

Referee's comments:

Overall the topic is of interest and fits well to the scope of the journal Biogeosciences.

Moreover, a budget using the LOICZ approach was constructed using measurements but mainly data from other studies. The budget balances sources and sinks of nitrate and is supported by stable isotope data of nitrate. As a central conclusion the overwhelming role of nitrification as the major source of nitrate is presented.

Authors' reply:

We thank the referee for his/her ideas on improving the manuscript and appreciate the careful review. In our opinion, the reviewer may not have appreciated the power of combined mass- and isotope budgets, which add a completely new dimension to standard mass-only budgets due to the process-specific isotope fractionation in the nitrogen cycle. This and an apparently poor choice of title on our side may have led to misunderstanding, which we hope to remedy in a revision. We address this point and others raised by the referee below.

Referee's comments:

The most significant error is the definition of equations (1) and (2). Sources and sinks are listed and supposed to be balanced. However, the source terms list nitrification and the loss terms list sedimentation. Both of these do not fulfill the criteria of a source or sink, respectively.

Nitrification is neither a source nor a sink for nitrate but simply a microbial process that converts ammonium via nitrite to nitrate. Nitrification does not generate new DIN for a system simply because the substrate of the nitrification process is ammonium and comes from internal turnover processes of organic matter. The LOICZ report (no 5 LOICZ BIOGEOCHEMICAL Modelling Guidelines, 1996) states "The important point to note with this reaction (nitrification) is that **carbon and phosphorus are not directly involved in the net reaction**. Again this makes the point that the relationship between NO₃ and NH₄ may be considered an "internal cycle" which need not be dealt with directly."

Authors' reply:

We are sorry that our approach is apparently open to misunderstanding, and indeed will change the title of our manuscript to "**A nitrate budget of the Bohai Sea based on an isotope mass balance model**" in order to make our focus on reactive nitrogen clearer. Because anthropogenic impacts on biogeochemical cycles of marginal seas is always seen in amplified inputs of reactive N, we focus on this cycle. The budget in the manuscript thus is basically a budget of nitrate ion in the water mass, neither organic particles nor the sediment are included as active compartments. Instead, we expand the mass-based budget with an isotope-based budget to employ the added possibilities of dual nitrate isotopes to quantify nitrate sources and sinks. That is why

nitrification and sedimentation are considered as sources and sinks, because they affect the isotope budget.

The “LOICZ approach” that the reviewer refers to links water- and salt-balance to construct carbon, nitrogen and phosphorus budget models and is an established methodology to standardize mass flux estimates of these biogeochemically important elements in coastal systems on regional to local scales (D.C. Gordon et al., 1996; Smith et al., 2005). The underlying box model approach diagnoses water, salt and CNP-fluxes, for example to decide if systems are autotrophic (production exceeds respiration) or heterotrophic (respiration exceeds production) on the basis of deviations from stoichiometric Redfield ratios. We do not aim to decide if Bohai Sea nutrient cycles indicate net autotrophy or net heterotrophy, and thus specifically do not aim to include the carbon balance associated with the LOICZ approach. We establish a more generic box model approach specifically of the reactive nitrogen pools to provide mass flux estimates of inputs and outputs to the nitrate pool. Our approach thus goes beyond a mass flux estimate (as done in previous LOICZ-type budgets for Bohai Sea, e.g., Zhang et al. (2004)) by constraining some of the branches of reactive nitrogen in this coastal sea based on the tell-tale changes in dual isotope composition of nitrate, and the dual isotopic properties of sources and sinks. This approach thus differs fundamentally from the solely mass-balance approach that have been done previously and that have large uncertainties specifically in the internal nitrogen turnover. In our opinion the approach taken in our study is significantly more specific and is diagnostic of several important pathways of reactive nitrogen.

Nitrification is indeed an “internal” source, as the referee says: “nitrification does not generate new DIN for a system simply because the substrate of the nitrification process is ammonium and comes from internal turnover processes of organic matter”, the initial source of newly nitrified nitrate is ammonium or organic matter which releases ammonium. However, nitrification affects the stable isotopic ratios and therefore, has to be included into our budget. For our study, N in organic matter is not involved in our box model because it is simply not present as nitrate ions.

Referee’s comments:

Sedimentation is also a problematic variable for a balanced budget because it is not a removal process for nitrate. Organic material in sediments is prone to remineralization and resuspension. Only if that organic matter is permanently buried it can be considered a long-term sink. The finding that nitrification in the Bohai Bay is a very active process – generating large quantities of nitrate - is not a surprise but rather typical for coastal eutrophied systems.

Authors’ reply:

We fully agree with the referee that “only if that organic matter is permanently buried it can be considered a long-term sink”. However, sedimentation in our model is defined as the nitrate removal from the water pool:

because the process converts the nitrate ion to particulate nitrogen (PN), it is a sink for inorganic N and importantly, it also is associated with isotope fractionation. We only need to consider the net amount of newly produced PN, namely the amount of consumed nitrate in our model.

The significance of nitrification may be unsurprising to the reviewer, but in terms of environmental management and legislation, it makes a lot of difference whether a nitrate “target threshold concentration” can be controlled by reducing river or atmospheric inputs, or whether the nitrate is generated by sources that cannot be controlled (as is the case in Bohai Sea nitrification – the largest nitrate source).

Referee’s comments:

Another problem I have with this manuscript is that it actually consists of two independent stories; one is the field study of nitrogen compounds and stable isotopes in the Bohai Sea and the other the budget. Both are rather disconnected although the authors try to include some measurements in the budget. The field data are rather distracting from the main scope because they suggest that part of the budget is based on measurements although, most data are taken from other publications. Of course the authors write very clearly where the numbers for the budget are from and which underlying assumptions were applied to derive mean values. Nevertheless, the field data and budget remain two different stories.

Authors’ reply:

The main objective of this manuscript is the budget of mass fluxes constrained by the isotope budget, and indeed both field data and literature data are used for completing the budget. The basic data are obtained through our investigations, including the basic hydrology data (salinity and temperature), nutrients and nitrate isotopes, the properties of the particles and sediments. They are the bulk of the data used here and constitute the backbone of our study. They cannot be excluded if the whole budget needed to be constrained.

Referee’s comments:

But data from only two seasons can hardly be used for a budget averaging annual mean fluxes.

Authors’ reply:

Using data from two seasons is not ideal to extrapolate to the annual situation, but our data set brackets the intra-annual variability in the Bohai Sea. That marginal sea and the eastern Chinese seas in general are dominated by the monsoon circulation that imposes characteristic end-member states in summer and winter driven by opposite directions of monsoon. During our cruises, the early spring pattern was that of the winter season, as reflected by the vertically mixed water column, and results of the second seasonal sampling images a typical summer situation when sea water temperature was quite high and biological activity has consumed most of the nutrients. The annual situation thus is represented by the two most typical seasons. Likewise, Yellow River, the

most important external riverine source of nitrate, was monitored over 5 months in order to register the dry and flood seasons.

Referee's comments:

The results of the HAMSON model were not used at all and in the discussion the field data are only briefly mentioned.

Authors' reply:

The HAMSON model is described in the method part, and as stated in the text we use the modeled water transports only to calculate the "net export" of nitrate from Bohai Sea to the Yellow Sea in our mass- and isotope balance model. Because our main purpose was to estimate transports and not to delve into details of hydrodynamic circulation, we only gave a brief text and do not see the point of expanding the manuscript.

Referee's comments:

The final major concern is the lacking error estimate of the budget. All field data are subject to some degree of major or minor inaccuracy, which is not analyzed and not included in the budget calculations. Point 4.3.3 is insufficient and only addresses single sources. What's needed is an error propagation estimate.

Authors' reply:

The errors coming from the measurement uncertainties could be done in more detail, and we will report the numbers in our revision. The errors of fluxes from the mass- and isotope balance are given as ranges in the manuscript.

The specific reply for the small issues.

L33: Reactive nitrogen is different to fixed nitrogen. While the first term summarises all bioavailable forms of nitrogen the latter is dedicated to diazotrophs.

Authors' reply:

Thank you and we will rephrase like "Reactive (N_r) is an essential nutrient of life on earth".

L52: what is a "dramatic" increase of N/P ratios?

Authors' reply: N/P ratio increased about 30 times, we now give this number.

L61: it should be avoided to merge the process of nitrification into budget considerations

Authors' reply: As explained above, we were trying to constrain a model of nitrate in the water of Bohai Sea, and even though nitrification is a internal cycling process, it leaves a significant imprint on the isotope balance.

L71: If a microbial process like nitrification is a major scope of a study it should have been measured during the field work. Including these rates could improve

the study significantly.

Authors' reply: The nitrification rates in both water column and sediments of Chinese marginal seas are not well documented, and our manuscript remedies that lack of information. We fully agree with referee's suggestion that one way to estimate nitrification the direct measurements of nitrification by incubation experiments (Ward, 2011). A second widely used approach (Wankel et al., 2007; DiFiore et al., 2009; Sigman et al., 2009) is mass- and isotope-based modeling that we use here.

L103: are the detection limits indeed as reported? They seem high to me.

Authors' reply: Thank you for catching this error: the detection limit for NO_x is $0.05 \mu\text{mol L}^{-1}$.

L133: the model has a depth resolution of 1.5m, the field data seem to have a spacing of 5-10m. This mismatch should be solved as the model validation can hardly be done with the data gathered.

Authors' reply: The upper 50 m of the HAMSOM model are resolved by layers of 5 m thickness. So, this coincides nicely with the resolution of our observational data. HAMSOM has been applied in the Bohai Sea since last century, we believe the HAMSOM was validated good in the Bohai Sea (Jia and Chen, 2021; Hainbucher et al., 2004; Huang et al., 1999).

L145: The authors may not use two seasons only to extrapolate to an entire year. Here the data of other studies could be used to generate a full annual data coverage.

Authors' reply: As mentioned above, the data from two seasons is not ideal to present the annual situation, but as we discussed in the manuscript, the Bohai Sea or even the eastern Chinese seas are monsoon-driven systems where most different seasons are summer and winter with opposite directions of monsoon. The isotope data are crucial for our approach and literature data of nitrate isotopes have to our knowledge not been published in Bohai Sea so far.

Fig 2 and 4 have blanks. How are does ODV generate these? Are the gradients of riparian data too large?

Authors' reply: ODV users can display their data in gridded form with the calculation method called "weighted-average gridding". Users can choose the extension scale of each data point, so that the blanks are places without interpolated values. By increasing the horizontal or vertical range of each datum the blanks can be filled if necessary, but the blanks do in our opinion not obscure the patterns.

Line 166 Here I do not agree. The nutrient concentrations in spring are highly variable from 15-5 micromol L⁻¹.

Authors' reply: Here we will rephrase to: "Nutrient concentrations in spring

were almost vertically uniform, consistent with temperatures and salinities, and no distinct nutricline was observed”.

Line 168 Fig 4 and 5 do not present any phosphate concentrations – the reference to the figures is not correct

Authors’ reply: Nitrate or dissolved inorganic nitrogen is our key point, so that we decided against showing phosphate profiles. We will delete the reference to figures.

Line 170ff average concentrations of all stations and depth have been calculated. Although I understand why this is done it makes of course no sense when a thermal stratification, a clear river plume and other features exist. Rephrasing and explaining this would help.

Authors’ reply: We fully realize that heterogeneous distribution of any parameters introduces errors. Thus, the patterns were briefly described and displayed as graphs to inform the reader.

Line 230 Sv unit should use superscript

Authors’ reply: We will correct it.

Line 244 there is a typo $r=$. . .

Authors’ reply: We will correct it.

Line 251 trace amounts are usually much lower than 0.5 micromol per liter which is the detection limit given.

Authors’ reply: Thanks again for noticing this typo, it should be 0.05 $\mu\text{mol L}^{-1}$ which is closer to the “trace amount”.

Line 270ff the assumption of similar nitrate fluxes in rivers without data based on the regional vicinity seems doubtful to me. Is the land use similar too?

Authors’ reply: In the manuscript, the nitrate concentrations of Shuangtaizi River, Daling River, and Xiaoling River were set to be the same as the Daliao River. Shuangtaizi River and Daliao River are quite near each other, their drainage basins are similarly populated and industrialized. Daling River and Xiaoling River are also close and both polluted by human activities (Wang et al., 2010). The nitrate concentration of these four rivers was reported to be similar (Zhang et al., 2007). Although all are quite polluted rivers, their water discharges are relatively small and only account for 4.1% of the discharge by the 8 biggest rivers into the Bohai Sea. Our estimate of nitrate concentrations for the three rivers is thus justified and erroneous estimates would only introduce small errors.

Point 4.2.2 this paragraph tries to explain away all uncertainties and assumptions but the potential error is likely very high. As said above – this and

the other fluxes need to be treated using error estimates.

Authors' reply: The error estimates could be done.

Point 4.2.3 was indeed the atmospheric deposition of entire China used? There should be tremendous differences across the country. May be I am misunderstanding something, but it seems that regional deposition data should be used. And again the uncertainty in the estimate needs to be included.

Authors' reply: We realise that the estimates may be problematic as well, but the results calculated by using different field data agree well and we are not aware of better data. The measurement-based estimates in the Bohai Sea are 3.4×10^9 mol yr⁻¹ (Zhang et al., 2004) and 3.1×10^9 mol yr⁻¹ (Liu et al., 2003), respectively. Other indirect estimates amount to 3.7×10^9 mol yr⁻¹ (Kim et al., 2019) and 3.6×10^9 mol yr⁻¹ (Zhao et al., 2017), respectively. We decided to use the number 3.4×10^9 mol yr⁻¹ because it was measured directly and is in the middle range of these estimates.

Line 326 unit

Authors' reply: We will correct it.

Page 18 and 19 the concerns explained above would need consideration to construct the budget differently

Authors' reply: We will make clear that we calculate the budget of “nitrate” instead of all reactive nitrogen.

Line 363 is not a hypothesis but a well known fact

Authors' reply: We will change the text “The sources of nitrate for BHS are river inputs, submarine fresh groundwater input, atmospheric deposition, and remineralization.”

Line 456 delta as Greek letter. What about sediment resuspension and transport? Wouldn't that also blur any isotope signature?

Authors' reply:

Our data show that the $\delta^{15}\text{N}$ values of sediment increase from the Yellow River estuary to the Bohai Strait along the pathway of water and particle transport (4.55‰-5.58‰) and mirror a decrease in terrestrial particles with increasing distance from the estuary. Importantly, the terrestrial signal of Yellow River particles disappears in short distance from the estuary. Furthermore, the isotope data suggest that resuspension of sediment with terrestrial signature is not significant.

Point 5 the conclusion would need a revision

Authors' reply: Thanks and will revise.

References:

- D.C. Gordon, J., Boudreau, P. R., Mann, K. H., Ong, J.-E., Silvert, W. L., Smith, S. V., Wattayakorn, G., Wulff, F., and Yanagi, T.: LOICZ BIOGEOCHEMICAL MODELLING GUIDELINES, LOICZ REPORTS & STUDIES, 5, 1996.
- DiFiore, P. J., Sigman, D. M., and Dunbar, R. B.: Upper ocean nitrogen fluxes in the Polar Antarctic Zone: Constraints from the nitrogen and oxygen isotopes of nitrate, *Geochem. Geophys. Geosyst.*, 10, <https://doi.org/10.1029/2009GC002468>, 2009.
- Hainbucher, D., Hao, W., Pohlmann, T., Sündermann, J., and Feng, S.: Variability of the Bohai Sea circulation based on model calculations, *J. Mar. Syst.*, 44, 153-174, <https://doi.org/10.1016/j.jmarsys.2003.09.008>, 2004.
- Huang, D., Su, J., and Backhaus, J. O.: Modelling the seasonal thermal stratification and baroclinic circulation in the Bohai Sea, *Cont. Shelf Res.*, 19, 1485-1505, [https://doi.org/10.1016/S0278-4343\(99\)00026-6](https://doi.org/10.1016/S0278-4343(99)00026-6), 1999.
- Jia, B., and Chen, X. e.: Application of an ice-ocean coupled model to Bohai Sea ice simulation, *Journal of Oceanology and Limnology*, 39, 1-13, 10.1007/s00343-020-9168-8, 2021.
- Kim, H., Park, G.-H., Lee, S.-E., Kim, Y.-i., Lee, K., Kim, Y.-H., and Kim, T.-W.: Stable isotope ratio of atmospheric and seawater nitrate in the East Sea in the northwestern Pacific ocean, *Mar. Pollut. Bull.*, 149, 110610, <https://doi.org/10.1016/j.marpolbul.2019.110610>, 2019.
- Liu, S. M., Zhang, J., and Jiang, W. S.: Pore water nutrient regeneration in shallow coastal Bohai Sea, China, *J. Oceanogr.*, 59, 377-385, <https://doi.org/10.1023/A:1025576212927>, 2003.
- Sigman, D. M., DiFiore, P. J., Hain, M. P., Deutsch, C., Wang, Y., Karl, D. M., Knapp, A. N., Lehmann, M. F., and Pantoja, S.: The dual isotopes of deep nitrate as a constraint on the cycle and budget of oceanic fixed nitrogen, *Deep-Sea Res. Pt. I*, 56, 1419-1439, <https://doi.org/10.1016/j.dsr.2009.04.007>, 2009.
- Smith, S. V., Buddemeier, R. W., Wulff, F., Swaney, D. P., Camacho-Ibar, V. F., David, L. T., Dupra, V. C., Kleyvas, J. A., San Diego-McGlone, M. L., McLaughlin, C., and Sandhei, P.: C, N, P Fluxes in the Coastal Zone, in: *Coastal Fluxes in the Anthropocene: The Land-Ocean Interactions in the Coastal Zone Project of the International Geosphere-Biosphere Programme*, edited by: Crossland, C. J., Kremer, H. H., Lindeboom, H. J., Marshall Crossland, J. I., and Le Tissier, M. D. A., Springer Berlin Heidelberg, Berlin, Heidelberg, 95-143, 2005.
- Wang, H., Li, Z., Lei, K., and Zhang, Z.: Analysis of Driving Forces and Variations of the Runoff and Suspended Sediment Discharge of the Daling and Xiaoling Rivers into the Sea over the Past Twenty Years, *Research of Environmental Sciences (in Chinese)*, 23, 1236-1242, 2010.
- Wankel, S. D., Kendall, C., Pennington, J. T., Chavez, F. P., and Paytan, A.: Nitrification in the euphotic zone as evidenced by nitrate dual isotopic composition: Observations from Monterey Bay, California, *Global Biogeochem. Cycles*, 21, <https://doi.org/10.1029/2006GB002723>, 2007.
- Ward, B. B.: Chapter thirteen - Measurement and Distribution of Nitrification Rates in the Oceans, in: *Methods Enzymol.*, edited by: Klotz, M. G., Academic Press, 307-323, 2011.
- Zhang, J., Yu, Z., Raabe, T., Liu, S., Starke, A., Zou, L., Gao, H., and Brockmann, U.: Dynamics of inorganic nutrient species in the Bohai seawaters, *J. Mar. Syst.*, 44, 189-212, <https://doi.org/10.1016/j.jmarsys.2003.09.010>, 2004.
- Zhang, J., Xia, B., Gui, Z., and Jiang, C.: Contaminative Conditions Evaluation of Sixteen Main Rivers Flowing into Sea Around Bohai Sea, in Summer of 2005, *Environmental Science (in Chinese)*, 28, 2409-2415, 2007.

Zhao, Y., Zhang, L., Chen, Y., Liu, X., Xu, W., Pan, Y., and Duan, L.: Atmospheric nitrogen deposition to China: A model analysis on nitrogen budget and critical load exceedance, *Atmos. Environ.*, 153, 32-40, <https://doi.org/10.1016/j.atmosenv.2017.01.018>, 2017.