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# Hydroxylamine (NH<sub>2</sub>OH) in the Baltic Sea

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**BGD**

1, 709–724, 2004

## Hydroxylamine (NH<sub>2</sub>OH) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004

## Abstract

The vertical distribution of dissolved hydroxylamine ( $\text{NH}_2\text{OH}$ ) was measured for the first time at 10 stations in the western, southern and central Baltic Sea during a cruise in February 2004. The distribution of dissolved  $\text{NH}_2\text{OH}$  was complex due to the interplay of in-situ production in the shallow western and southern Baltic Sea and the hydrographical setting in the central Baltic Sea caused by the major North Sea water inflow event in January 2003. We conclude that nitrification might be the major source of  $\text{NH}_2\text{OH}$ , whereas anaerobic ammonium oxidation (anammox) appeared to be negligible. We suggest that a “fresh” nitrifying system, in which the  $\text{NH}_4^+$ -oxidation rates exceeded the  $\text{NO}_2^-$ -oxidation rates, favoured the build-up of  $\text{NH}_2\text{OH}$ .

## 1. Introduction

Hydroxylamine ( $\text{NH}_2\text{OH}$ ) is an intermediate in two important microbial processes of the nitrogen cycle: It is formed during nitrification ( $\text{NH}_4^+ \rightarrow \text{NH}_2\text{OH} \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$ ) (e.g. Arp and Stein, 2003) as well as during anaerobic ammonium oxidation (anammox:  $\text{NO}_2^- \rightarrow \text{NH}_2\text{OH} + \text{NH}_4^+ \rightarrow \text{N}_2$ ) (Jetten, 2001). Furthermore,  $\text{NH}_2\text{OH}$  is a precursor of nitrous oxide ( $\text{N}_2\text{O}$ ) as a side product during nitrification (e.g. Arp and Stein, 2003). Oceanic nitrification is a major formation pathway of dissolved  $\text{N}_2\text{O}$  in the ocean (Bange and Andreae, 1999). Since oceanic  $\text{N}_2\text{O}$  emissions are of significant importance for the Earth’s climate (Montzka et al., 2003; Prather et al., 2001), deciphering the distribution of potential precursors such as  $\text{NH}_2\text{OH}$  is important to understand the formation pathways of  $\text{N}_2\text{O}$ . However, there are only a few published measurements of dissolved  $\text{NH}_2\text{OH}$  in oceanic environments such as the Yaquina River estuary in Oregon (Butler et al., 1987), a coastal lagoon in California (Butler et al., 1988) and the continental shelf off Oregon (Von Breyman et al., 1982). Results from an early laboratory study and the Yaquina Bay suggested that nitrification might be the principal formation process of  $\text{NH}_2\text{OH}$  (Butler et al., 1988; Rajendran and Venugopalan, 1976).

**BGD**

1, 709–724, 2004

## Hydroxylamine ( $\text{NH}_2\text{OH}$ ) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004

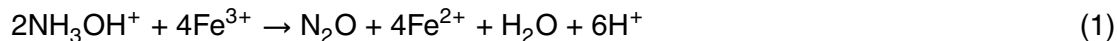
The Baltic Sea consists of a series of basins (Arkona, Bornholm, western and eastern Gotland Basins; see Fig. 1) with restricted horizontal water exchange. The fresh-water supply from the rivers and the discontinuously inflowing saline North Sea water result in a surface layer with lower salinity, and more saline deep and bottom water masses. The permanent halocline between these layers restricts the vertical exchange and is the reason for the development of stagnant deep waters accompanied by oxygen depletion and anoxia with accumulation of hydrogen sulphide. A major inflow of North Sea water, terminating the ongoing stagnation period in parts of the central Baltic Sea basins, occurred in January 2003 (Feistel et al., 2003; Nausch et al., 2003).

Here we present our measurements of dissolved  $\text{NH}_2\text{OH}$  from 10 stations in the western, southern and central Baltic Sea. The cruise took place on board the German research vessel Gauss (expedition no. 11/04/01) from 11 February to 22 February 2004 as part of the Cooperative Monitoring in the Baltic Sea Environment (COMBINE) program of the Baltic Marine Environment Protection Commission (the so-called Helsinki Commission, HELCOM, see <http://www.helcom.fi>). The locations of the stations are shown in Fig. 1.

## 2. Methods

### 2.1. Principle

$\text{NH}_2\text{OH}$  was determined with an adaptation of the method first described by Von Breyman et al. (1982) and later modified by Butler and Gordon (1986). The method is based on the oxidation of  $\text{NH}_2\text{OH}$  by  $\text{Fe(III)}$  to  $\text{N}_2\text{O}$  (Bengtsson et al., 2002):



The final concentration of  $\text{NH}_2\text{OH}$ ,  $[\text{NH}_2\text{OH}]$ , was computed as

$$[\text{NH}_2\text{OH}] = 2 * r^{-1} * ([\text{N}_2\text{O}] - [\text{N}_2\text{O}]^0), \quad (2)$$

**BGD**

1, 709–724, 2004

## Hydroxylamine ( $\text{NH}_2\text{OH}$ ) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004

where  $r$  stands for the recovery factor (for the determination of  $r$  see section below),  $[\text{N}_2\text{O}]$  is the total concentration of dissolved  $\text{N}_2\text{O}$  in the sample after the oxidation of  $\text{NH}_2\text{OH}$  and  $[\text{N}_2\text{O}]^\circ$  is the background concentration of dissolved  $\text{N}_2\text{O}$  in the sample. In the original method, Butler and Gordon (1986) used a purge-and-trap system to extract the  $\text{N}_2\text{O}$  from the sample. Here we used a headspace equilibration technique, which is routinely applied to measure oceanic  $\text{N}_2\text{O}$  depth profiles (Bange et al., 2001). Thus,  $\text{N}_2\text{O}$  concentrations,  $[\text{N}_2\text{O}]$  in  $\text{nmol L}^{-1}$ , were calculated as:

$$[\text{N}_2\text{O}] = (\beta x' P V_{wp} + \frac{x' P}{RT} V_{hs}) / V_{wp}, \quad (3)$$

where  $x'$  is the measured dry mole fraction of  $\text{N}_2\text{O}$  (in ppb) in the headspace of the sample,  $P$  is the pressure in the headspace (estimated to be constant at  $1.01325 \times 10^5 \text{ J m}^{-3}$ ),  $V_{hs}$  is the volume of the headspace,  $T$  is the equilibration temperature (in K),  $R$  is the gas constant ( $8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $\beta$  is the Bunsen solubility (in  $\text{nmol L}^{-1} \text{ atm}^{-1}$ ) as a function of  $T$  and the salinity of the sample (Weiss and Price, 1980), and  $V_{wp}$  is the volume of the water phase.

## 2.2. Sample treatment and analysis

All chemicals used were analytical reagent grade supplied by Merck KGaA, Darmstadt, Germany. We always used deionised water (Milli-Q). Triplicate water samples for the determination of  $[\text{N}_2\text{O}]^\circ$  and  $[\text{N}_2\text{O}]$  from various depths were taken from a 5 L-bottle rosette, equipped with a CTD-sensor. The samples for  $[\text{N}_2\text{O}]^\circ$  (24 mL sample volume) were immediately poisoned with 0.5 mL 1.7 mM aqueous  $\text{HgCl}_2$  solution. The samples for  $[\text{N}_2\text{O}]$  (118 mL sample volume) were acidified with 1 mL glacial acetic acid (final pH was 3). Then 1 mL of a 25 mM aqueous ferric ammonium sulphate (FAS,  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) solution was added. After 3 h (which is the required time to complete the  $\text{NH}_2\text{OH}$  oxidation reaction, see Butler and Gordon, 1986), the samples were poisoned with 0.5 mL 1.7 mM aqueous  $\text{HgCl}_2$  solution. All samples were stored in the dark at  $5^\circ\text{C}$  until measurement in our laboratory in Kiel. In order to create the headspace,

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

10 mL of sample were replaced with pure Helium (>99.999%, Messer Griesheim, Germany). Then the samples were allowed to equilibrate at least for 2 hours at room temperature (temperature was recorded). After equilibration, a subsample of 9 mL was drawn from the headspace with a gastight syringe. The subsample was injected through a phosphorus pentoxide (Sicapent® by Merck KGaA, Darmstadt, Germany) drying column to purge a stainless steel 2 mL sample loop connected to a gas stream selecting valve. After switching the valve, the sample was injected onto the separation column (prewashed, packed molsieve 5A column, 1.83 m length, Alltech GmbH, Unterhaching, Germany) with a argon/methane (95/5) mixture (ECD quality by Messer Griesheim, Germany) as carrier gas (flow 20 mL min<sup>-1</sup>). The separation was performed isothermally at 190°C. N<sub>2</sub>O was detected with an electron capture detector (ECD, Fisons model 800). The ECD was run in the constant current mode at 320°C with a pulse width of 1 µs, a reference current of 1 nA and a pulse voltage of 25 V. Signal processing and chromatogram integration was done with Chromstar (SCPA, Bremen, Germany) software. For the calibration procedure we used certified standard gas mixtures with 100±2 ppb and 318±6 ppb N<sub>2</sub>O in synthetic air (DEUSTE Steininger GmbH, Mühlhausen, Germany). The check of the ECD response curve (by dilution of pure N<sub>2</sub>O with He) revealed a linear response for N<sub>2</sub>O in the range from 76 ppb to 11,320 ppb thus no correction for non-linearity was applied for this range. For N<sub>2</sub>O mole fractions <76 ppb we applied the correction for non-linearity as described in Bange et al. (2001). Repeated measurements of the standard gas mixtures resulted in a mean relative error of 2.4%. The relative errors of the mean [NH<sub>2</sub>OH] were in the range from 5 to 15%. The detection limit for [NH<sub>2</sub>OH] was estimated to be approximately 2 nmol L<sup>-1</sup>.

### 2.3. Determination of the recovery factor

The recovery factor *r* (see Eq. 2) was defined as the ratio of the measured NH<sub>2</sub>OH to the theoretical NH<sub>2</sub>OH. In order to determine the recovery factor, a series of NH<sub>2</sub>OH standard solutions were prepared as follows: A NH<sub>2</sub>OH stock solution was prepared by dissolution of 347.7 mg of dry NH<sub>2</sub>OH HCl in 1 L water which was previously acidified

**BGD**

1, 709–724, 2004

## Hydroxylamine (NH<sub>2</sub>OH) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004

with 1 mL 1N HCl. The stock solution was stored in the dark at 5°C. 1 L of Baltic Sea water (from the Kiel Fjord) was filtered and acidified with 1 mL 1N HCl. Then 1 mL of the stock solution was added. This solution was diluted with Baltic Sea water to prepare a  $5 \mu\text{mol L}^{-1}$   $\text{NH}_2\text{OH}$  solution. In a further dilution step, standard solutions with concentrations of 2, 5, 10, 30 and  $50 \text{ nmol L}^{-1}$   $\text{NH}_2\text{OH}$  were prepared. The solution was acidified with 3 mL glacial acetic acid to a final pH of 3. After adding 1 mL of the FAS solution (see Sample treatment and analysis) the samples were allowed to react for 16 h in order to complete the  $\text{NH}_2\text{OH}$  oxidation to  $\text{N}_2\text{O}$ . Finally,  $\text{N}_2\text{O}$  was analysed as described above. The combined natural background of  $\text{N}_2\text{O}$  and  $\text{NH}_2\text{OH}$  concentrations of the used Baltic Sea water was also determined. The procedure was repeated two times. The results are shown in Fig. 2. The resulting mean recovery factor was 0.31. For the computation of  $[\text{NH}_2\text{OH}]$  we used 0.31 for the recovery factor  $r$  in Eq. (2). Our recovery factor is at the lower end of the values reported by Butler and Gordon (1986), which ranged from 0.40 (Big Lagoon, California) to 0.83 (coast off Oregon). It appears that  $r$  strongly varies with the water matrices used (Butler and Gordon, 1986). We may speculate that dissolved trace metals and/or other dissolved constituents of the Baltic Sea water reduce the yield of the  $\text{NH}_2\text{OH}$  oxidation.

## 2.4. Nutrients

Concentrations of the dissolved inorganic nitrogen compounds nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), ammonium ( $\text{NH}_4^+$ ), and oxygen ( $\text{O}_2$ ) were determined using standard methods (Grasshoff et al., 1983).

## Hydroxylamine ( $\text{NH}_2\text{OH}$ ) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

### 3. Results and Discussion

#### 3.1. Water column distribution

NH<sub>2</sub>OH concentrations were in the range from 2 nmol L<sup>-1</sup> up to 179 nmol L<sup>-1</sup> (at station #22). Generally, NH<sub>2</sub>OH concentrations were higher at the shallow, well-mixed stations (the mean for stations #360, #22 and #133 was 108 nmol L<sup>-1</sup>) than in the mixed layer (ML, defined as temperature difference of <0.5°C between surface and depth) of the central Baltic Sea (26±12 nmol L<sup>-1</sup>, n=7). Our measurements are comparable with the NH<sub>2</sub>OH concentrations found in the Yaquina River (Oregon) and Big Lagoon (California) which were in the range from 0 to 362 nmol L<sup>-1</sup> and 0 to 175 nmol L<sup>-1</sup>, respectively (Butler et al., 1987; Butler et al., 1988).

The vertical distributions of NH<sub>2</sub>OH in the water column were highly variable and partly showed complex structures (Figs. 3a–d). Enhanced NH<sub>2</sub>OH concentrations at stations #22 and #360 were associated with high salinities indicating a significant contribution of North Sea water, however, a clear relationship was not detectable. Obviously there was no correlation of NH<sub>2</sub>OH with N<sub>2</sub>O or O<sub>2</sub> suggesting that (i) a direct coupling of N<sub>2</sub>O formation via NH<sub>2</sub>OH was negligible and (ii) NH<sub>2</sub>OH formation was not directly influenced by O<sub>2</sub>. Our results are partly in contrast to the results of Butler et al. (1987; 1988) who reported a reasonable correlation of NH<sub>2</sub>OH with N<sub>2</sub>O. However, Butler et al. (1987) stated that the observed correlation does not necessarily prove N<sub>2</sub>O formation via NH<sub>2</sub>OH.

In the anoxic deep waters of the western Gotland Basin (stations #284 and #245), NH<sub>2</sub>OH concentrations rapidly decreased close to 0 nmol L<sup>-1</sup> when O<sub>2</sub> was exhausted (Fig. 3d). The effect of the recent North Sea water inflow event is illustrated by the distribution of NH<sub>2</sub>OH at station #286 (Fig. 3c) in the northern Gotland Basin. Below the mixed layer (>50 m) the dramatic decrease of NH<sub>2</sub>OH and N<sub>2</sub>O at 80 m is associated with the steep gradient of the O<sub>2</sub> concentrations (down to 7.9 μmol L<sup>-1</sup> at 90 m). Below 90 m the oxygen concentrations were enhanced due to the presence of O<sub>2</sub>-rich North

**BGD**

1, 709–724, 2004

## Hydroxylamine (NH<sub>2</sub>OH) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004



Sea water which ventilated the previously anoxic deep waters except for a narrow (now suboxic) depth range between 80–100 m. Therefore, the extremely low  $\text{NH}_2\text{OH}$  and  $\text{N}_2\text{O}$  concentrations at 80 m most probably were the residual signal of the “old” anoxic condition before the inflow event which is still found at station #284 (Fig. 3d).

### 5 3.2. Formation

$\text{NH}_2\text{OH}$  concentrations at the shallow, well-mixed stations in proximity to the coast (especially stations #22 and #133) were associated with high  $\text{NO}_3^-$  concentrations (Fig. 4a).  $\text{NH}_2\text{OH}$  in the ML was well correlated with  $\text{NO}_2^-$  (Fig. 4b). High  $\text{NH}_2\text{OH}$  in conjunction with enhanced  $\text{NO}_2^-$  concentrations were found at stations #360, #22 and #133. The data from station #113 seem to support the correlation, however, in this case the enhanced  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$  concentrations were found below the ML (Figs. 3a and 4b). The high  $\text{NH}_2\text{OH}$  concentrations in the western and southern Baltic Sea (i.e. stations #360, #22, #133) might result from two effects: (i) input via rivers or North Sea water and (ii) in-situ formation via nitrification.

15 Seike et al. (2004) observed  $\text{NH}_2\text{OH}$  concentrations in the range from 21 up to  $3614 \text{ nmol L}^{-1}$  in the Hii and Iu Rivers in Japan indicating indeed that rivers may serve a potential source of high  $\text{NH}_2\text{OH}$  concentrations. Since we did not find any indications for an input of high  $\text{NH}_2\text{OH}$  by riverine sources (we found no correlation with salinity) we conclude that  $\text{NH}_2\text{OH}$  input by rivers at the time of our measurements was negligible.  $\text{NH}_2\text{OH}$  measurements in the North Sea are not known, thus, the question whether  
20  $\text{NH}_2\text{OH}$  might be brought into the Baltic Sea by North Sea waters remains speculative.

Most probably,  $\text{NH}_2\text{OH}$  was formed in-situ during nitrification at the shallow stations in the western and southern Baltic Sea. At a first glance this seems surprising because:

- 25 1. Both steps of the nitrification process are light inhibited (Olson, 1981; Ward, 1985). However, Horrigan and Springer (1990) found that “photoinhibition of  $\text{NH}_4^+$  oxidation may be less important in estuarine environments than in oceanic ones”. Since the Baltic Sea is an estuarine system, light inhibition of the nitrification is

## Hydroxylamine ( $\text{NH}_2\text{OH}$ ) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

most likely of minor importance.

2. Most microbial process rates show a pronounced seasonality, which follows the annual temperature cycle (ML temperatures during our study were in the range from 1.2 to 3.2°C). According to Ward (2000), however, nitrifying bacteria can easily adapt to low temperatures, thus we might expect nitrification even at the low temperatures during our study. This is in agreement with the results of Enoksson (1986) who found a significant seasonality of the nitrification rates in the ML of the western Gotland Basin (stations #284 and #245) indicating that the rates in November were considerably higher than in June. Additionally, during the time of our cruise, nitrifiers were not outcompeted by phytoplankton since the phytoplankton bloom, competing for  $\text{NH}_4^+$ , usually starts a month later (in March).

Thus, we conclude that  $\text{NH}_2\text{OH}$  in the western and southern Baltic Sea (stations #360, #22, #133) was most likely formed by nitrification. This is in agreement with the results of Butler et al. (1987) who found a correlation between  $\text{NH}_4^+$  oxidation rates and  $\text{NH}_2\text{OH}$  concentrations for the Yaquina River system.

Since high  $\text{NH}_2\text{OH}$  concentrations were associated with enhanced  $\text{NO}_2^-$  concentrations we may speculate that nitrification during our study was incomplete. Possibly the rates of the second nitrification step (i.e.  $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$ ) were lower than the rates of the  $\text{NH}_4^+$  oxidation (typical for a “fresh” nitrifying system, Philips et al. (2002)) or the second step was inhibited by the rather high concentrations of  $\text{NH}_2\text{OH}$  (Castignetti and Gunner, 1982).

Anammox, as an alternative formation process for  $\text{NH}_2\text{OH}$ , should only occur at the oxic/anoxic interface in the western Gotland Basin. Comparable conditions favouring anammox were found in the Black Sea and Golfo Dulce, Costa Rica (Dalsgaard et al., 2003; Kuypers et al., 2003). However, the formation of  $\text{NH}_2\text{OH}$  by anammox in the Baltic Sea could not be verified. At the oxic/anoxic interface in the western Gotland Basin (see e.g. station #284, Fig. 4d) no distinct depletion or enhancement was observed.

**BGD**

1, 709–724, 2004

## Hydroxylamine ( $\text{NH}_2\text{OH}$ ) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004

## 4. Conclusions

The water column distribution of  $\text{NH}_2\text{OH}$  was measured for the first time in the Baltic Sea enlarging considerably the existing data set of oceanic  $\text{NH}_2\text{OH}$  measurements. The distribution of dissolved  $\text{NH}_2\text{OH}$  in Baltic Sea in February 2004 was complex due to the interplay of in-situ production in the shallow western and southern Baltic Sea and the hydrographical setting in the central Baltic Sea caused by the major North Sea water inflow event in January 2003. We found no correlation of  $\text{NH}_2\text{OH}$  with  $\text{N}_2\text{O}$  or  $\text{O}_2$  suggesting (i) that a direct coupling of  $\text{N}_2\text{O}$  formation via  $\text{NH}_2\text{OH}$  was negligible and (ii) that  $\text{NH}_2\text{OH}$  formation was not influenced by  $\text{O}_2$ . Nitrification appeared to be the major  $\text{NH}_2\text{OH}$  source, whereas  $\text{NH}_2\text{OH}$  formation via anammox was not detectable. We suggest that a “fresh” nitrifying system, in which the  $\text{NH}_4^+$ -oxidation rates exceeded the  $\text{NO}_2^-$ -oxidation rates, favoured the build-up of  $\text{NH}_2\text{OH}$ .

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**BGD**

1, 709–724, 2004

## Hydroxylamine ( $\text{NH}_2\text{OH}$ ) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004

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**BGD**

1, 709–724, 2004

## Hydroxylamine (NH<sub>2</sub>OH) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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## Hydroxylamine (NH<sub>2</sub>OH) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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## Hydroxylamine ( $\text{NH}_2\text{OH}$ ) in the Baltic Sea

S. Gebhardt et al.

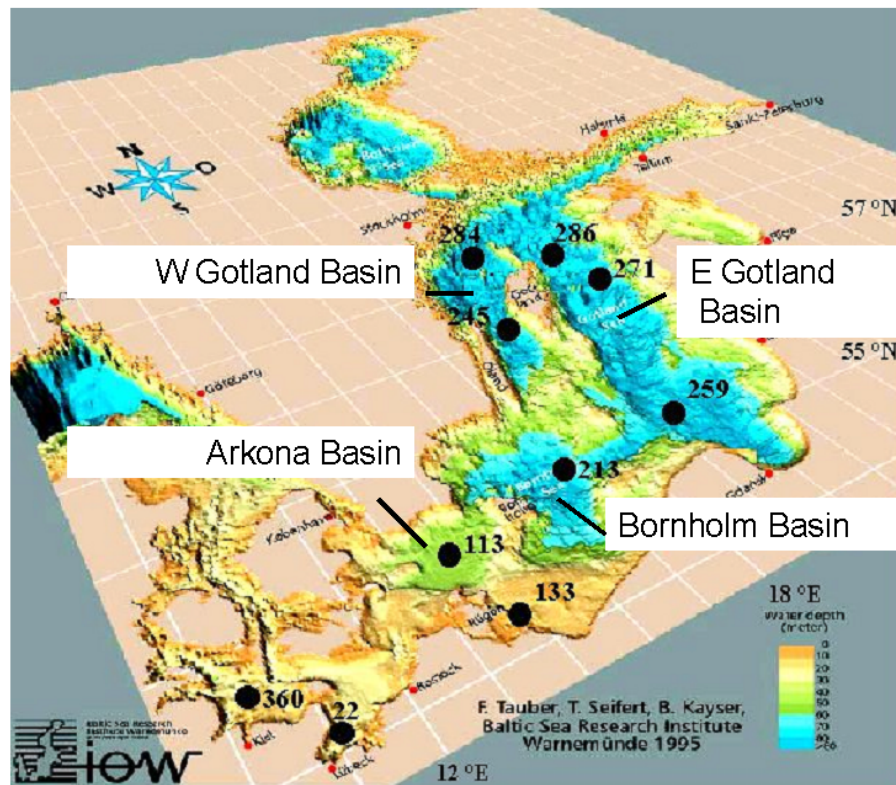


Fig. 1. Map of the Baltic Sea. Sampling stations are indicated.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

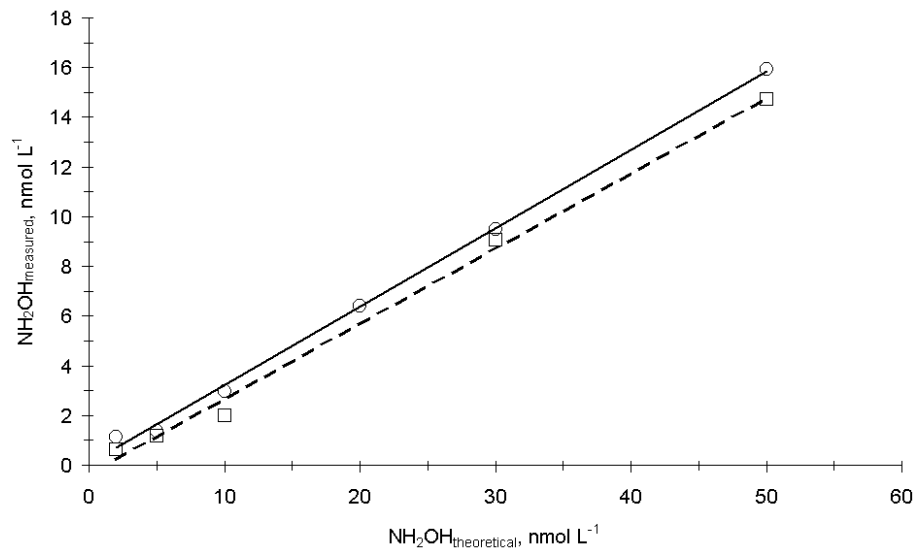
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Print Version

Interactive Discussion

## Hydroxylamine ( $\text{NH}_2\text{OH}$ ) in the Baltic Sea

S. Gebhardt et al.



**Fig. 2.** Determination of the recovery factor based on two independent experiments. Data points represent mean of triplicate samples. (solid line:  $y = 0.32x + 0.054$ ,  $r^2 = 0.998$ ; dashed line:  $y = 0.30x - 0.37$ ,  $r^2 = 0.995$ )

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

# Hydroxylamine (NH<sub>2</sub>OH) in the Baltic Sea

S. Gebhardt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

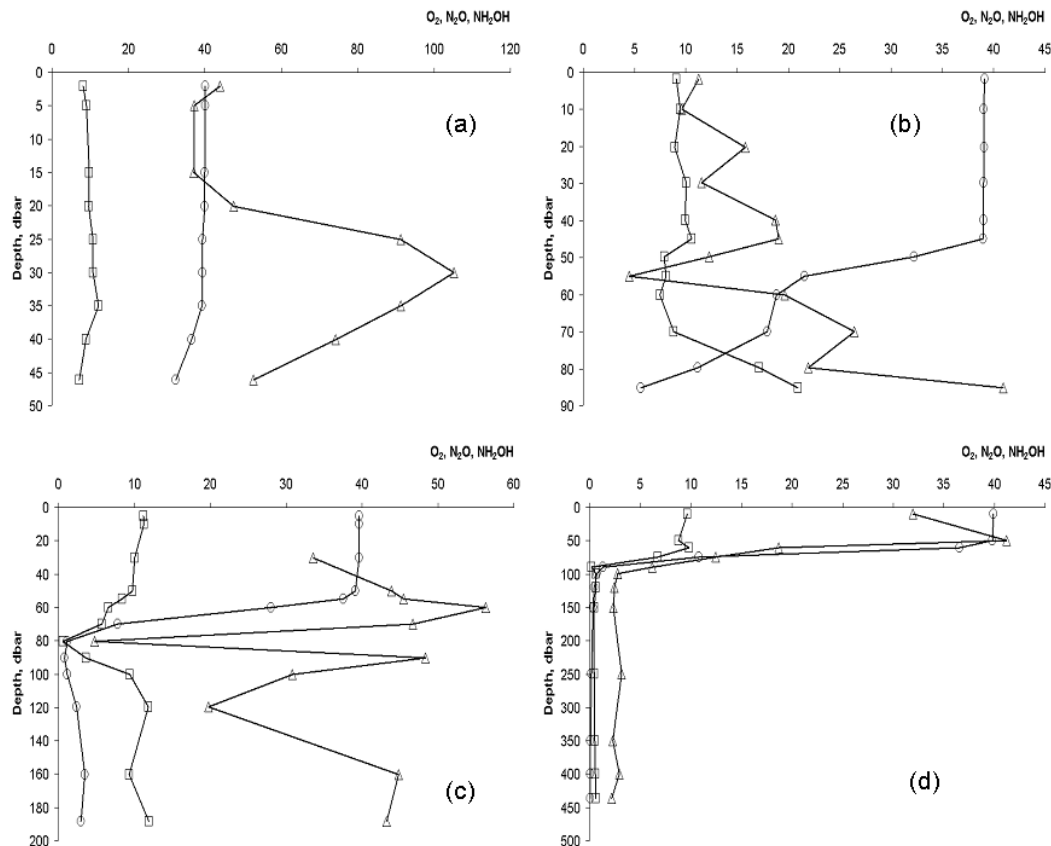
Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

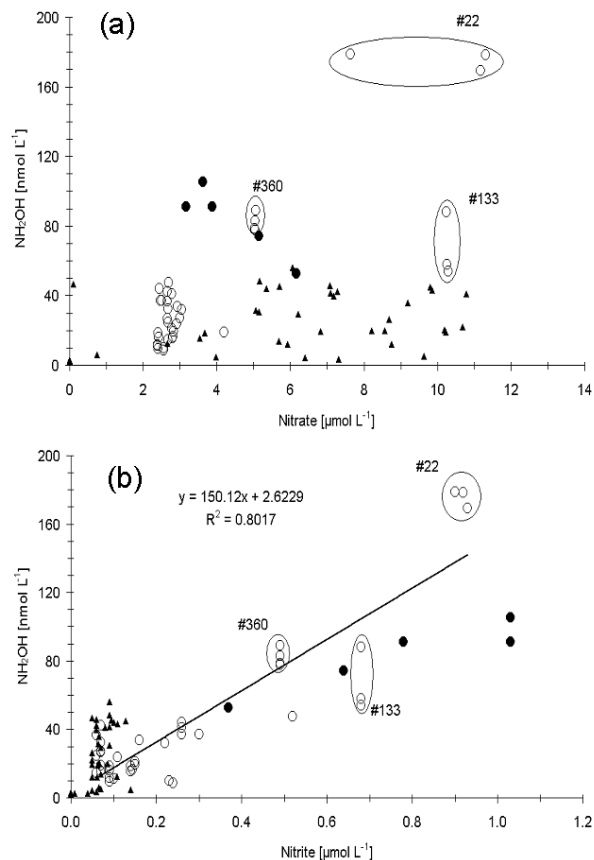


**Fig. 3.** NH<sub>2</sub>OH (in nmol L<sup>-1</sup>, triangles), N<sub>2</sub>O (in nmol L<sup>-1</sup>, squares) and O<sub>2</sub> (in μmol L<sup>-1</sup>/10, circles) in the central Baltic Sea: **(a)** station #113 Arkona Basin, **(b)** station #213 Bornholm Deep, **(c)** station #286 Farö Deep, and **(d)** station #284 Landsort Deep.



# Hydroxylamine (NH<sub>2</sub>OH) in the Baltic Sea

S. Gebhardt et al.



**Fig. 4.** (a) NH<sub>2</sub>OH vs. NO<sub>3</sub><sup>-</sup> and (b) NH<sub>2</sub>OH vs. NO<sub>2</sub><sup>-</sup>. Open circles stand for data from the mixed layer, filled triangles stand for data from below the mixed layer and Filled circles indicate data below the mixed layer from station #113. Data from stations #360, #22, and #133 are marked.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion