

Interactive comment on “Technical Note: Simultaneous measurement of sedimentary N₂ and N₂O production and new ¹⁵N isotope pairing technique” by T.-C. Hsu and S.-J. Kao

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Received and published: 20 May 2013

The paper is presented as a technical note and whereas as I think the technical advance presented which enables the simultaneous cryo-focusing and quantification of N₂ and N₂O from the same sample is good, the claims of a new ¹⁵N isotope pairing technique are somewhat overstated. For example, the abstract and introduction describe the various processes within the N cycle that may produce both N₂ and N₂O and how to disentangle the contribution from each pathway is indeed challenging. Whereas Nielsen's original isotope pairing technique (IPT 1992) was perfectly suited to measuring denitrification, it came undone with the advent of anammox; though if

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anammox is absent it is still absolutely ok. The logic behind the IPT was then reworked by Risgaard-Petersen et al (2003) to include the key parameter r₁₄ and they proposed two techniques for its quantification – one direct (V in intact sediment cores) and one indirect (r_a% from parallel homogenous sediments). Later, in collaboration with Trimmer et al (2006), they proposed the combined N₂ and N₂O technique for direct quantification of r₁₄ and thereby the simultaneous quantification of anammox and denitrification in intact sediment cores. At around the same time, Master et al (2005) proposed a purely theoretical framework for the combined quantification of N₂O and N₂ in a pure denitrification assay. This latter framework did not include N₂ from anammox, which, as at that time the occurrence of anammox was being reported in more and more marine and estuarine sediments, the new framework of Master was, in effect, already out of date when published – though the rationale behind wanting to quantify both N₂ and N₂O was, and still is, fully justified.

The authors here claim advances on both of these new formulations as 1: the reworking by Risgaard-Petersen/Trimmer overlooked N₂O production and 2: Master did not include anammox. While the shortfall in Master et al (2005) is true, as described above, Trimmer et al (2006) did indeed show the production of N₂O over time in their time series incubations (Fig 3b 45,46N₂O nmol m⁻² against time). The point to appreciate is that the focus of the 2006 paper was to simply focus on N₂ production by both anammox and denitrification and NOT the fractional split in N₂ to N₂O in the denitrification pathway but it was quantified. Admittedly, we take two samples from the head-space of the helium equilibrated gas tight vial - one for cryo-focusing of ¹⁵N-N₂O and one for quantification of ¹⁵N-N₂. If this can be done in a single step, then yes, that is an advance, but I don't think that in itself qualifies as a new ¹⁵N isotope pairing technique – but what the authors do propose is a simple reformulation to include both N₂O and N₂ (equation 10 page 6871).

What is interesting, however, is the very high ratio of N₂O to N₂ in the denitrification pathway in these sediments. Most studies report some 2% but here the authors record

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66% of denitrification gases as N₂O –yet there is very little consideration of what other studies have shown for estuarine sediments or indeed (beyond the sulphide story) what may actually cause this. If, indeed, 66% of the ¹⁵N gases are accumulating as N₂O in the denitrification pathway, then the formulation that includes this would obviously be necessary but it seems quite out of the ordinary.

Finally, the direct quantification of the production of ⁴⁴N₂O by IRMS should enable any additional production or excess production above and beyond that traced with ¹⁵N to be assigned to nitrification but I think it might be helpful to simply term this as N₄₄ as a logical contrast to that ascribed to denitrification as D₄₄, rather than P'₄₄ (which would just be the total?) as the authors currently have it. In relation to this point, the title and the abstract may lead the reader to believe that all of the N₂O and N₂ coming from denitrification, anammox and nitrification can be accounted for in one measurement and formulation but the quantification of N₂O from nitrification (i.e. equations 16 and 17) is not included in the overall estimate of N₂ and N₂O as P₁₄-anaN₂O (equation 10) ? – if I am wrong then please clarify this point. Also, if it is possible to measure the production of ⁴⁴N₂O i.e. without a tracer, then, with cryo-focusing, is it not also possible to measure ²⁸N₂ directly and check that against the ¹⁵N –traced estimates in P₁₄-anaN₂O?

Interactive comment on Biogeosciences Discuss., 10, 6861, 2013.

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