is this right - you need to flush 5hrs? Why so long? Have you tested that this is needed?

Reply: Since we simply applied the flushing routine of the denitrifier method, the headspace vials were indeed flushed for 5 hrs. Later testing showed, that 3 hrs would also suffice. However, several hours of flushing seem to be necessary to reduce the blank value to acceptable levels, in particular when sample size is low.

L315: you mean Fig. 6 here?

Reply: We thank the reviewer for pointing this out and apologize for the mistake! Indeed, in L315 it should read Fig. 6. We will change this in the manuscript!

L315: Such a value seems rather not plausible, pleas double check your measurements and check how reliable is this value. There is no known process which could result in such negative value. Similarly, in 6C - I'd even doubt the value of -40 permil, unless you have ideas to explain this.

Reply: As already mentioned, we carefully checked the raw data as well as the corrected data files again and we have to admit that these values are indeed outliers caused by very high peak areas (concentration effect). We corrected the graphs accordingly (see Figure 1 "Site Preference (SP; A, C) and δ15Nbulk (B, D) values of N2O produced in experiments amended with mineral + dead biomass (red) and mineral-only (grey)").

L346: Is further N2O reduction to N2 also possible? If not, please explain why.

Reply: Considering previous publications (Rivallan et al., 2009; Doane, 2017; Phillips

et al, 2016), an abiotic reduction of N2O to N2 is indeed possible, particularly in the presence of a reactive surface.

See L559-570: “Abiotic decomposition of N2O to N2 in the presence of Fe-bearing zeolites has been investigated previously (Rivallan et al., 2009). However, it remains unclear if this process could also occur here. Fractional N2O reduction is also not explicitly indicated by the SP values, which would reflect an increase with N2O reduction (Ostrom et al., 2007; Winther et al., 2018) [...] However, since N2O concentrations, even if minor, are increasing towards the end of the experiments, production and possible decomposition as well as ongoing sorption mechanisms might also serve as possible explanation leading to these rather low SP values.”

However, with regards to the rather low N2O concentrations and given the relatively constant δ15Nbulk-N2O values, abiotic N2 production seems plausible. First, the N2O produced here accounts only for $\sim$0.7% of the total NO2- reduced in the experiments. This large difference might be caused by sorption processes or simply by the fact that N2O is not the final product (Note: accumulation of the intermediates e.g. NO, is quite unlikely since they are extremely reactive). Furthermore, if N2O were indeed the final and only product, its δ15Nbulk values should approximate the δ15N-NO2- values (starting off lighter than δ15N-NO2- and increasing over incubation time). However, here the δ15Nbulk-N2O values remained relatively steady or did not increase much throughout the experiment, which might indicate that N2O is not just produced but possibly also further reduced (multistep-reaction). Therefore, the production of N2, although abiotic, seems quite likely. We clarify this in the revised MS.

As written in L597-601: “Considering that the N2O concentrations measured in our experiments were comparatively low and that δ15Nbulk N2O values did not noticeably change throughout the experiments, formation of N2 via abiotic interactions between NO2- and NO may also be involved (Doane, 2017; Phillips et al., 2016). Hence, N2O is possibly involved in the reaction either as an intermediate or as a side product, and can thereby influence the overall N and O isotope dynamics.”.

L484: This is not clear: d15N decrease and initial decrease?

Reply: Here, we meant the decrease in δ15N and an observed initial decrease in the concentration of NO2-. We will add “concentration” to avoid further confusion.

L547: "was calculated is based" - sentence to be rewritten

Reply: Again, we thank the reviewer for reading our manuscript so carefully. This will of course be corrected.

L548: What do the arrows mean? (in table 3)

Reply: The arrows were added to indicate an overall increase (arrow up) or decrease (arrow down) from the initial delta value. We will correct a mistake (line for δ15N NO2- values - arrow for DB+mineral setup should point up) that we only now detected, and we will add the explanation in the caption of the table.

L614: This last sentence is not stated in the discussion - in discussion you just say it is unsure if abiotic N2 production is possible. Please explain this more detailed. It is not said in the discussion what is the isotope effect of abiotic N2O reduction to N2 (is this known?) - so I do not understand how N2O isotopic results can suggest its occurrence.

Reply: Generally, N2 production is still assumed to be caused mainly by enzymatic reactions. However, there are studies providing evidence for abiotic N2 production (e.g., Rivallan et al., 2009; Phillips et al, 2016). In our manuscript, we choose to only cautiously refer to the possible abiotic N2O reduction to N2, since most N cycling studies still do not account for abiotic N2 production. Furthermore, our SP values do not explicitly indicate the occurrence of fractional N2O reduction (N2O accumulates, SP values remain rather steady). Unfortunately, we did not analyse N2 samples, hence we do not know the range of N2 concentrations and/or isotope values, which would help to better address this aspect. To the best of our knowledge, the isotope effect of abiotic N2O reduction to N2 is unknown. As already mentioned above, N2O accumulates throughout the experiments but overall accounts only for a small fraction of the NO2-

reduced. Furthermore, the δ15Nbulk-N2O values remained rather steady throughout the experiments, which indicates that other processes may influence the reaction dynamics and that N2O may simply be an intermediate. If, again, N2O were the final and only product, δ15N-bulk values would be expected to increase with decreasing NO2- concentrations (and thus increasing δ15N-NO2-). However, δ15Nbulk-N2O values to not really change much toward the end of the experiments, and remain steady for quite some time. Thus they do not reflect the patterns expected for a final product.

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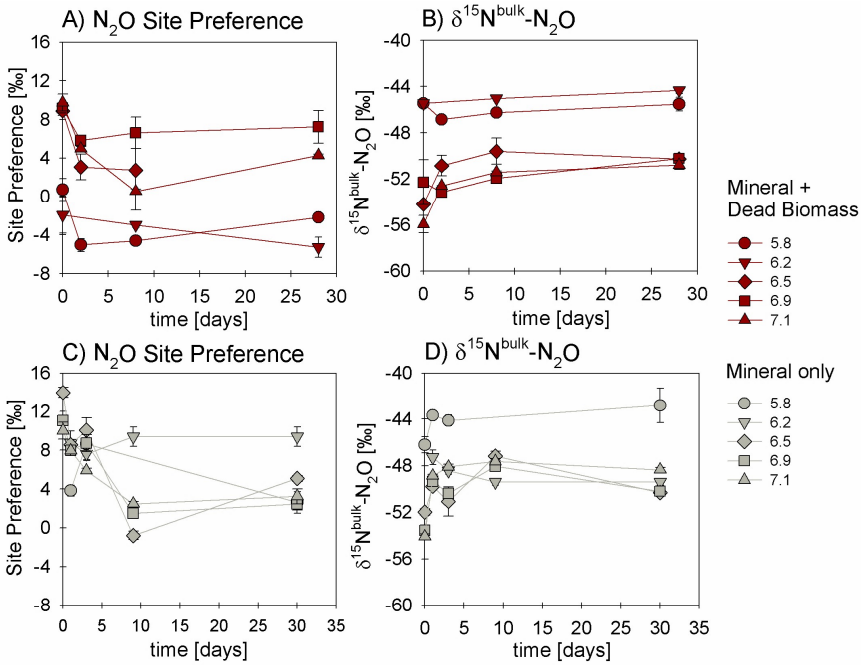

Fig. 1. N2O vs NO2- concentrations in (A) mineral plus dead biomass and (B) mineral only experiment