

Interactive comment on “Hydroxylamine (NH₂OH) in the Baltic Sea” by S. Gebhardt et al.

Anonymous Referee #1

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Data are presented for dissolved hydroxylamine and nitrous oxide at a range of sites in the Baltic Sea with the aim of establishing the processes that determine their distribution. This is of value as the first such dataset in this region, but the authors present little in the way of robust and supportable new insights into the source and cycling of hydroxylamine. This is partly due to the physico-chemical complexity of this region and also methodological shortcomings. They present a less than thorough analysis and discussion of the dataset and poorly-supported conclusions, and I cannot recommend publication in its present form. The authors should consider the following points.

Specific comments The methodology is based upon the oxidation of hydroxylamine by Fe (III), and is applied to waters with a range of oxygen concentration. Fe concentration and redox status vary significantly between oxygenated surface and sub-oxic waters at depth in the Baltic, as shown by Brugmann et al (Applied Geochemistry, 13:359-368, 1998). This has consequences for the hydroxylamine measurement and the data presented. Firstly, the recovery factor, and so effectiveness of the methodology, may vary

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dependent upon ambient Fe(III) level and redox status. The authors identify this at the end of Section 2.3, but do not examine it in any detail. The only confirmation of the recovery factor is two experiments using the same water from a single site, (which I assume was oxic). Thus the accuracy of the method is open to question, and the presented hydroxylamine distribution may reflect variation in the recovery efficiency under different redox conditions, rather than real differences in hydroxylamine concentration. The authors need to undertake and present further tests to confirm validity in different redox matrices and water of variable Fe concentration.

The impact of Fe availability on hydroxylamine also has implications for interpretation of the data. Bruggmann et al (1998) show that influx of seawater in the deeper sub-oxic water in the Gotland Deep caused an 80-fold decrease in dissolved iron. Such a shift in Fe availability suggests that the observed hydroxylamine distribution may be more strongly influenced by this sink process, as opposed to source process such as nitrification. At the very least this requires consideration in the discussion, as it may negate any conclusion on the source of the hydroxylamine. Presentation of Fe data (if available) and revision of the discussion to consider the role of Fe in determining hydroxylamine distribution are essential.

North Sea water intrusion is identified at Station 286, one of the most north-easterly stations; but there is no explanation, or T-S data shown, to examine the contribution of N. Sea water at the other sites. The authors note that a source of hydroxylamine in North Sea waters is speculative, and do not find a relationship in their data. The highest hydroxylamine values were all in the south-west Baltic - mainly in the mixed layer at Stations 22, 360, & 133, and from just below the mixed layer at Station 113 - which suggests a localised source, that could be freshwater input (or N. Sea water?). The elevated hydroxylamine concentration between 20 and 40m at 113 Station may be an intrusion of water, possibly from the mixed layer at Stations 22, 360 & 133. Presentation, further analysis and interpretation of the associated hydrographic data is required to identify trends and explain the higher levels of hydroxylamine and nitrite in

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the water in this region.

The authors do not present hard evidence that hydroxylamine was produced by nitrification, though their data includes some factors against, it such as the lack of relationship between hydroxylamine and O₂ and N₂O. Instead, they opt to refute arguments against active nitrification per se, rather than focussing upon whether nitrification could explain the observed hydroxylamine distribution. There is much data in the literature regarding rates, depth distributions, and controls of nitrification and the nitrogen budget of the Baltic that would be of considerably more value to consider than issues such as light inhibition. The strongest piece of evidence, that of a correlation between nitrite and hydroxylamine, is merely noted and not followed up in the discussion of potential hydroxylamine sources. The authors should look at the literature regarding nitrite (NO₂⁻) accumulation in upwelling regions for insights into the potential hydroxylamine source mechanisms.

Technical

It is difficult to do the data justice in such a short paper, particularly across such a range of conditions. The lack of inclusion of profiles from Station 22 and 360 in Fig 3 is an oversight, as these are identified as important in Fig 4 and in the discussion in identifying the source of the hydroxylamine.

The lack of hydrographic data hinders interpretation. Temperature, salinity or density data should be included in all profiles, particularly in Fig 3c to identify the position of the N. Sea water intrusion.

Fig 3c shows sharply contrasting hydroxylamine concentration at almost identical O₂ concentrations at 80 and 90m at Station 286, which should be mentioned.

There is no relationship between hydroxylamine and nitrate and so Fig 4a should be removed.

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