Biogeosciences Discuss., 7, C3295–C3300, 2010
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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 #2

Received and published: 12 October 2010

Summary

In the introduction, the authors state that they wish to use PN d15N, NO3 d15N and d18O, and river water d18O to answer the following questions: 1) what the sources of NO3 are in the rivers, 2) How does river discharge and water residence time influence nitrate concentration and its isotopic composition? (3) Do we find evidence for biological processes within the rivers that influence nitrate loads and nitrate isotopic variability?

Comments

Unfortunately, additional work is necessary to interpret the authors' data to answer the questions outlined in the introduction. There are multiple potential explanations for the

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authors' observations, many of which are not explored in this manuscript. Additionally, the authors come to many of their conclusions based on assumptions that I would argue are not valid. The authors spend a lot of text explaining the work that others have done, and assuming the conclusions of others' work can be extrapolated to theirs, without having made the necessary measurements to do so. Fundamentally, this study is under-constrained; not enough measurements were made to make meaningful, rigorous interpretations of the data in the ways the authors wish.

In particular, measuring [NH4] and NH4 d15N would help support their claims and rule out alternative explanations for their observations. A more complete study would at least identify what the dominant N species in the river are – how high is [NH4] relative to [NO3], and does it vary throughout the year? On p. 6071, the authors claim that [NH4] are high during winter – this would seem to support high rates of nitrification being the source of increased [NO3] during winter, not decreased rates of NO3 assimilation, as is suggested on p. 6067-6068. What about [DON]? In order to justify ignoring these other dissolved N species as the authors have done in this text, the authors need to show that these species are not quantitatively relevant, which they have not done – instead they sometimes suggest other N species are quantitatively relevant, and even seem to have the data, but don't include it. Similarly, what is the [PN] in these samples? Is it quantitatively relevant? If [PN] are small relative to changes in [NO3], why do the authors use PN as an indicator of the degree of NO3 assimilation? If PN is not a quantitatively relevant term, why bother measuring it, since a pool with a small mass is unlikely it can tell you anything about the dominant fluxes through the system? Additionally, the authors contradict themselves throughout the text (i.e., characterization of the d15N of NO3 from agricultural fertilizer as between 4 to 9‰ on page 6054, but then quote it as having a d15N from -5 to 8‰ per mil on p. 6061).

The authors claim nitrification of soil ammonia is the dominant source of NO3 in river water; have the authors confirmed that their results are consistent with the work of Casciotti, 2009; Buchwald and Casciotti, 2010, Casciotti et al., 2010? Did the authors

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measure changes in [NH4] and d15N to confirm this supposition? [NH4] data would go a long way towards bolstering the authors' conclusions, but none is provided. Additionally, the authors claim that in nitrification, 2 oxygen atoms come from water, and 1 comes from dissolved O2 gas; this is an old explanation, and newer evidence has shown that this is not the case; see work of Casciotti.

It's not clear to me that just because [NO3] and NO3 d15N are inversely correlated that anthropogenic inputs are the cause of this variation – certainly this inverse correlation exists in the open ocean, away from anthropogenic influence of the marine N cycle, as in the Southern Ocean (e.g., Sigman et al., 1999; Sigman et al., 2000). This anti-correlation alone does not mean that NO3 in the river is dominated by anthropogenic sources.

p. 6054, lines 10-12: I disagree with this statement; the d15N of NO3 produced by nitrification depends on 1) the d15N of the NH4 being nitrified, and 2) the degree to which the substrate pool (NH4) is nitrified; nitrification itself does not have an inherent d15N associated with the NO3 produced from that process. Only sources of N (like precipitation or N2 fixation) have a characterizable d15N; nitrification is a transformation of N from one form (NH4) to another (NO3).

p. 6054, lines 16-18: similarly, is the reported range in d15N of fertilizer, 4 to 9‰ that of NO3 in streams affected by fertilizer, in which case denitrification may have elevated the d15N of the NO3, or is it the d15N of directly measured fertilizer?

p. 6054, lines 21-23: it would be more appropriate to provide the formal definition of ε here

p. 6058, line 22: rephrase to "summer maxima were observed each year"

p. 6058, lines 23-25: are these seasonal differences statistically significant?

p. 6059-6060, lines 25-1: There is not enough evidence to support the claim that the inverse relationship between [NO3] and NO3 d15N is due to in-river NO3 assimilation;

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this could also be caused by in-river denitification, or the addition of NO3 with a low-d15N during times of high N load. The authors need to constrain the problem more before they can make this claim.

p. 6060, top paragraph; a correlation between PN d15N and degree of anthropogenic impact does not mechanistically explain the absolute value of PN d15N; this would require knowledge of the d15N of the sources of N to the rivers (i.e., direct measurement of the d15N of the fertilizer being applied, the d15N of the NO3 in rain, etc.), as well as rate measurements of the processes (denitrification, NO3 assimilation, etc.), to explain the absolute value of PN d15N.

p. 6060, lines 16-20: denitrification in the rivers could also raise the NO3 d15N to the observed values; it is not clear that NO3 d15N is high because of anthropogenic impact

p. 6060-6061: "All these sources are known to contribute to nitrate stocks in surface and groundwater, and each has more or less specific isotopic compositions"; I disagree with this assumption; this is an oversimplified interpretation of the cited reference.

p. 6061, this is a confusing summary of the d15N of fertilizer, and more over, it is not relevant to the interpretation of the data; as the authors describe elsewhere, the initial d15N of fertilizer will not necessarily be reflected by the d15N of NO3 (or PN, NH4, etc) measured in a river, because of 1) the potential for incomplete conversion of substrate (fertilizer) to product (NO3, in this case), 2) mixing with other sources, such as atmospheric deposition, groundwater, etc., with different isotopic compositions, and 3) removal of NO3 by fractionating processes such as denitrification and/or assimilation. None of these other sources or processes are quantified or constrained in this manuscript, making it difficult to interpret the data with any degree of certainty. Moreover, the lack of a mass and isotopic balance (i.e., the authors do not measure the concentration of other dissolved N species in the river, so we do not know what the dominant form of N is; in particular [NH4] would have been very useful in this study) makes it impossible to interpret the data. Indeed, even though the authors measured

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[PN], they do not report it – if they felt that the relationship between PN d15N and NO3 d15N was due to NO3 assimilation alone, they should have shown a mass and isotopic balance whereby all of the change in [NO3] and NO3 d15N could be accounted for by a corresponding change in [PN] and PN d15N; they do not provide the [PN] data that is critical to this explanation, even though they presumably have the data.

p. 6063-6064: the discussion of nitrifying bacteria, especially the discussion of groups of nitrifying bacteria, seems unnecessary, since the authors do not use genomics to identify which nitrifiers may be active in their samples. This discussion is distracting and should be cut.

p. 6066, lines 17-25: the [NO3] (and [NH4]) in precipitation can be quite high in anthropogenically affected areas like the ones in this study; additionally, the d15N of this NO3 and NH4 in rain is low (Hastings et al., 2003; Knapp et al., 2010); however, this source of N to the rivers is not addressed in this text (even though the d18O of NO3 in rain is). If the authors wish to understand what the sources of the NO3 in their rivers are, it would help to quantify the potential importance of precipitation – how much N may rain contribute? If N in rain contributes a small fraction of N in rivers, it could be safely ignored; however, if rain contributes a significant fraction of N in rivers, its d15N should be considered. If the authors are going to the trouble of addressing the d18O of NO3 in rain, they should also address the quantitative importance of N in rain, and its d15N, on their river samples; alternatively, they should drop the whole section – as is it is inconsistent.

p.6067, lines 14-17: “Because assimilation is low in winter (as indicated by the indirect, but significant, negative correlation between NO3 concentration and water temperature; Table 2), the more intense soil source and low consumption rates result in higher nitrate loads in winter.” I argue that this is a bad assumption; the negative correlation between NO3 concentration and water temperature could be due to the introduction of a different water mass with a different [NO3], rather than result from biological activity. Alternatively, the negative correlation could be due to another biological process domi-

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nating during the winter season, such as increased rates of nitrification, or decreased rates of denitrification. The authors have not done enough work to substantiate their conclusion that higher [NO3] in winter result from lower rates of NO3 assimilation.

p. 6068: the authors assume that sedimentary denitrification has no isotope effect, and so it should not play a role in producing NO3 with a high d15N in these samples. That would be true if, as is the case in ocean sediments, rates of denitrification were diffusion-limited; however, given the high loading of NO3 in soil pore waters in agricultural soils, this may not be a good assumption. Indeed, the isotope effect for denitrification may be expressed to some degree in soil waters, which would impact the d15N of NO3 in these samples.

p. 6068: "Seasonal variation in both d15N and d18O combined with decreasing NO3 concentrations in Rhine, Weser, and Ems have similar trends with maxima in summer and minima in winter for all sampling periods (Fig. 2a–c), suggesting that NO3 is consumed during summer months when biological activity increases." I assume that the authors are claiming that eukaryotic biological activity decreases in the winter (although they provide no direct evidence of this); however, they show no evidence that prokaryotic activity decreases in the winter. Since bacterial transformations of N are likely to dominate, this statement seems misleading/poorly supported.

The figures are hard to read – please make them bigger, especially Figs 3, 5

Fig 6 – use ln (f) on the x axis instead of f to get a linear relationship to estimate fractionation factor.

Interactive comment on Biogeosciences Discuss., 7, 6051, 2010.