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3, S282-S286, 2006

Interactive Comment

# 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.

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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 redox environments in the region, ranging from fully oxic to anoxic. Since nitrous oxide cycling is highly sensitive to ambient oxygen levels in the low range, the prevailing conditions made the Baltic a natural laboratory to investigate pathways of its production and consumption.

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Consequently, the results being reported here will be of considerable interest to those engaged in marine nitrous oxide research.

Some of the findings of this study are a bit unexpected and the nitrous oxide concentrations generally lower than one would expect from the prevailing oxygen deficiency. In the shallow western basins, the vertically homogenous, near-equilibrium concentrations 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 characterized by a nitrite maximum located just above the anoxic deep water is also consistent 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 probably 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.

### Specific Comments

Title: Could be rearranged to "Distribution of nitrous oxide in the Baltic Sea water column during the transition from anoxic to oxic conditions".

# **BGD**

3, S282-S286, 2006

Interactive Comment

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Interactive Discussion

**Discussion Paper** 

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 ~10 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.

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

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").

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

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

Page 734, line 5: Change "affected" by "inflowing".

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

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

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".

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".

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).

# **BGD**

3, S282-S286, 2006

Interactive Comment

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Interactive Discussion

**Discussion Paper** 

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

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

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 local 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, possible contribution of denitrification to the formation of nitrous oxide peaks below and above the nitrous oxide minimum cannot be ruled out.

Page 744, lines 14-15 and the following discussion: The decrease in nitrous oxide concentration below about 20 micromolar oxygen (red symbols in Fig. 8) is intriguing. Elsewhere 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 accounting 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 ambient 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. 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 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

## **BGD**

3, S282-S286, 2006

Interactive Comment

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**Discussion Paper** 

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.

#### References

Naqvi, S. W. A. and Noronha, R. J.: Nitrous oxide in the Arabian Sea, Deep-Sea Res., 38, 871-890, 1991.

Naqvi, S. W. A., Naik, H., and Narvekar, P. V., The Arabian Sea, in: Biogeochemistry of marine systems, edited by: Black, K. and Shimmield, G., p. 157-207, Blackwell Publishing, Oxford, 2003.

Senga, Y., Mochida, K., Fukomori, R., Okamoto, N., and Seike, Y.: N2O accumulation in estuarine and coastal sediments: The influence of H2S on dissimilatory nitrate reduction, Estuar. Coast. Shelf Sci., 67, 231-238, 2006.

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

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3, S282-S286, 2006

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