

***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

Received and published: 3 July 2020

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 N<sub>2</sub>O 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.

Printer-friendly version

Discussion paper



L98: "hold the potential to disentangle abiotic and biotic NO<sub>2</sub>- 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, please 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  $\delta^{15}\text{N}_{\text{bulk}}$  (B, D) values of N<sub>2</sub>O produced in experiments amended with mineral + dead biomass (red) and mineral-only (grey)").

L346: Is further N<sub>2</sub>O reduction to N<sub>2</sub> also possible? If not, please explain why.

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

[Printer-friendly version](#)[Discussion paper](#)

et al, 2016), an abiotic reduction of N<sub>2</sub>O to N<sub>2</sub> is indeed possible, particularly in the presence of a reactive surface.

See L559-570: “Abiotic decomposition of N<sub>2</sub>O to N<sub>2</sub> 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 N<sub>2</sub>O reduction is also not explicitly indicated by the SP values, which would reflect an increase with N<sub>2</sub>O reduction (Ostrom et al., 2007; Winther et al., 2018) [...]. However, since N<sub>2</sub>O 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 N<sub>2</sub>O concentrations and given the relatively constant  $\delta^{15}\text{N}_{\text{bulk-N}_2\text{O}}$  values, abiotic N<sub>2</sub> production seems plausible. First, the N<sub>2</sub>O produced here accounts only for  $\sim 0.7\%$  of the total NO<sub>2</sub><sup>-</sup> reduced in the experiments. This large difference might be caused by sorption processes or simply by the fact that N<sub>2</sub>O is not the final product (Note: accumulation of the intermediates e.g. NO, is quite unlikely since they are extremely reactive). Furthermore, if N<sub>2</sub>O were indeed the final and only product, its  $\delta^{15}\text{N}_{\text{bulk}}$  values should approximate the  $\delta^{15}\text{N-NO}_2^-$  values (starting off lighter than  $\delta^{15}\text{N-NO}_2^-$  and increasing over incubation time). However, here the  $\delta^{15}\text{N}_{\text{bulk-N}_2\text{O}}$  values remained relatively steady or did not increase much throughout the experiment, which might indicate that N<sub>2</sub>O is not just produced but possibly also further reduced (multistep-reaction). Therefore, the production of N<sub>2</sub>, although abiotic, seems quite likely. We clarify this in the revised MS.

As written in L597-601: “Considering that the N<sub>2</sub>O concentrations measured in our experiments were comparatively low and that  $\delta^{15}\text{N}_{\text{bulk N}_2\text{O}}$  values did not noticeably change throughout the experiments, formation of N<sub>2</sub> via abiotic interactions between NO<sub>2</sub><sup>-</sup> and NO may also be involved (Doane, 2017; Phillips et al., 2016). Hence, N<sub>2</sub>O 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.”

[Printer-friendly version](#)[Discussion paper](#)

L484: This is not clear:  $\delta^{15}\text{N}$  decrease and initial decrease?

Reply: Here, we meant the decrease in  $\delta^{15}\text{N}$  and an observed initial decrease in the concentration of  $\text{NO}_2^-$ . 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  $\delta^{15}\text{N}$   $\text{NO}_2^-$  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  $\text{N}_2$  production is possible. Please explain this more detailed. It is not said in the discussion what is the isotope effect of abiotic  $\text{N}_2\text{O}$  reduction to  $\text{N}_2$  (is this known?) - so I do not understand how  $\text{N}_2\text{O}$  isotopic results can suggest its occurrence.

Reply: Generally,  $\text{N}_2$  production is still assumed to be caused mainly by enzymatic reactions. However, there are studies providing evidence for abiotic  $\text{N}_2$  production (e.g., Rivallan et al., 2009; Phillips et al., 2016). In our manuscript, we choose to only cautiously refer to the possible abiotic  $\text{N}_2\text{O}$  reduction to  $\text{N}_2$ , since most N cycling studies still do not account for abiotic  $\text{N}_2$  production. Furthermore, our SP values do not explicitly indicate the occurrence of fractional  $\text{N}_2\text{O}$  reduction ( $\text{N}_2\text{O}$  accumulates, SP values remain rather steady). Unfortunately, we did not analyse  $\text{N}_2$  samples, hence we do not know the range of  $\text{N}_2$  concentrations and/or isotope values, which would help to better address this aspect. To the best of our knowledge, the isotope effect of abiotic  $\text{N}_2\text{O}$  reduction to  $\text{N}_2$  is unknown. As already mentioned above,  $\text{N}_2\text{O}$  accumulates throughout the experiments but overall accounts only for a small fraction of the  $\text{NO}_2^-$

Printer-friendly version

Discussion paper



reduced. Furthermore, the  $\delta^{15}\text{N}_{\text{bulk-N}_2\text{O}}$  values remained rather steady throughout the experiments, which indicates that other processes may influence the reaction dynamics and that  $\text{N}_2\text{O}$  may simply be an intermediate. If, again,  $\text{N}_2\text{O}$  were the final and only product,  $\delta^{15}\text{N}$ -bulk values would be expected to increase with decreasing  $\text{NO}_2$ -concentrations (and thus increasing  $\delta^{15}\text{N}$ - $\text{NO}_2$ -). However,  $\delta^{15}\text{N}_{\text{bulk-N}_2\text{O}}$  values do 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.

---

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-73>, 2020.

**BGD**

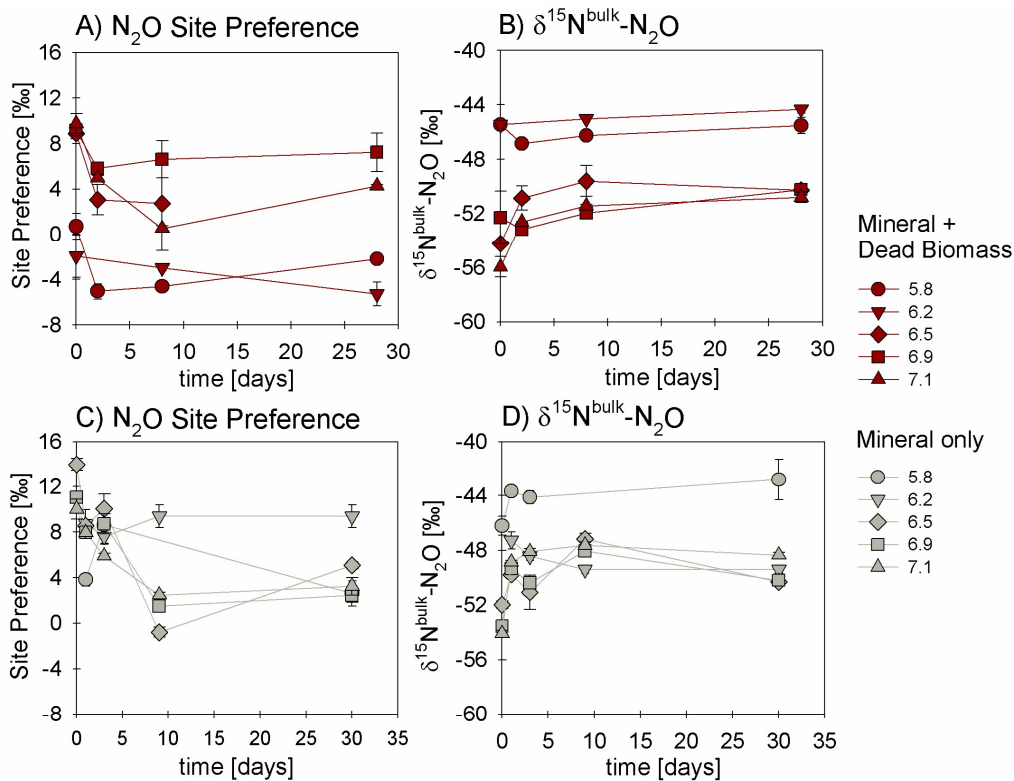
---

Interactive  
comment

Printer-friendly version

Discussion paper





**Fig. 1.**  $\text{N}_2\text{O}$  vs  $\text{NO}_2^-$  concentrations in (A) mineral plus dead biomass and (B) mineral only experiment

Printer-friendly version

Discussion paper

