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Biogeosciences Discussions

Interactive comment on "Seasonal variations in nitrate isotope composition of three rivers draining into the North Sea" *by* A. Deek et al.

Anonymous Referee #1

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Seasonal variations in nitrate isotope composition of three rivers draining into the North Sea bg-2010-211 Authors: unsure... Deek, A., K. Emeis, and U. Struck Or Johannssen, A., K. Emeis, and U. Struck

The authors present a time series of nitrate N and O isotope ratio measurements (15N/14N and 18O/16O) in three European rivers that discharge in the German Bight, as well as ancillary measurements, including d18O H2O and d15N of suspended particulate N.

The authors monitored the rivers bi-weekly for two years to identify nitrate sources, sinks and turnover. The reported findings of the study, as per the abstract, are as follows (1) O isotopes of nitrate in rivers attests that it originates chiefly from nitrification of catchment ammonia (2) Nitrate N and O isotopes in rivers also bear evidence

of enrichment due to assimilation (3) particulate d15N mirrors the d15N of nitrate in rivers (4) assimilation of nitrate in rivers correlates with the residence time of nitrate in rivers (5) the higher enrichment in d15N of nitrate indicates the constant additional diffuse nitrate inputs deriving from soil nitrification. (6) an observed inverse relationship between d15N of nitrate and nitrate concentrations intimates that there is a strong influence of human activites on nitrate consumption efficiency and the isotopic composition of riverine nitrate.

I find all of the 6 'findings' above problematic, for reasons that I outline below. The interpretation of the results is based largely on assumptions that are either unfounded or not supported by the data, yielding an analysis that is superficial and conclusions that are likely erroneous:

Assumption #1: Nitrate d15N delivered to rivers from the catchment is invariant interseasonally. The authors present no evidence that this is so. What if...: denitrification were occurring in soils? What would that do to the d15N and d18O of nitrate delivered to rivers? Assumption #2: Assimilation of nitrate in rivers accounts for the seasonal decrease in nitrate concentrations What if...: the lower nitrate concentrations were to reflect lower nitrate loading into rivers from the catchement. Given less precipitation or snow-melt in summer, it seems plausible that less nitrate would make it to rivers from the catchment. The authors hint at this but then state that the decrease in nitrate in summers reflects assimilation. Moreover, the longer residence time of nitrate in soils in summer could make it more likely to be denitrified directly in soils, thereby delivering even less nitrate per rain event. And... what if sediment denitrification in rivers caused some of the decrease in nitrate? And... Assimilation does not, in and of itself, cause a net loss of reactive N from rivers. In the riverine N mass balance, what happens to PN produced from nitrate? Does it disappear, does it get trapped upstream and remineralized there, is it recycle in the water column into ammonia, or is it remineralized right back to nitrate? In the latter case, denitrification in soils or in riverine sediment would need to be invoked to account for the loss of fixed N evidenced by the decrease in nitraet. In order for there to be a loss of nitrate only to assimilation, the nitrate-N assimilated needs to be in another pool, for which the authors do not account. The authors need to consider other more plausible scenarios to account for the decrease in river nitrate in summers. Assumption #3: Nitrate assimilation in rivers accounts for 15N-enrichment of nitrate in summers relative to winter What if…: denitrification in soils imparted 15N and 18O enrichment to nitrate that is delivered to rivers? Assumption #4: the d15N of reactive N in rivers reflects that of the source(s), directly (i.e. more elevated d15N of PN among rivers reflects more elevated d15N of N sources to the cathement), implying that the d15N is not modified while in the catchment relative to its initial source d15N. Catchement biological N transformations must hence be non-fractionating, although the opposite is clearly stated by the authors (p. 6061, lines10 and 28). What if…: the d15N of nitrate delivered to rivers we 15N-enriched in soils by denitrification, in proportion, in part, to the residence time of reactive N in soils before entering the river? Then scenarios could emerge where riverine d15N were particularly elevated in spite of a relatively lower source d15N, due to soil N dynamics. Seems plausible to me. Assumption # 5: the d18O of nitrate is determined by that of atmospheric oxygen (1/3) and that of water (2/3), as per Equation (2), which was prevalent in older literature. However, Equation (2) has been demonstrated as inaccurate. More recent studies involving careful investigation of mono-cultures have clearly illustrated that this is an oversimplification that is likely to yield erroneous prediction of the d18O of nitrate anticipated for nitrification (Casciotti 2002, Casciotti et al. 2008, Buchwald and Casciotti, 2009). While the value is not determined with absolute certainty, a number of studies narrow the range anticipated (Casciotti et al. 2002, Casciotti et al. 2007, Sigman et al. 2009, Pantoha 2009, Buchwald and Casciotti 2009).

What if…: The authors determined the d18O of nitrate anticipated for newly nitrified nitrate based on the d18O of ambient water, and were then able to assess d18O enrichment relative to newly nitrified nitrate.

Assumption #6: The d15N of PN is determined by the d15N of riverine nitrate. What

if…: primary production relies largely on regenerated N in rivers, and thus reflects the d15N of regenerated N primarily?

Specific comments: Abstract, line 20: "…both are uncorrelated in time series due the lateral and temporal mixing of PN." Not clear to me what this means or how that works. Abstract, line 27: "human dominated land use" how is that measured. It's the first we hear of it in the abstract. Learn later in the text that it's in reference to another paper… Abstract, last sentence: The meaning is unclear. And what is nitrate consumption efficiency? What is it about humans that cause higher nitrate consumption efficiency?

p. 6053 line 15: the Rhine and Elbe are considered large rivers, I surmise? p. 6053 line 27: What is the meaning of sources of nitrate within rivers have been overlooked? N2-fixation? p. 6054, line 11: It seems to me that the d15N of nitrate produced by nitrification is not a "range" per se, but rather determined by (1) the N isotope composition of ambient ammonia (2) the isotope effect and (3) the extent to which ammonium is nitrificed to nitrate. p. 6054, line 27: shed light on assimilation of what? Nitrate, ammonium, reactive N? p. 6055:, paragraph 1: What did the previous study contribute and how does this one differ, or how can it improve findings, other than being a longer time series? p. 6055, line13: loads of what? To what? Would "N loading" be a more appropriate term here? p. 6055, line 23: the pore size of a GF/F is 0.7 μm p. 6056: How can the d18O of nitrate be compared to that of H2O knowing that the correction is off? p. 6058, line 7: "load" and "N discharge" are used interchangeably to mean N loading and or water discharge – should stick to single term for single process. And units should be specific (kt per year, rather than kt between this and that time). p. 6059, line 3: too vague a description of d18O nitrate p. 6060, line 19: the d18O of which direct sources? And what are these values?

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