

## A time series of hydroxylamine (NH<sub>2</sub>OH) in the southwestern Baltic Sea

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[1] Hydroxylamine (NH<sub>2</sub>OH) is an intermediate of the marine nitrogen cycle and in marine environments dissolved NH<sub>2</sub>OH is short-lived. In order to investigate the distribution of NH<sub>2</sub>OH under varying oxygen conditions, its seasonal variability was investigated on a monthly basis from July 2005 to May 2006 at the time series station Boknis Eck located in the Eckernförde Bay (southwestern Baltic Sea). NH<sub>2</sub>OH concentrations were generally low and close to the detection limit. However, a pronounced increase was observed after the seasonal thermohaline stratification period with low oxygen/anoxic conditions in the deep layers was terminated in November 2005. The increase of NH<sub>2</sub>OH was associated with the re-oxygenation of the water column. We conclude that NH<sub>2</sub>OH was produced in-situ during nitrification. We suggest that the detection of significant amounts of NH<sub>2</sub>OH can be used as an indicator for a “fresh” nitrifying system. **Citation:** Schweiger, B., H. P. Hansen, and H. W. Bange (2007), A time series of hydroxylamine (NH<sub>2</sub>OH) in the southwestern Baltic Sea, *Geophys. Res. Lett.*, *34*, L24608, doi:10.1029/2007GL031086.

### 1. Introduction

[2] Hydroxylamine (NH<sub>2</sub>OH) is an intermediate in the natural nitrogen cycle. It is formed during microbial nitrification [Arp and Stein, 2003; Rajendran and Venugopalan, 1976], where ammonium (NH<sub>4</sub><sup>+</sup>) is oxidized via NH<sub>2</sub>OH to nitrite (NO<sub>2</sub><sup>-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>): NH<sub>4</sub><sup>+</sup> → NH<sub>2</sub>OH → NO<sub>2</sub><sup>-</sup> → NO<sub>3</sub><sup>-</sup>. Other suggested NH<sub>2</sub>OH formation pathways such as anaerobic ammonium oxidation as well as dissimilatory nitrate reduction to ammonia have not been verified [Strous *et al.*, 2006; Yordy and Ruoff, 1981]. In marine environments dissolved NH<sub>2</sub>OH is not stable and therefore has a half-life of only a few hours [Butler *et al.*, 1987, 1988]. First measurements of NH<sub>2</sub>OH in marine environments were made in 1981 on the continental shelf off Oregon [Von Breyman *et al.*, 1982], followed by studies in the Yaquina River estuary, Oregon, in 1984 [Butler *et al.*, 1987] and a coastal lagoon in California, in 1985 [Butler *et al.*, 1988]. In February 2004, NH<sub>2</sub>OH was measured at 10 stations in the western, southern and central Baltic Sea [Gebhardt *et al.*, 2004].

[3] The Baltic Sea is an ideal natural laboratory to study the influence of changing environmental conditions on the marine nitrogen cycle: Especially the frequently occurring natural oscillations between oxic and anoxic conditions

allows to study the variability of oxygen-sensitive processes such as nitrification and others [see, e.g., Hannig *et al.*, 2007; Walter *et al.*, 2006]. Here we present the first time series of dissolved NH<sub>2</sub>OH at station Boknis Eck in the Eckernförde Bay (Baltic Sea). Samples were taken on a monthly basis between July 2005 and May 2006 on board of the German research vessel Littorina. The sampling period covered a shift from anoxic to oxic conditions at Boknis Eck, allowing us to study the influence of varying oxygen condition on the NH<sub>2</sub>OH distribution.

### 2. Study Site Description

[4] The time series station Boknis Eck (BE) is located at the entrance of the Eckernförde Bay (54°31′N, 10°02′E; Figure 1). It has a water depth of about 28 m. The hydrographic setting of BE is dominated by the inflow of North Sea water via the Kattegat and the Great Belt. These deepwater inflows of high salinity North Sea waters result in stable stratification. Seasonal stratification is associated with the development of a pycnocline at about 15 m water depth from mid of March until mid of September. During this period, vertical mixing is restricted and deep water bacterial decomposition of organic material causes pronounced oxygen depletion and sporadically occurring anoxia during late summer [Hansen *et al.*, 1999]. Salinity, temperature, and oxygen data from BE have been recorded on a monthly basis since 1957. Monthly nutrient data are available since 1979 [Hansen *et al.*, 1999].

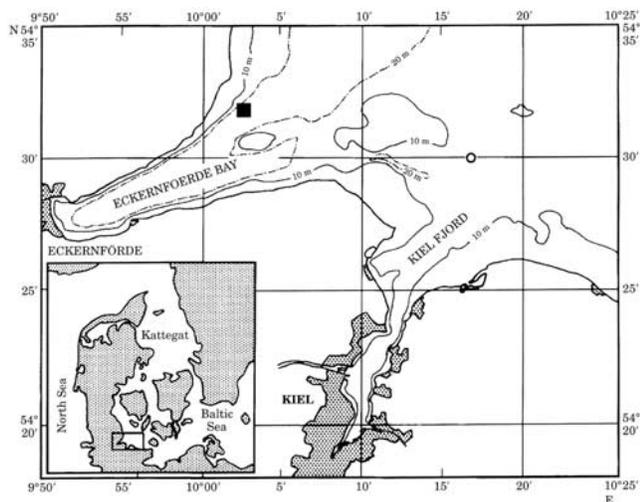
### 3. Methods

[5] For the determination of dissolved NH<sub>2</sub>OH we applied the analytical method described by Gebhardt *et al.* [2004], which is a modification of the technique reported by Butler and Gordon [1986]. NH<sub>2</sub>OH concentrations, [NH<sub>2</sub>OH], were calculated with the following equation:

$$[\text{NH}_2\text{OH}] = 2([\text{N}_2\text{O}] - [\text{N}_2\text{O}]^0) \cdot R^{-1}.$$

[6] Where [N<sub>2</sub>O] is the concentration of N<sub>2</sub>O in the sample after oxidation, [N<sub>2</sub>O]<sup>0</sup> is the background concentration of dissolved N<sub>2</sub>O in the sample, and R stands for the recovery factor. The recovery factor was determined with water samples, which were taken from 15 m depth at BE during the monthly sampling campaigns from August 2005 to May 2006. The recovery factors (slope ± error of slope) varied between 0.44 ± 0.01 and 0.64 ± 0.02 (see Table 1). They are in agreement with previously reported recovery factors, which range from 0.31 to 0.83 [Butler and Gordon, 1986; Gebhardt *et al.*, 2004]. The monthly variations of the recovery factor did not correlate with salinity, water tem-

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**Figure 1.** Location (filled square) of the time series station Boknis Eck in the Eckernförde Bay.

perature, nutrients, and O<sub>2</sub>. We may speculate that dissolved trace metals such as copper and mercury and/or other dissolved constituents of the Baltic Sea water reduce the yield of the NH<sub>2</sub>OH oxidation [Butler and Gordon, 1986]. However, the recovery factor did not influence the seasonal pattern of NH<sub>2</sub>OH because its seasonal variability was low (Table 1).

[7] Triplicate water samples for the determination of [N<sub>2</sub>O] and [N<sub>2</sub>O]<sup>0</sup>, respectively, were taken from six standard depths (1, 5, 10, 15, 20 and 25 m) with a 5 L Niskin bottle. The standard deviations of [N<sub>2</sub>O] and [N<sub>2</sub>O]<sup>0</sup> were approximated with (C<sub>max</sub> - C<sub>min</sub>)/1.91, where C<sub>min</sub> and C<sub>max</sub> stand for the minimal and maximal N<sub>2</sub>O concentrations of the triplicate samples of [N<sub>2</sub>O] and [N<sub>2</sub>O]<sup>0</sup>, respectively. The factor 1.91 is derived from the statistical method by David [1951]. The overall mean analytical error of [N<sub>2</sub>O] and [N<sub>2</sub>O]<sup>0</sup> was ±3%. A rough estimate of the mean error of [NH<sub>2</sub>OH], introduced by the uncertainties of [N<sub>2</sub>O], [N<sub>2</sub>O]<sup>0</sup>, and R, was calculated according to the following equation:

$$\Delta[\text{NH}_2\text{OH}] = \pm \sqrt{\left(\frac{2}{R} \Delta[\text{N}_2\text{O}]\right)^2 + \left(\frac{-2}{R} \Delta[\text{N}_2\text{O}]^0\right)^2 + \left(\left(\frac{-2}{R^2} [\text{N}_2\text{O}] + \frac{2}{R^2} [\text{N}_2\text{O}]^0\right) \Delta R\right)^2}$$

[8] For a strict treatment of the error propagation, the standard deviation of each parameter should be known. Since this was not the case, we replaced the standard deviation partly with best estimates of the mean error (depicted by the  $\Delta$  symbol). For  $\Delta[\text{N}_2\text{O}]$  and  $\Delta[\text{N}_2\text{O}]^0$  we used the mean relative error of 3% (see above). Based on the data listed in Table 1 we calculated a mean R of  $0.55 \pm 0.05$  (mean  $\pm$  standard deviation,  $n = 10$ ). For the maximum [NH<sub>2</sub>OH] observed (18.5 nmol L<sup>-1</sup> in November 2005) we computed a mean error  $\pm 3.6$  nmol L<sup>-1</sup> (which gives a mean relative error of  $\pm 19.5\%$ ). Lower [NH<sub>2</sub>OH] are associated with larger errors: [NH<sub>2</sub>OH] concentrations of about 1.6 nmol L<sup>-1</sup> have a relative error of about  $\pm 100\%$ .

[9] Concentrations of dissolved nitrate (NO<sub>3</sub><sup>-</sup>) and oxygen (O<sub>2</sub>) were determined using standard methods [Grasshoff *et al.*, 1999].

#### 4. Results and Discussion

[10] NH<sub>2</sub>OH concentrations showed a pronounced seasonal variability (Figure 2a). In the period from July to October 2005, NH<sub>2</sub>OH concentrations were low (ranging from not detectable up to 5 nmol L<sup>-1</sup>) and about uniform throughout the water column. In November 2005 we observed a remarkable increase of NH<sub>2</sub>OH in the entire water column with maximum concentrations of about 18.5 nmol L<sup>-1</sup> in 5 m depth. NH<sub>2</sub>OH concentrations started to decline rapidly in December 2005 and continued to decline until March 2006. During the period from December 2005 to May 2006, NH<sub>2</sub>OH concentrations in the depth range 0–20 m were low and ranged from not detectable to 5 nmol L<sup>-1</sup> (Figure 2a).

[11] Our measurements are comparable with the NH<sub>2</sub>OH concentrations found in the Yaquina River (Oregon) and Big Lagoon (California): The seasonal study by Butler *et al.* [1987] of NH<sub>2</sub>OH along the salinity gradient of the Yaquina River consisted of 5 measurement campaigns from October 1983 to August 1984. Butler *et al.* [1987] found maximum values in November (39–326 nmol L<sup>-1</sup>) and minimal concentrations in January (0–20 nmol L<sup>-1</sup>). The study of NH<sub>2</sub>OH in the stratified Big Lagoon revealed comparably low concentrations (0–18 nmol L<sup>-1</sup>) in the upper water column, whereas maximum values (up to 175 nmol L<sup>-1</sup>) were found at the water/sediment interface [Butler *et al.*, 1988].

[12] Our measurements are lower than the mean NH<sub>2</sub>OH concentration ( $82 \pm 5$  nmol L<sup>-1</sup>) measured by Gebhardt *et al.* [2004] at the shallow, well-mixed station #360 (54°36'N 10°27'E, water depth 15 m) in the western Baltic Sea in February 2004. However, this discrepancy might be caused by the fact that the hydrographic setting of the western Baltic Sea in February 2004 was significantly different: For example, the overall mean NO<sub>3</sub><sup>-</sup> concentration in the water

column at station #360 in February 2004 ( $5.05 \pm 0.01$   $\mu\text{mol L}^{-1}$ ) was considerably higher than at BE in February 2006 (ranging from 0.03  $\mu\text{mol L}^{-1}$  at the surface to 4.3  $\mu\text{mol L}^{-1}$  in 25 m). Moreover, Gebhardt *et al.* [2004] reported an unusual low R of 0.31. Scaling their measurements to the average R of this study (0.55) would reduce their mean NH<sub>2</sub>OH concentration by a factor of about 1.8.

[13] It is obvious that the seasonal variability of NH<sub>2</sub>OH was closely associated with a sudden change of the environmental conditions at BE: A stagnation period lasted until October and led to low oxygen and even anoxic conditions in 25 m water depth in September and October (Figure 2b). In November the stagnation period was terminated after a

**Table 1.** NH<sub>2</sub>OH Recovery Factors

Sampling Date	NH <sub>2</sub> OH Recovery Factor <sup>a</sup>
28 Jul 2005	Nd <sup>b</sup>
11 Aug 2005	0.53 ± 0.04
14 Sep 2005	0.57 ± 0.01
26 Oct 2005	0.64 ± 0.02
15 Nov 2005	0.55 ± 0.02
13 Dec 2005	0.55 ± 0.02
17 Jan 2006	0.51 ± 0.01
14 Feb 2006	0.54 ± 0.02
14 Mar 2006	0.56 ± 0.02
21 Apr 2006	0.44 ± 0.01
17 May 2006	0.57 ± 0.02

<sup>a</sup>Given as slope of regression ± error or of the slope.

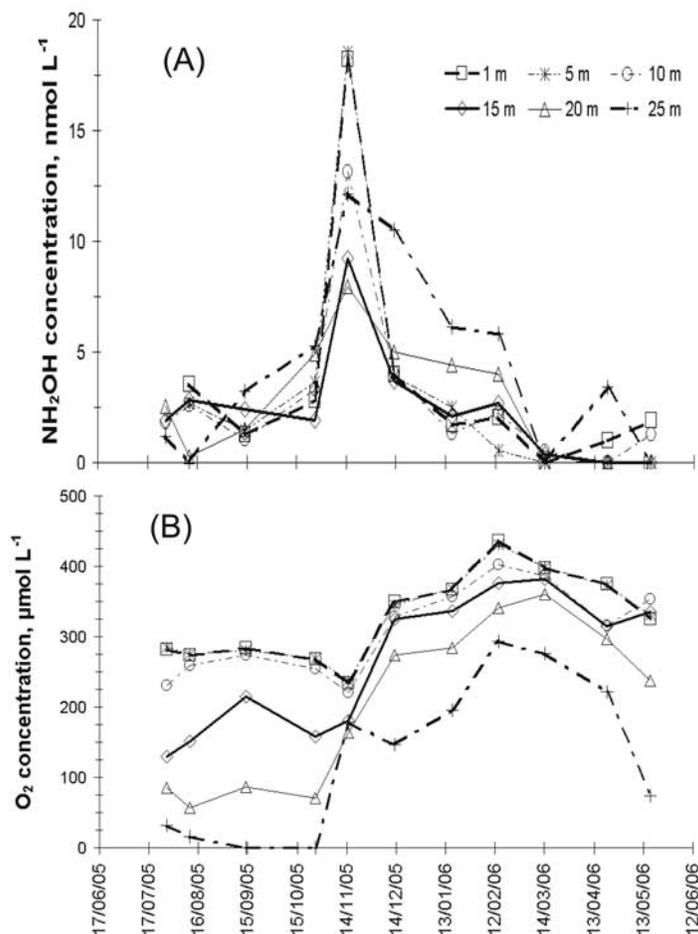
<sup>b</sup>Nd stands for not determined.

period of 14 days with steady winds from Southwest to South blowing parallel to the coastline of Eckernförde Bay and thus triggering a coastal upwelling event at BE [Hansen *et al.*, 1999] (wind data were recorded by the German Weather Service at Schleswig, 54°31'N, 09°33'E). The upwelling resulted in complete mixing and re-oxygenating of the water column at BE (Figure 2b). Since dissolved

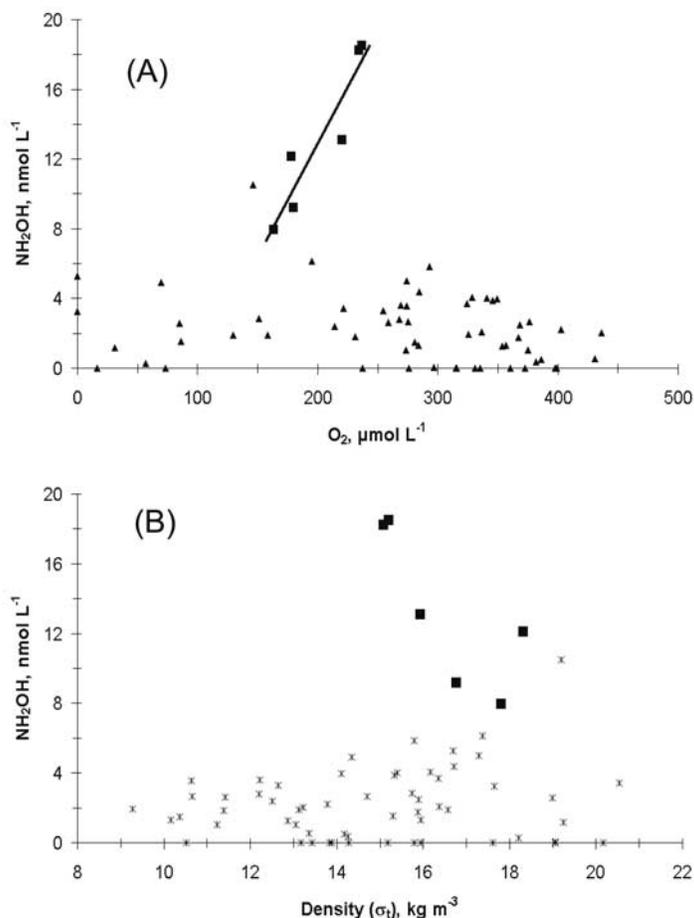
NH<sub>2</sub>OH has a half-life of only 3 to 10 hours [Butler *et al.*, 1987], the observed pronounced increase in November is resulting mainly from in-situ processes with a minor contribution of NH<sub>2</sub>OH advected to BE from the adjacent areas: In November the maximum NH<sub>2</sub>OH concentrations were associated with increasing O<sub>2</sub> concentrations and decreasing densities (Figure 3), which implies that during upwelling the mixing of high density water with low density water at the surface triggered an in-situ NH<sub>2</sub>OH production. A simple mixing of O<sub>2</sub>- and NH<sub>2</sub>OH- enriched dense water with low density surface water could not explain the fact that the maximum NH<sub>2</sub>OH concentrations were measured at the surface between 1–10 m (Figure 2a).

[14] Interestingly, NH<sub>2</sub>OH concentrations at the water/sediment interface (25 m) are slightly increasing already during the anoxic period before the ventilation and the decline of NH<sub>2</sub>OH in 25 m is much slower during the months after the ventilation than in the rest of the water column (Figure 2a). Thus, the possibility of an additional sedimentary release of NH<sub>2</sub>OH cannot be excluded but remains speculative because a sedimentary formation of NH<sub>2</sub>OH has not been described in the literature.

[15] The most plausible production pathway for NH<sub>2</sub>OH in marine system is nitrification (see introduction): Butler *et al.* [1987] found that NH<sub>2</sub>OH concentrations were positively



**Figure 2.** (a) NH<sub>2</sub>OH and (b) dissolved O<sub>2</sub> at Bognis Eck. (Please note that O<sub>2</sub> concentrations in 1 and 5 m are almost identical. No O<sub>2</sub> was detected at 25 m during the September and October sampling.)



**Figure 3.** (a)  $\text{NH}_2\text{OH}$  vs.  $\text{O}_2$ . The filled squares depict the data points from November 2005 ( $r = 0.93$ ,  $\alpha = 0.01$ ,  $n = 6$ ) and (b)  $\text{NH}_2\text{OH}$  concentrations and density. The filled squares depict the data points from November 2005.

correlated to  $\text{NH}_4^+$  oxidation rates in Yaquina Bay (but found no correlation in the Big Lagoon [Butler *et al.*, 1988]). The results of the study by Gebhardt *et al.* [2004] indicated nitrification as the main  $\text{NH}_2\text{OH}$  production pathway in the Baltic Sea. During our study the occurrence of nitrification was supported by the fact that during July and August a linear correlation between  $\text{N}_2\text{O}$  and  $\text{O}_2$  ( $r = -0.99$ ,  $\alpha = 0.01$ ,  $n = 12$ ) was observed which is indicative for  $\text{N}_2\text{O}$  production via nitrification [Nevison *et al.*, 2003]. However, the  $\text{N}_2\text{O}/\text{O}_2$  relationship broke down when  $\text{O}_2$  concentrations in the deep decreased during September and October. After the ventilation in November, the linear  $\text{N}_2\text{O}/\text{O}_2$  relationship ( $r = -0.93$ ;  $\alpha = 0.01$ ,  $n = 6$ ) was restored. It is well known that a shift from anoxic to oxic conditions (or vice versa) causes a change of the nitrification activities [Boontanon *et al.*, 2000; Goreau *et al.*, 1980]. Thus, we conclude that re-oxygenating of the water column in November restored nitrification, which in turn was associated with increasing  $\text{NH}_2\text{OH}$  concentrations. We might speculate that nitrification during the shift from low oxygen/anoxic to oxic conditions was incomplete leading to the temporary accumulation of  $\text{NH}_2\text{OH}$  at BE. 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 which is typical for a “fresh” nitrifying system [Philips *et al.*, 2002].

## 5. Summary

[16] Monthly measurements of  $\text{NH}_2\text{OH}$  at the station Boknis Eck (southwestern Baltic Sea) were performed from July 2005 to May 2006. A pronounced increase of  $\text{NH}_2\text{OH}$  concentrations was measured when a stagnation period with low oxygen/anoxic conditions in the deep layers was terminated by an upwelling event in November 2005 resulting in a re-oxygenation of the water column. We suggest that detection of a significant increase of  $\text{NH}_2\text{OH}$  concentrations might serve as an indicator for the presence of a “fresh” nitrifying system. Enhanced production of  $\text{NH}_2\text{OH}$  is especially expected to occur in coastal systems with pronounced changes in the oxygen concentrations.

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