Biogeosciences Discuss., 12, C7712–C7715, 2015
www.biogeosciences-discuss.net/12/C7712/2015/

Biogeosciences Discussions

BGD

12, C7712–C7715, 2015

Interactive Comment

Interactive comment on "The mechanism of oxygen isotope fractionation during N_2O production by denitrification" *by* D. Lewicka-Szczebak et al.

Anonymous Referee #4

Received and published: 16 November 2015

Review of "The mechanism of oxygen isotope fractionation during N2O production by denitrification" by Lewicka-Szczebak et al.

Summary

The authors present an analysis of oxygen isotope dynamics and fractionation during biological N2O production in soils. Using a variety of approaches, they aim to discern the location and magnitude of fractionation mechanisms including 1) equilibration of N-oxyanion intermediates with water, 2) kinetic isotope effects during each step of denitrification, as well as 3) branching isotope effects during abstraction of oxygen atoms at each of these steps. The authors incorporate both a 17O approach and 18O

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

labeled water experiments as well as acetylene inhibition in the context of both batch and flow-through incubations. In particular, I feel that this manuscript does a good job of laying out the oxygen isotope dynamics involving both 'intra-' and 'inter-molecular' fractionation mechanisms and clarifying the meaning behind 'branching' isotope effects in the context of denitrification. In general, I think the discussion about intra- and inter-molecular isotope effects is among the most valuable parts of this manuscript. The idea of fungi contributing to N2O production is also intriguing, especially if there is the possibility of teasing their role apart from bacteria. Overall, I think the paper could benefit from some clarifications in many areas – as I have noted below.

[Although the presentation of the results and interpretation is generally clear – there are sections of the text (especially, the discussion) that would benefit from editing by a native-English speaker.]

General Comments

Based on my understanding (and also the reading of Casciotti et al., (2007)), the exchange of O atoms between nitrite and water occurs as the result of the chemical dissociation of nitrous acid and is enhanced depending on their respective equilibrium concentrations. With a pKa value of $\sim$3.4, a lower pH accelerates the exchange of oxygen atoms because the pool size of nitrous acid increases, increasing the rates of forward/reverse equilibrium reactions between nitrite and nitrous acid (during which O atoms are lost/gained). This pH influence is well-known in other oxy-anion systems as well (sulfate, carbonate and phosphate, etc.). Given this important control on oxygen isotope equilibrium dynamics, I am surprised that the authors have not reported pH values for their soil incubations and solutions. Can more consideration be included about the pH of these soils and the porewaters – and their possible role in the oxygen isotope dynamics?

The authors report traditional 'delta' and 'epsilon' values in units of 'permil,' yet in all of the equations the authors use 'un-normalized' delta and epsilon values. Perhaps this

BGD
12, C7712–C7715, 2015

is simply style issue – but I feel that it can lead to confusion. For example – in the text when the branching isotope effect is estimated as '17‰'- this is not the numerical value that is used in the equations throughout. At a minimum, some clarity might be provided by stating how the values should be converted (e.g., not multiplied by 1000). For example, on P 18, L 16 – here the epsilon values which were reported on P 15, L 2 as "18.2‰' and "17.1‰' are being reported as equal to 0.0181 and 0.0172. While I understand the desire to somewhat simplify the equations – there appears to be some inconsistency – which I think would be very confusing to the casual reader.

P 4 L5-10: In general I think it would be good to be clearer about how epsilon-n here is calculated (e.g., I think it would be useful to see this mathematically expressed).

P 5 L 11-13: This sentence seems out of place.

I think the use of the word "Dynamic" incubations seems a little misleading – perhaps consider using 'steady-state' or 'open-system' or 'flow-through' experiments instead? I think of 'dynamic' as indicating an important changing parameter – whereas here conditions are held constant (with the exception of the temperature and perhaps soil moisture).

Does one need to account for the non-random 17O in the calculations of Site Preference? Or does the low abundance of 17O not impact the accuracy?

P 20 L 11: Here the authors conceptualize oxygen isotope exchange as occurring 'later than' the branching isotope effect. However, in the equations – they are mathematically occurring simultaneously. Indeed, would it not be probable that the O abstraction and exchange with water are occurring as the result of the same enzymatic process – and that the 'intra-' and 'inter-molecular' isotope effects are related (while not necessarily their fractional contributions). At least for a single organisms or class of enzymes – I would think this would be the case.

P 20, L 25: "Out of plausible range of values" – please include reference to your line of reasoning here (e.g., based on what?).

P21 L 10-15: Something is not clear about these statements. I understand how the effect observed by Casciotti (2007) represents only the 'intra-molecular' effect – (e.g., the O abstraction) – and that Casciotti (2007) refers to this as the branching effect. Here the authors then refer to this as being the 'maximal possible branching effect' – which also makes sense. Then, referring to the work by Rohe et al (2014), since the NO3- pool is not completely consumed – both the 'inter-' and 'intra-molecular effects' should be observed. But I fail to understand the next statement about the values of e-NIR of 10‰ and eNAR assumed to be 0‰ – and how this supports their observations. Please clarify.

Regarding the source of the positive Δ17O values others have observed in atmospheric N2O, this would imply denitrification of specifically atmospherically derived NO3-. Is this a reasonable assumption? Their data indeed show that a large degree of the original NO3- oxygen isotope composition is erased during equilibration with water – which has important implications for the transfer (or not) of this signal to N2O. So – to the degree that this signal is not erased, it would be possible to retain some amount of this Δ17O signal. However, does the size of the Δ17O signal in N2O represent a reasonable fraction of N2O derived from NO3- of atmospheric origin? I think these are open questions that may not be easily addressed with their data.

Specific Comments

The title could be a little more specific (e.g., referring to soils).

P 17 L 11: 'Oxygen fractionation' = not clear whether you are referring here to molecular O2 , O in water or O in N-bearing species.

P21 L 17 and L19: I think this should be 'inter-molecular effects.'

Interactive comment on Biogeosciences Discuss., 12, 17009, 2015.