

## ***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.***

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General comments-

In this study, the authors perform denitrification rate measurements using the isotope pairing approach in sediments from a variety of subbasins in the Baltic Sea. Sediment characteristics (organic carbon content and porosity) as well as water column chemistry (oxygen, dissolved inorganic nitrogen) were also determined at the sampling sites. Nitrogen removal was then extrapolated using a number of different approaches to the entire Baltic Sea using maps of sediment characteristics.

Denitrification is a critical process that controls N loss in coastal marine ecosystems.

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As the authors point out, few studies have incorporated direct rate measurements into a N mass balance of entire enclosed marine basins. Thus, this study is timely and will be of interest to the biogeosciences community. The authors have used a straightforward approach, the isotope pairing technique (IPT), to measure denitrification rates that is appropriate when applied so that all of the necessary assumptions as outlined by the original method (Nielsen, 1992; cited in ms) and the modifications outlined by Risgaard-Petersen et al. (2003; cited in ms) are satisfied. Rates were measured in sandy and muddy sediments from a number of subbasins in the Baltic. Rates showed a good correlation with the organic carbon content of the sediments. Nitrogen removal for the entire Baltic Sea was then estimated by calculating a sediment specific denitrification rate that was then extrapolated over large areas of the seafloor using maps of sediment characteristics. Drawbacks to the study are that the rate measurements do not capture the natural temporal and spatial variability of the Baltic and the experimental design requires further explanation. Due to these drawbacks, conclusions of the study could be questioned. Substantive comments are provided below.

Specific comments-

Were assumptions of the IPT method satisfied? In section 2.2 of the methods, the authors state that they used three replicate incubation cores per site. Was this just 3 cores total? Was a time course conducted and were linear rates of N<sub>2</sub> achieved? Were only end points examined? More detail on the core incubations should be provided to show the strength of the rate determinations. IPT should be conducted by sampling replicate cores over a time course and then regressing the concentration of excess <sup>29</sup>N<sub>2</sub> and <sup>30</sup>N<sub>2</sub> with time. Linearity of N<sub>2</sub> production should be tested in a time course for each sample site. If this was not done, the confidence in the rates would be lessened and that should be identified by the authors.

In section 2.3, the authors provide few details on how the assumptions of IPT were satisfied. Incubations at multiple tracer concentrations are a plus. However, these incubations should be carried out with adequate replication in a time course (see above

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comments). Also, how was the contribution of anammox determined? Were slurry incubations conducted? If so, slurries were not mentioned. Anammox and dissimilatory nitrate reduction to ammonia (DNRA) are both processes that have been identified to occur in the Baltic Sea. Based on the information provided in this paper, it is unclear whether these processes were accounted for in the experimental design. The authors should further describe how the assumptions of IPT were satisfied in the methods section. Then in the discussion section, a qualifying statement should be made if anammox and DNRA were not completely addressed.

As the authors admit in the discussion section, a drawback to this study is that spatial and temporal variation is not incorporated into the experimental design. Rates were not measured during the winter and only once during the spring. Water column nitrate is likely to be elevated during winter/ spring due to runoff inputs to this heavily industrialized area. Thus, the impacts/ controls of seasonal variation (temperature, organic matter inputs) and overlying water column nitrate concentration are not fully addressed in this study. This is a substantial concern. According to the author's own statements in the discussion section, these are the major factors likely to control denitrification rates in the Baltic and yet they are not fully incorporated into the study.

A substantial number of the sites studied contain permeable or sandy sediments. Advective flow has been shown in a large number of previous studies to have a large effect on the rates of biogeochemical processes, including denitrification, in permeable sediments (DeBeer et al., 2005; Rao et al., 2008a&b; Gihring et al., 2010; Gao et al., 2010). However, again by the authors own admission, 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.

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

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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.

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.

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.

Section 4.3 Uncertainties. The uncertainties revealed by the authors and the above-mentioned comments raise questions about the accuracy of the authors calculations of N removal and their N budget. These questions should be addressed.

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 N<sub>2</sub> production were observed by Gihring et al and others using the N<sub>2</sub>/Ar method in core incubations exposed to continuous advective flow, which more effectively mimics the in situ pressure and flow conditions. Thus, the authors

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should state that much higher rates have been measured in permeable or sandy marine sediments when advective flow has been adequately taken into account. In addition to the references given, studies by Rao et al. should also be cited and incorporated into the discussion:

RAO, A. M. F., M. J. MCCARTHY, W. S. GARDNER, AND R. A. JAHNKE. 2007. Respiration and denitrification in permeable continental shelf deposits on the South Atlantic Bight: Rates of carbon and nitrogen cycling from sediment column experiments. *Continental Shelf Res.* 27: 1801–1819.

RAO, A. M. F., M. J. MCCARTHY, W. S. GARDNER, AND R. A. JAHNKE. 2008. Respiration and denitrification in permeable continental shelf deposits on the South Atlantic Bight: N<sub>2</sub> : Ar and isotope pairing measurements in sediment column experiments. *Continental Shelf Res.* 28: 602–613.

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.

The citation of Gao et al. should also be modified. The correct reference is:

Gao, H., F. Schreiber, G. Collins, M. M. Jensen, J. E. Kostka, G. Lavik, D. de Beer, H. Zhou, M. M. M. Kuypers. 2010. Aerobic denitrification in permeable Wadden Sea sediments. *The ISME Journal* 4: 417-426.

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