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Biogeosciences Discussions

Interactive comment on "Nitrous oxide water column distribution during the transition from anoxic to oxic conditions in the Baltic Sea" *by* S. Walter et al.

S. Walter et al.

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General Comments This manuscript describes nitrous oxide variability in the Baltic Sea about nine months after an event of inflow from the North Sea had occurred in January 2003. This intrusion carried oxygen to the otherwise anoxic subsurface waters of the Baltic, and at the time the study was carried out, it had resulted in a variety of re-dox environments in the re-gion, ranging from fully oxic to anoxic. Since nitrous oxide cycling is highly sensitive to ambient oxygen levels in the low range, the prevailing con-ditions made the Baltic a natu-ral laboratory to investigate pathways of its production and consumption. Consequently, the results being reported here will be of consider-able interest to those engaged in ma-rine nitrous oxide research. Some of the findings of this study are a bit unexpected and the nitrous oxide concentra-tions generally lower

than one would expect from the prevailing oxygen deficiency. In the shallow western basins, the vertically homogenous, near-equilibrium concentra-tions are as per expectations, as is the non-linear increase in nitrous oxide concentration as the ambient oxygen content approaches (but does not reach) suboxic levels in bottom waters of the Bornholm Basin. Farther to the east and to the north in the eastern and western Gotland Basin where the deep water was still anoxic, low nitrous oxide values occurred, again as expected, in the bottom water. Moreover, the local minimum in nitrous oxide associated with the denitrifying layer char-acterized by a nitrite maximum located just above the anoxic deep water is also consis-tent with the pattern observed in the open-ocean suboxic zones. But the nitrous oxide peaks located above and below this feature are much smaller. One would expect large nitrous oxide accumulation at the suboxic-anoxic interface given the inhibition of nitrous oxide reduction by sulphide (e.g. Senga et al., 2006), but proba-bly the hydrogen sulphide levels are not high enough for this to happen. One relatively major point that I wish to make is that the conclusion that nitrification is mainly responsible for the production of nitrous oxide may be correct, but it is not fully supported by the data. Moreover, even if such is the case, there would still be consumption of nitrification-produced nitrous oxide in reducing waters. Thus, among other things (e.g. assumed yield of nitrous oxide during nitrification), given the possible production of nitrous oxide through processes other than nitrification and its consumption in reducing waters the nitrification rate estimate probably has a very large error bar.

We agree with the referee that our data are only indirectly indicating nitrification as the main production pathway and therefore they are not a direct proof for nitri-fication. Our conclusions are mainly based on the fact that we found positive cor-relations between N2O excess and oxygen utilization. However, we appreciate that other possibilities such as denitrification cannot be excluded definitely. So we modified the term “production rate” to a “net production” rate, which includes consumption processes as well.

Specific Comments Title: Could be rearranged to “Distribution of nitrous oxide in the

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Baltic Sea water column during the transition from anoxic to oxic conditions".

We agree with the referee and changed the title.

Page 730, line 20: The statement, "No indications for advection of nitrous oxide by North Sea Water were found" is a little misleading. With a concentration of Ÿ10 nM in the North Sea Water, nitrous oxide is definitely advected into the Baltic even though it may not raise the inventory for the Baltic.

We agree with the referee and changed the text.

Page 731, line 15: The authors probably mean nitric oxide instead of nitrate, which of course is not an intermediate of nitrogen redox chemistry.

We agree with the referee and changed the text.

Page 731, line 24: Change "and depletion in anoxic layers" to ", a general depletion within the core of suboxic water column, and invariably near-zero values in anoxic waters" (I believe the authors regard "suboxic" as "denitrifying").

We agree with the referee and changed the text.

Page 732, line 4: Change "Oceans emit more than 25% of natural produced nitrous ox-ide" to "Oceans account for over 25% of total natural emissions of nitrous oxide to the atmosphere".

We agree with the referee and changed the text.

Page 733, line 8: Change "highly depends" to "strongly depends".

We agree with the referee and changed the text.

Page 734, line 5: Change "affected" by "inflowing". We do not agree with the referee. The term "affected bottom water" describes Bal-tic Sea bottom water, which is affected by the inflowing North Sea water, not the inflowing North Sea water itself.

Page 736, line 7: Change "single basins" to "each basin".

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We agree with the referee and changed the text.

Page 736, line 9: Change “the single basins” to “any given basin”.

We agree with the referee and changed the text.

Page 736, lines 10-11: Change “mole weight of nitrous oxide (44 g mol-1)” to “molecular weight of nitrous oxide (44)”, and “single basins” to “basin”.

We agree with the referee and changed the text.

Page 736, line 22 and elsewhere in the manuscript: I assume the unit “ton” is the metric ton, in which case it should be spelled as “tonne”.

We agree with the referee and changed it throughout the text.

Page 736, lines 25, continued on the next page, line 1: Change “Vbasin is the calculated volume of the basins (km3)..., n is the mole weight of nitrous oxide (44 g mol-1)” to “Vbasin is the calculated volume of the basin (km3), n is the mole weight of nitrous oxide (44)” (note reference is already given in lines 12-13).

We agree with the referee and changed the text.

Page 737, line 15: Include saturation values for stations 360 and 22 as for other basins.

The given saturation value for the Mecklenburg Bight includes the values for the Kiel and Lübeck Bights. We changed the sentence to clarify our statement.

Page 739, line 7: To me complete oxygenation means 100% saturation, which is not the case; will “well oxygenated” not be better?

We agree with the referee and changed the text.

Page 743, line 18 - Page 744, line 7: The observed local minimum in nitrate is presumably caused by denitrification (and/or anaerobic ammonium oxidation). The geochemical signal such as this is a cumulative feature, and the lack of denitrification activity within this layer, only indicates the absence of this process at the time of observations. The

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lo-cal nitrous oxide minimum associated with the minimum in nitrate is typical of most suboxic zones suggesting its reduction to molecular nitrogen (e.g. Naqvi and Nornha, 1991), and may not be caused by the inflow as suggested by the authors. Similarly, pos-sible contribution of denitrification to the formation of nitrous oxide peaks below and above the nitrous oxide minimum cannot be ruled out.

We agree with the referee that cumulative signals might be possible. However, due to the complete absence of the typical, very pronounced N2O peaks as ob-served at the oxic/suboxic interfaces of the Arabian Sea and the ETNP, we think that denitrification is of minor importance.

Page 744, lines 14-15 and the following discussion: The decrease in nitrous oxide con-centration below about 20 micromolar oxygen (red symbols in Fig. 8) is intriguing. Else-where in the ocean such a decrease normally occurs at oxygen $<$ 1 micromolar, the threshold from the oxic to suboxic metabolism (see Naqvi et al., 2003). Even ac-counting for the insensitivity of Winkler procedure at low oxygen concentrations, this difference is too large to be attributed to analytical errors. On page 745, the authors invoke differential response of various microorganisms to am-bient oxygen. This part of the discussion is a little confusing. It is not clear to me if the authors are implying that nitrifier-denitrification leads to nitrous oxide consumption. I do not think this would be the case.

In this part we tried to make clear, that there is no distinct threshold due to differ-ent O2 requirements of bacteria and their enzymes, the possibility of other con-verting processes and due to mixing processes. Especially in environments with rapid changes of conditions, organisms should be able to react very quickly. It cannot be expected that all of them are adapted in the same way what might lead to similar but not exactly the same thresholds.

The alternative explanation that the trend observed might result from spatio-temporal evolution of oxic conditions as the inflowing water advects through the Baltic also raises

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some questions. As the authors have shown the anomalies are found in anoxic basins. But the waters in the Gotland Basin are derived from the Bornholm Basin where the deep waters are nitrous oxide enriched. What happens to the high nitrous oxide content of this water when it mixes with anoxic waters? Can the mixing alone lead to a depletion of nitrous oxide while its dissolved oxygen is not fully consumed? If not then the signature of its high nitrous oxide content should still be preserved even if enough time has not elapsed for (further) production of nitrous oxide.

We assume that it is possible to preserve a previous signal. Beside the possibility of a preserved previous denitrification signal, it might also be possible, that these local N2O minima are caused by uplifted (from the inflow event in August 2002) previously anoxic Bottom Water with low N2O concentrations. The water layers can be clearly identified (Feistel et al. 2003), thus, here it seems to be not a ques-tion of mixing to explain the anomalies. However, in general we agree that mixing processes might play a role for the N2O profiles.

Interactive comment on Biogeosciences Discuss., 3, 729, 2006.