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Biogeosciences
Discussions

Interactive comment on "Denitrification in sediments as a major nitrogen sink in the Baltic Sea: an extrapolation using sediment characteristics" *by* B. Deutsch et al.

B. Deutsch et al.

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We thank Prof. Joel Kostka and Dr. Matthew Schwartz for their very constructive comments and suggestions.

Please note, that we found some misspelled units in the results section (μmol N m-2 h-1 instead of μmol N2 m-2 h-1), a misspelling in table 2 ('Trask sorting coefficient' instead of 'Task sorting coefficient'), a wrong cited value in the introduction section (15810 μmol N m-2 h$-$1 instead of 3400 μmol N l-1 h-1), and a misspelling in the discussion section (p.2530, l. 19, Dn > 70% instead of Dw > 70%) that were corrected.

Please find our comments to the reviews below (RC: reviewer comment; AC: author

comment):

Response to the comments and suggestions of J. Kostka (Rev#1):

RC#1: Were the assumptions of the IPT method satisfied?

AC: The assumptions of the IPT are well described in the review of Steingruber et al. (2001): 1. The added 15NO3- does not interfere with denitrification of in-situ NO3-. This assumption is not valid if anammox is present, in which case an increase of N2 production with tracer concentration is observed. 2. Total denitrification of NO3- from the water column should increase linearly with the NO3- concentration in the overlying water (first order kinetics of denitrification). 3. Labelling of in-situ NO3- with 15NO3- in the water column and in the sediment must be homogenous. 4. A stable NO3- concentration gradient across the sediment water interface must be established shortly after 15NO3- addition.

All four conditions are met when genuine N2 production is independent of tracer concentration and the production of 15N-N2 increases linearly with tracer concentration. There was no tracer concentration dependency of genuine N2 production detected at any of the study sites (p»0.05). Therefore, the first assumption of the IPT could be validated and provides a negative proof of anammox for all study sites. Furthermore, the linear regression of the 15N-N2 production versus tracer concentration yielded a significant positive linear relationship for all stations (R2 > 0.88). Thus, the assumptions underlying the IPT could be assumed to be valid. We will add additional information to the text.

RC#2: How was the contribution of anammox determined?

AC: The contribution of anammox was determined according to Risgaard-Petersen et al. (2003). By conducting a concentration series tracer experiment with at least four concentrations, the existence of the anammox process (or other processes leading to an unsuccessful application of the IPT) can be tested by checking for a positive correlation between the genuine N2production and the amount of 15NO3- added. Since none of our experiments showed this positive correlation, we concluded that anammox did not exist. Slurry incubations were not carried out.

RC#3: The impacts/ controls of seasonal variation (temperature, organic matter inputs) and overlying water column nitrate concentration are not fully addressed in this study.

AC: These issues have been addressed to some extend in the discussion sections 4.1 (p. 2498, l. 16-28) and 4.3 (p. 2502, l.19-27, p. 2503, l. 18-28), however, not clearly enough as it seems.

While several studies point out that there is a summer to fall maximum, the one by Kähler identifies spring as a short – one month – peak rate of denitrification, albeit measured with the acetylene block method at the time. Peak rates triggered by river runoff may occur in spring and actually cause a shift to more Dw than we observed throughout the year. Rates would have to be much higher then, if a significant overall yearly increase was to be expected: a doubling of the activity, as observed by Kähler, during one month results in a yearly increase of but 1/12 or ∼8 %. Organic fresh material sedimenting in a bloom situation may enhance denitrification rates over the level sustained by the more refractory carbon depicted in the surface sediment carbon contents. On the other hand studies of Graf (1987) in the Baltic have shown that post-bloom redox conditions in sediments are often such, that oxygen supply is no longer favorable and therefore strong C-supply may well reduce denitrification rates. Overall the controls are manifold and sometimes antagonistic in effect and we may expand somewhat on this part of the discussion, since the lack of data from spring season is the most likely bias to our extrapolation.

RC#4: The impact of advective flow was not incorporated into the experimental approach. Sandy sediments tend to have low organic carbon contents. Thus, calculation of basin-wide denitrification rates that include sandy sediments, without consideration of advection, is likely to underestimate N removal.

AC: The reviewer is correct, that in sandy sediments the rates of denitrification are often underestimated by experimental setups without simulation of advective flow. This was shown in several studies by Gao et al. (2010) and Gihring et al. (2010), which we cited in our text. We addressed this in our section ‘uncertainties’ and added also measured rates from other studies. However we think that in the Baltic Sea the underestimation of the denitrification rate without simulating advective flow is much lower than in the other areas which are mentioned in the above cited publications (Wadden Sea, Gulf of Mexico). The major differencees between these sites and the Baltic Sea are that the Baltic Sea is not or only marginally influenced by tides. This means that advective flow is only forced by baroclinic transport and wind waves, which cause advective flow down to water depths of wavelength/2 m (Precht & Huettel, 2004). Furthermore permeability in Baltic sediments is almost an order of magnitude lower than in other seas, reflecting lower hydrodynamic energy. Thus, k is on the order of 2–8 x 10ˆ-12 mˆ-2 along much of the southern areas representative for this extrapolation (Forster et al. 2003) reaching maximum values of around 10ˆ-11 mˆ-2. By contrast the North Sea has k well in excess of 10ˆ-11 mˆ-2 (Janssen et al. 2005) and Gihring et al. (2010) also reports values well above 10-11 for the investigation at the Gulf of Mexico. But nevertheless we are aware that our estimated N-removal rates from sandy sediments might mark the lower limit because of an underestimation. We will add more information to the text.

RC#5: In the first paragraph of the discussion, the authors state that an increase in temperature would “automatically” result in an increase in the nitrification rate and an increased supply of nitrified nitrate. This statement should be revised. Nitrification rate would also depend on a number of other factors including bioturbation, organic matter loading, and oxygen supply to the ammonium oxidation zone.

AC: The reviewer is correct, that an increase in the temperature does not automatically lead to an increased nitrification rate, unless all other conditions are favorable. However, experiments presented in the study of Gihring et al. (2010) showed a linear correlation between potential rates of nitrification and the temperature. Given no other constraints by regulating factors such as bioturbation we would anticipate an increase of internal nitrate supply to coupled denitrification. We will reformulate the statement.

RC#6: In the second paragraph of the discussion, the authors state that their rate measurements indicate that denitrification is primarily controlled by organic carbon content of the sediments. This statement should be toned down and revised. The factors likely to control denitrification rate were not completely addressed as evidenced by the authors own statements in the discussion section.

AC: The reviewer is correct that we cannot draw this conclusion that the denitrification rate in the Baltic Sea is generally controlled by the organic carbon content. Since we only measured roughly during 2 seasons (summer, autumn) we can hardly say anything about the temporal variation of denitrification at our stations. We modify the text and now argue that the spatial variation of denitrification seems to be controlled by the organic carbon content.

RC#7: From line 16 page 2500 to line 11 page 2502, the authors provide a speculative interpretation of water column denitrification and the expansion of the hypoxic/ anoxic zones. I recommend that this section be removed from the discussion. Further, I recommend that the calculation of the response of nitrogen removal rates due to expansion of the anoxic zone be removed from the paper. No new rates from the water column are provided in this study, and the rate measurements used in the author's calculations were not direct rate measurements. The estimate of the expansion of the anoxic zone is equally based on speculation. Water column anoxia is likely to be dependent on regional factors such as nutrient inputs which are not addressed in this study.

AC: The anoxia in the Baltic Sea is only partly dependent on regional factors. The narrow connection to the North Sea, the high (intensive) freshwater input into the central parts of the Baltic in combination with the specific structure (several deep basins separated by shallow sills) favors water column stratification and consequently the oc-

currence of water column anoxia in the central Baltic Sea. Because of these characteristics, the Baltic Sea in its current form always suffered from – a kind of – natural anoxia. The extension of the anoxic area is primarily controlled by the non-periodical salt water intrusions from the North Sea. This natural phenomenon is strongly enhanced by eutrophication and is one of the major threats for the Baltic Sea ecosystem (see papers of Conley et al. 2009). After long periods of stagnation, the oxycline is located predominantly at depths of around 100m (e.g. Conley et al. 2009b). Since future scenarios assume an increase in nutrient emissions because of increased population and increased meat consumption (Darraq et al. 2005) an increase in the oxycline and consequently an extension of the anoxic area seems realistic. We therefore think that this section in our manuscript where we examine the loss in N-removal capacity via sedimentary denitrification by a realistic extension of the anoxic zone is an important part of our manuscript. We will add more information about anoxia in the Baltic Sea and our motivation for examining a shift from 100 to 80 m to the introduction section.

The rates from Brettar & Rheinheimer (1991) which we used for our calculation of the total N-removal in the Baltic Proper were determined with the Acetylene Block method, which – as far as we know – is a direct method to calculate rates of denitrification and was used in many studies before the IP method was developed. The calculation of the water volume with O2 concentrations in the range in which Brettar & Rheinheimer measured denitrification was done by using data from routine monitoring cruises from the period 01.01.2005 – 31.12.2006. Since we wanted to compare our benthic data with results from other studies (e.g. Shaffer & Rönner, 1984; Voss et al. 2005) which all present combined estimates from sediment and water column denitrification together, it was necessary to calculate water column denitrification. We know that the Acetylene Block method is known to underestimate the true denitrification rates because of an inhibition of the coupled nitrification-denitrification, but, in our opinion these were the best rates that could be used in an extrapolation.

RC#8: The uncertainities revealed by the authors and the abovementioned comments raise questions about the accuracy of the authors' calculations of N removal and their N budget. These questions should be addressed.

AC: We are aware that our extrapolation approaches – like every other extrapolation approach - are based on some assumptions and are subject to a certain level of uncertainty. By adding the paragraph uncertainties to our manuscript we explicitly addressed this topic and discussed there the missing seasonal aspect, the missing consideration of advective flow in our IP measurements in sands, and finally our choices of the 100m and 80m depth for the oxycline.

RC#9: Statements that refer to the impacts of advective flow and nitrate supply on page 2503 need to be modified. It is true that the maximum rate reported in the present study is similar to the maximum rate reported by IPT in the Gihring et al. study. However, much higher rates of N2 production were observed by Gihring et al and others using the N2/Ar method in core incubations exposed to continuous advective flow, which more effectively mimics the in situ pressure and flow conditions. Thus, the authors should state that much higher rates have been measured in permeable or sandy marine marine sediments when advective flow has been adequately taken into account.

AC: We will modify the text (see our response to comment #4).

RC#10: In addition to the references given, studies by Rao et al. should also be cited and incorporated into the discussion.

AC: We thank the reviewer for suggesting these two publications. We incorporate the study of Rao et al. (2008) to the manuscript.

RC#11: The authors state that the external supply of nitrate was not important in their study. This statement should be removed. Since temporal and seasonal variation has not been addressed, the authors cannot be certain about the influence of external nitrate supply.

AC: As written in the text (p.2498 l. 22-28) at 8 of our 12 stations the share of the

coupled nitrification-denitrification (Dn) was >70%, which indicates to us, that during our investigation the external supply of nitrate was of minor importance. The reviewer is right, that we cannot be certain about the influence of external nitrate supply in other areas or during other seasons. We addressed this topic on p.2503 l.18-21. If requested we can expand this part of the discussion section. We furthermore apologize for a misprint in the text (p.2503, l. 19) where Dw >70% was written instead of Dn > 70%. The term was corrected.

RC#12: The citation of Gao et al. should also be modified.

AC: We will modify the citation.

Response to the comments and suggestions of M. Schwartz (Rev#2):

RC#1: The authors would strengthen the article by further justifying their rationale for each of the five methods used to extrapolate data across the Baltic Sea region. As it stands, the lack of such discussion leaves the impression that the models were chosen without an intentional purpose in mind.

AC: Extrapolation of the denitrification rates to larger scales was based on the current knowledge of the factors governing the process, explicitly organic carbon content in sediments, and grain size which are both closely related. We used the datasets that were available to us in order to investigate the variability of the results derived from the different approaches. Both datasets on sediment distribution were relatively new and seemed to be the best available for the Baltic Sea region. The set of Corg data was the largest and only one available of Corg of surface sediments. We will add additional information to the text.

RC#2: I remain somewhat confused as to why the authors chose to model the oxicline from 100m to 80m. Why was the latter depth chosen? Was it based on actual model results or observatiosn from sub-basins? This discussion can/should be expanded at the bottom of page 12.

AC:For a detailed description why we had chosen these two depths, see our response to the comment #7 of J. Kostka. We will expand the discussion to address this question.

RC#3: Two general editorial suggestions: 1) the formatting for new paragraphs is inconsistent and should be indicated by a distinct line break; 2) many sentences that start with a leading clause are missing a required comma before the main sentence. Similarly, many in-sentence parenthetical references require the use of either commas or parentheses to distinguish them from the main text. Many cases of missing commas leading to confused sentences were identified throughout the paper.

AC: We will carefully revise the manuscript.

RC#4: On page 10 (line 10), I think that the term "indicates" overstates the certainty of the conclusion drawn and suggest replacing it with "suggests".

AC: The term will be replaced.

RC#5: On page 12 (lines 6 and 7), I do not understand the parenthetical phrase between the dashes. Do you mean that N-fixation is important in areas other than the central Baltic Sea?

AC: Nitrogen fixation occurs mainly in the central Baltic (Baltic Proper) and in the southern Bothnian Sea but also – less intensive - in other parts like the western Baltic.

Other specific editorial comments/questions:

p.1, l. 28: delete ",too" from end of Abstract.

Term will be deleted.

p. 2, l 2: I am not familiar with the prefix "Mio" used in "Mio tons".

We will replace 'Mio' with 10ˆ6

p. 2, l 8: make a subscript the "r" in Nr.

Term will be corrected.

p. 2, 112: delete "the study of" before "Voss et al. (2005)".

Term will be deleted.

p.4, l.11: I am unfamiliar with the use of the letter Ø in this context.

We replace Ø by 'diameter'

p.5, l. 6: to what does the "p15" refer?

p15 is the production rate of 15N-N2. We replaced p15 by the more common term 'production rate of 15N-N2'.

p.6, l.2 and 12: spell out "5" as "five".

Term will be corrected.

p.7., ll 20-23: place into parentheses the station names used to define each set of stations (e.g., "..with muddy sediments (Kreidesegler and NS14), dentrification rates: : :")

Station names will be added.

p.9 ll 22-23 and 28: replace" very often" with "frequently" or "commonly".

Term will be replaced.

p. 11, l.8: replace "nowadays" with "now".

Term will be replaced.

p.11, ll21-23: not a complete sentence.

Will be changed to: 'The largest hypoxic water-body of the Baltic Sea is located in that area, and water-column denitrification might play an important role for the total N-losses from the system.'

p.13, l 3: change ": : :demonstrate that anoxic sediments: : :" to ": : :demonstrate that increasing the areal coverage of anoxic sediments: : :."

Term will be corrected.

p.13, l. 5: change "remarkable" to "remarkably".

Term will be corrected.

p. 13, l. 13" insert "of" into "the question OF whether: : :"

Term will be inserted.

p. 13, l. 23: change sentence to read ": : :in Baltic sediments are high, implying: : :"

Sentence will be corrected.

Table 3: format to better separate/differentiate between different approached (i.e., rows).

Table 3 will be revised.

Table 5: Gulf of Finland mis-spelled.

Term will be corrected.

Additional literature cited:

Forster, S., B. Bobertz, and B. Bohling (2003). Permeability of Sands in the Coastal Areas of the Southern Baltic Sea: Mapping a Grain-size Related Sediment Property. Aquatic Geochem. 9: 171 – 190.

F. Janssen, P. Faerber, M. Huettel, V. Meyer, and U. Witte (2005) Pore-water advection and solute fluxes in permeable marine sediments (I): Calibration and performance of the novel benthic chamber system Limnol. Oceanogr., 50(3): 768–778.

Graf G (1987) Benthic response to the annual sedimentation pattern; In: Rumohr, J.; Walger, E.; Zeitschel, B. (ed.) Lecture notes on coastal and estuarine studies, Vol. 13. Seawater-sediment interactions in coastal waters. An interdisciplinary approach.

Springer-Verlag, New York, p. 84-92.

A. Darracq, F. Greffe, F. Hannerz, F. Destouni, V. Cvetkovic (2005). Nutrient transport scenarios in a changing Stockholm and Mälaren valley region. Water. Sci. Technol. 51: 31-38.

E. Precht, M. Huettel (2004). Rapid wave driven advective pore water exchange in a permeable coastal sediment. Journal of Sea Research 51: 93-107.

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