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Interactive comment on "Nitrate sources and dynamics in the salinized rivers and estuaries – a δ^{15}N- and δ^{18}O-NO_3^- isotope approach" *by* D. Xue et al.

Anonymous Referee #2

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General: This paper presents some interesting results about the use of nitrate isotopes to study DIN dynamics in human influenced river- estuary. Generally, the text is clearly written but some important shortcomings were identified. First, there is a lack of information about the study area – especially hydrology of the systems is poorly described - and about the sampling (see below). However most important, the interpretation of the data mainly based on comparisons towards mixing lines, present important weaknesses. This is mainly linked to the authors choice of considering a continuous water body from the most upstream station to the most downstream station (2 extreme end-members) while the system is characterized by non-continuous hydrological characteristics such as the presence of gates or river confluences. When

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performing Nitrogen budgets, this clearly needs to be taken into consideration in order to avoid misinterpretation. More details and suggestions here bellow.

Important comments:

Introduction

P4564, Line 26 - “Seldom researchers carried out research in small estuarine systems (Caffrey et al., 2007; Teixeira et al., 2010; Kaiser et al., 2013). Even more, less is known about small estuarine systems with salinization from sea-water intrusion upstream the estuarine channel (Graas and Savenije, 2008).” These statements should be checked carefully. To my knowledge, studies on N dynamics in small estuaries are not so seldom (many studies on small tropical estuaries for example), and most (all) of small studied estuaries have salinity gradients inside the estuarine-river bed because of low freshwater discharge and tidal mixing. I do not know any freshwater small estuary:

Material and methods

Study area P4566. Missing useful information: What are the average freshwater river discharge of the 3 rivers? Climate characteristics of the study area (seasons)? Tidal amplitude at river mouth? How are the gates functioning? Info about geometry (depth?, width?, residence times?) Population in Tianjin(density)? Presence of Wastewater treatment facilities?

Sampling

P4566 . How do you take the samples? From a ship? From bridges? With a bucket (surface water)? With a Niskin bottle? Is the water column well mixed? At which moment of the tide? What was the river discharge (dry weather condition or not) and seasonal condition? Please give more details. . . P4566, Line 25: what physico-chemical property do you analyze on the frozen sample?

Results

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P4570, Line 13 “The specific reasons to cause such variations could be potentially linking to internal/external NO3 source contributions and different NO3 dynamics in the rivers and the estuaries”. Not only nitrate – also NH4, organic N, etc. . .

Discussion

P4571 – Potential dominant nitrate sources: what is the influence of internal processes in changing the original signal of the nitrate source? The use of the dual approach to identify major sources may be biased in a system with active Nitrate transformation pathways as here . . .

P4572, L6: What is the “initial sampling location”? The most upstream station? Similar: “last sampling location” should be “most downstream sampling location”. There is a general problem with the mixing lines in river HH as presented. Actually, there is no continuity between the water masses located in the different river stretches separated by gates. So you cannot consider a mixing line crossing the gates because you do not have a continuous mixing pattern between your chosen end-members. . . If you want to compare observed concentration with conservative mixing lines, you should do this separately in each of your stretches: (1) Freshwater HH = before gate 1, (2) region between gate 1 and 2, and (3) estuary below gate 2

P4572- Line 16. In the upstream HH river you have freshwater and you should look at the evolution of concentration as a function of the distances as plotted in you figure 3. Line 18 and on: discussion about anaerobic-aerobic denitrification. You can have anaerobic denitrification in the sediments of your river. This is probably more likely than aerobic denitrification in the water column, which although may occur. Do not neglect sediment-water interaction in your system – especially as it is a small river.

P4574 L 4: NH4 is not only the preferred nutrient, it also inhibits NO3 assimilation by phytoplankton. Hence, assimilation cannot be ignored but may be considered as unlikely to be significant.

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P4574 L 9: replace “aerobic denit” by “denit” (see comment above). You cannot exclude nitrification, especially as the O2 levels are relatively low which favors the unbalance between the 2 groups of nitrifiers (ammonium oxidizers more sensitive to low O2 than nitrite oxidizers –see old paper by Helder and de Vries 1983 - Netherlands Journal of Sea Research, 17(1) 1–18). For example in the Scheldt estuary in the 1970’s, NH4 levels where up to 750 μM and still nitrification was intense (Somville, 1984 – APPLIED AND ENVIRONMENTAL MICROBIOLOGY, Feb. 1984, p. 424-426)

P4574 L18: for CB and JY rivers and estuaries: here also you cannot consider continuity between most upstream river station and most downstream marine station as you have another important end-member coming into your system. Thus, you should separate the 2 freshwater rivers from the mixed estuary. Evaluate the 2 freshwater zones by looking at evolution of C as a function of distance (there is almost no salinity gradient there), and then the estuary by plotting a mixing line between most upstream station after the confluence with the marine end-member. This will make evaluation much more clear – and change the story... Hence freshwater rivers: sink of NO2, source of NO3, sink of NH4 (JY) or scattered distribution of NH4 (CB-difficult to say if there is a source or sink). Estuary: sink of NH4, conservative NO2 and sink of NO3 (and not a source as you conclude...). Please rewrite your discussion ad hoc and reconsider your conclusion.

P4576, line 3 – how do you practically calculate the removal efficiency? This is not clear at all.

P4576 line 28: what is the water residence time?

Small remarks

P4548 – “Normally, a mixture (MIX) can be calculated via a basic mixing model”– should be: “ The concentration of a mixture can be calculated ...” P4565, Line 10: replace “are converged” by “converge” P4565, Line 12 “and is separated into three parts by two floodgates cross the river” replace by “... crossing the river” or “...that

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cross the river" Fig3 and 4: no info in the legend about the small graphs inside the NH4, NO2 and NO3 figures (I guess a plot across distance in the freshwater zones)

Interactive comment on Biogeosciences Discuss., 11, 4563, 2014.