

# Distribution of N<sub>2</sub>O in the Baltic Sea during transition from anoxic to oxic conditions

S. Walter<sup>1,\*</sup>, U. Breitenbach<sup>1</sup>, H. W. Bange<sup>1</sup>, G. Nausch<sup>2</sup>, and D. W. R. Wallace<sup>1</sup>

<sup>1</sup>Forschungsbereich Marine Biogeochemie, IFM-GEOMAR, Leibniz-Institut für Meereswissenschaften, Kiel, Germany

<sup>2</sup>Leibniz-Institut für Ostseeforschung, Warnemünde, Germany

\* now at: Institute for Marine and Atmospheric Research Utrecht, Utrecht University, Utrecht, The Netherlands

Received: 22 February 2006 – Published in Biogeosciences Discuss.: 26 June 2006

Revised: 23 October 2006 – Accepted: 14 November 2006 – Published: 21 November 2006

**Abstract.** In January 2003, a major inflow of cold and oxygen-rich North Sea Water terminated an ongoing stagnation period in parts of the central Baltic Sea. In order to investigate the role of North Sea Water inflow in the production of nitrous oxide (N<sub>2</sub>O), we measured dissolved and atmospheric N<sub>2</sub>O at 26 stations in the southern and central Baltic Sea in October 2003.

At the time of our cruise, water renewal had proceeded to the eastern Gotland Basin, whereas the western Gotland Basin was still unaffected by the inflow. The deep water renewal was detectable in the distributions of temperature, salinity, and oxygen concentrations as well as in the distribution of the N<sub>2</sub>O concentrations: Shallow stations in the Kiel Bight and Pomeranian Bight were well-ventilated with uniform N<sub>2</sub>O concentrations near equilibrium throughout the water column. In contrast, stations in the deep basins, such as the Bornholm and the Gotland Deep, showed a clear stratification with deep water affected by North Sea Water. Inflowing North Sea Water led to changed environmental conditions, especially enhanced oxygen (O<sub>2</sub>) or declining hydrogen sulphide (H<sub>2</sub>S) concentrations, thus, affecting the conditions for the production of N<sub>2</sub>O. Pattern of N<sub>2</sub>O profiles and correlations with parameters like oxygen and nitrate differed between the basins. Because of the positive correlation between  $\Delta$ N<sub>2</sub>O and AOU in oxic waters the dominant production pathway seems to be nitrification rather than denitrification.

Advection of N<sub>2</sub>O by North Sea Water was found to be of minor importance. A rough budget revealed a significant surplus of in situ produced N<sub>2</sub>O after the inflow. However, due to the permanent halocline, it can be assumed that the N<sub>2</sub>O produced does not reach the atmosphere. Hydrographic

aspects therefore are decisive factors determining the final release of N<sub>2</sub>O produced to the atmosphere.

## 1 Introduction

### 1.1 Nitrous oxide

Nitrous oxide (N<sub>2</sub>O) is an important atmospheric trace gas which influences, directly and indirectly, the Earth's climate: In the troposphere, it acts as a greenhouse gas with a relatively long atmospheric lifetime of 114 years (Prather et al., 2001). In the stratosphere it is the major source for nitric oxide radicals, which are involved in one of the main ozone reaction cycles (WMO, 2003).

N<sub>2</sub>O is mainly formed during microbial processes such as nitrification and denitrification. Nitrification is an aerobic two-step process in which ammonium is oxidized to nitrate. In this process, in which typically two groups of bacteria are involved, N<sub>2</sub>O is assumed to be a by-product, the exact metabolism however is still under discussion (Ostrom et al., 2000). In suboxic habitats, nitrate can be reduced by denitrification to molecular nitrogen, with N<sub>2</sub>O as an intermediate (Cohen and Gordon, 1978). N<sub>2</sub>O may also be produced by coupled nitrification and denitrification at oxic/suboxic boundaries, due to the transfer of intermediates such as nitrite (Yoshinari et al., 1997). Other possibilities are the production of N<sub>2</sub>O during nitrifier-denitrification or aerobic denitrification (Wrage et al., 2001). Both processes enable nitrifiers to oxidize NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup>, followed by the reduction of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub>O or N<sub>2</sub> (Robertson and Kuenen, 1984; Robertson et al., 1988; Richardson, 2000). In anoxic habitats N<sub>2</sub>O is used, instead of oxygen, as an electron acceptor (Elkins et al., 1978; Cohen and Gordon, 1978).

Correspondence to: S. Walter  
(s.walter@phys.uu.nl)

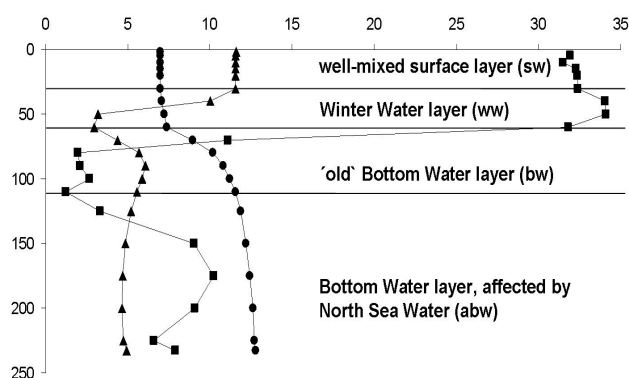


creasing salinity. In this water mass, located below the Winter Water, oxygen concentrations decreased rapidly, to anoxic conditions at some stations. A permanent halocline between Winter Water and Bottom Water strongly restricts the vertical exchange and is the reason for the development of stagnant deep waters with oxygen depletion culminating in anoxia as indicated by the accumulation of hydrogen sulphide (H<sub>2</sub>S). Bottom Water, affected by the North Sea Water inflow in January 2003 (*abw*) was characterized by decreasing temperature and enhanced oxygen concentrations compared to previous Bottom Water (*bw*) values. Due to its higher density the affected Bottom Water lifts up the “old” Bottom Water.

## 2 Methods

Samples of dissolved N<sub>2</sub>O were measured at 26 stations in the western, southern and central Baltic Sea. The cruise took place on board the German research vessel Gauss (expedition no. 11/03/04) from 13 October to 25 October 2003 as part of the Cooperative Monitoring in the Baltic Sea Environment (COMBINE) program of the Baltic Marine Environment Protection Commission (Helsinki Commission, HELCOM, see <http://www.helcom.fi>). The locations of sampled stations are shown in Fig. 1.

Water samples were taken using a combined Seabird SBE911 CTD and Hydrobios rosette sampler equipped with 13 Niskin bottles. Samples for N<sub>2</sub>O analysis were collected in triplicate from various depths. The analytical method applied was a modification of the method described by Bange et al. (2001). Bubble free samples were taken immediately following oxygen sampling from the rosette in 24 mL glass vials, sealed directly with butyl rubber stoppers and crimped with aluminium caps. To prevent microbial activity, samples were poisoned with 500 μL of a 2 mM mercury (II) chloride solution. 10 mL of the sample were then replaced with a helium headspace for each vial, and the samples were equilibrated for at least two hours at room temperature (temperature was recorded continuously). A 9 mL subsample from the headspace was used to flush a 2 mL sample loop after passing through a moisture trap (filled with Sicapent, Merck Germany). Gas chromatographic separation was performed at 190°C on a packed molecular sieve column (6 ft × 1/8" SS, 5 A, mesh 80/100, Alltech GmbH, Germany). The N<sub>2</sub>O was detected with an electron capture detector. A mixture of argon and methane (95:5 by volume) was used as carrier gas with a flow of 21 mL min<sup>-1</sup>. For the two-point calibration procedure we used standard gas mixtures with 311.8 ± 0.2 ppb and 346.5 ± 0.2 ppb N<sub>2</sub>O in synthetic air (Deuste Steininger GmbH, Mühlhausen Germany). The standard mixtures have been calibrated against the NOAA (National Oceanic and Atmospheric Administration, Boulder, Co.) standard scale in the laboratories of the Air Chemistry Division of the Max Planck Institute for Chemistry, Mainz, Germany.



**Fig. 2.** Characterization of different water masses in the Baltic Sea, for example at station 271 in the Eastern Gotland Basin (triangles: temperature (°C), circles: salinity, squares: oxygen ( $\mu\text{mol } 10^1 \text{ L}^{-1}$ )).

### 2.1 Calculations

N<sub>2</sub>O water concentrations ( $c_{\text{N}_2\text{O}}$ ) were calculated as follows:

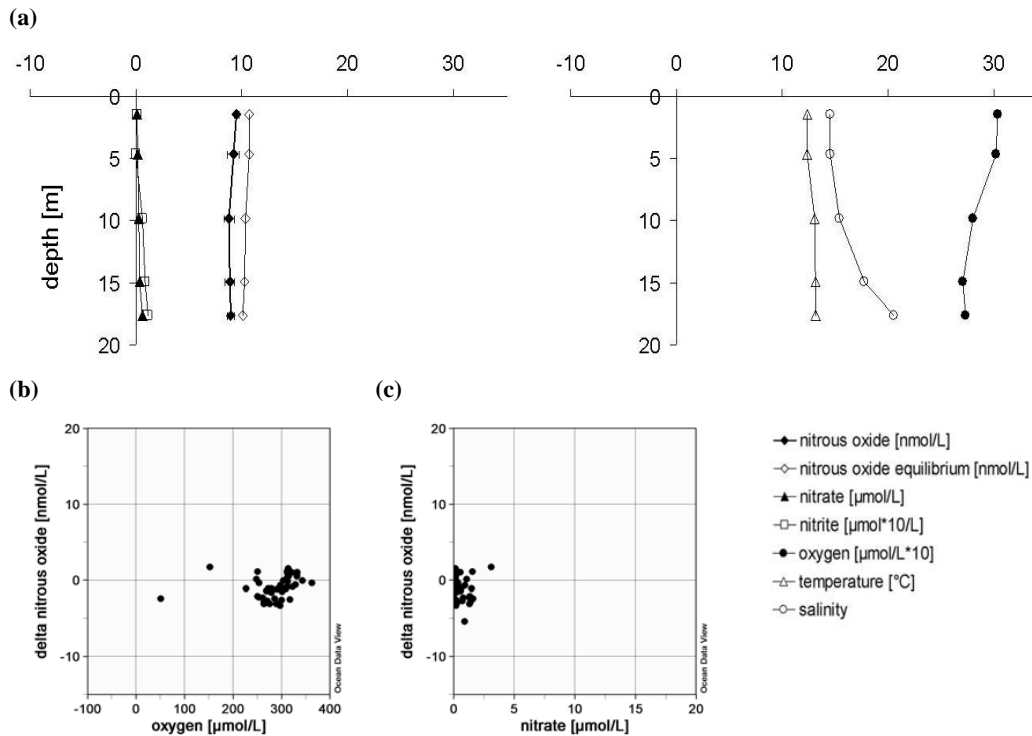
$$c_{\text{N}_2\text{O}} \left[ \text{nmol L}^{-1} \right] = \left( \beta x P V_{wp} + \frac{x P}{RT} V_{hs} \right) / V_{wp} \quad (1)$$

where  $\beta$  stands for the Bunsen solubility in  $\text{nmol L}^{-1} \text{ atm}^{-1}$  (Weiss and Price, 1980),  $x$  is the dry gas mole fraction of N<sub>2</sub>O in the headspace in ppb,  $P$  is the atmospheric pressure in atm,  $V_{wp}$  and  $V_{hs}$  stand for the volumes of the water and headspace phases, respectively.  $R$  is the gas constant ( $8.2054 \cdot 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the equilibrium temperature. The conductivity was measured by the CTD-Sensor during water sample collection; the temperature was measured while subsampling the headspace of the sample vial. The overall relative mean analytical error was estimated to be ±1.8%.

The excess N<sub>2</sub>O ( $\Delta\text{N}_2\text{O}$ ) was calculated as the difference between the calculated N<sub>2</sub>O equilibrium concentration and the measured concentration of N<sub>2</sub>O as follows

$$\Delta\text{N}_2\text{O} (\text{nmol L}^{-1}) = \text{N}_2\text{O} (\text{observed}) - \text{N}_2\text{O} (\text{equilibrium}). \quad (2)$$

Since the water masses in the Baltic Sea are comparably young (e.g. 11 years for the oldest bottom water at the Landsort Deep) (Meier, 2005) it is reasonable to calculate the equilibrium value with the actual atmospheric N<sub>2</sub>O mole fraction. The mean atmospheric concentration measured by us on the cruise was 318 ppb (±3 ppb, n=84), which is in good agreement with the monthly mean of  $318.5 \pm 0.2$  ppb in October 2003 measured at Mace Head, Ireland. This value was taken from the Advanced Global Atmospheric Gases Experiment (AGAGE) data set (updated version from May 2005, available at <ftp://cdiac.esd.ornl.edu> (subdirectory `pub/ale_gage_Agage/Agage/gc-md/monthly`) at the Carbon



**Fig. 3.** Well mixed basins; (a) left plot with profiles of N<sub>2</sub>O, calculated N<sub>2</sub>O equilibrium concentration, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> at station 41 in the Mecklenburg Bight and right plot with profiles of temperature, salinity and oxygen at station 41 in the Mecklenburg Bight; (b) ΔN<sub>2</sub>O plotted against oxygen at all stations <30 m; c) ΔN<sub>2</sub>O plotted against NO<sub>3</sub><sup>-</sup> at all stations <30 m.

Dioxide Information Analysis Center in Oak Ridge, Tennessee).

The apparent oxygen utilization (AOU) was calculated as follows:

$$\text{AOU}(\mu\text{mol L}^{-1}) = \text{O}_2(\text{equilibrium}) - \text{O}_2(\text{observed}). \quad (3)$$

The equilibrium values of dissolved oxygen (O<sub>2</sub>) were calculated with the equation given by Weiss (1970). The concentration of H<sub>2</sub>S is expressed as the negative oxygen equivalent (1 μmol L<sup>-1</sup> H<sub>2</sub>S = -2.00 μmol L<sup>-1</sup> O<sub>2</sub>). Dissolved nutrients and CTD data were provided by the participating working groups. Concentrations of the dissolved inorganic nitrogen compounds nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), and oxygen (O<sub>2</sub>) were determined using standard methods (Grasshoff et al., 1983).

The N<sub>2</sub>O inventory of each basin  $m_{\text{N}_2\text{O}}$  was calculated as follows:

$$m_{\text{N}_2\text{O}} [\text{tons}] = \bar{C}_{\text{N}_2\text{O}} * n_{\text{N}_2\text{O}} * V * 10^{-3} \quad (4)$$

where  $\bar{C}_{\text{N}_2\text{O}}$  is the mean measured N<sub>2</sub>O concentration in any given basin from the upper part of the halocline to the bottom (nmol L<sup>-1</sup>),  $n_{\text{N}_2\text{O}}$  is the molecular weight of N<sub>2</sub>O (44 g mol<sup>-1</sup>) and  $V$  is the water volume of each basin (km<sup>3</sup>).

The water volumes are based on data published in chapter 4.4.1 (HELCOM, 1996), available at: [www.vtt.fi/inf/baltic/balticinfo/index.html](http://www.vtt.fi/inf/baltic/balticinfo/index.html).

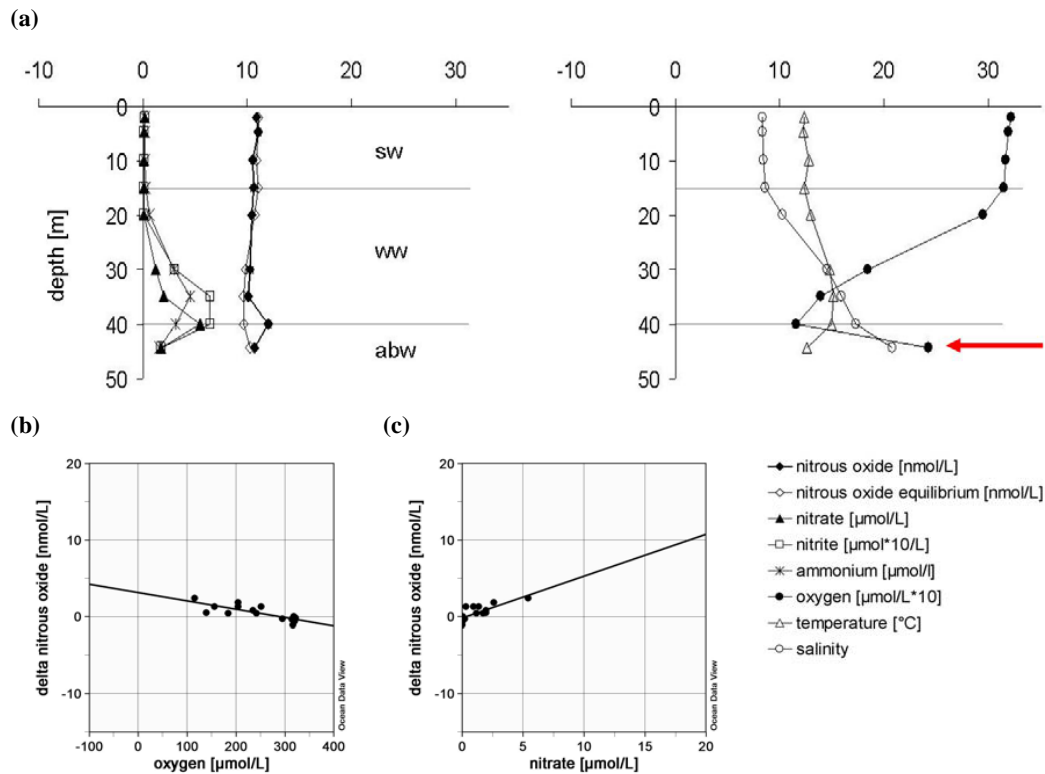
The N<sub>2</sub>O content of basins was calculated with data of the following stations: Bornholm Basin: station 140, 200, 213, 222, eastern Gotland Basin: station 250, 259, 260, 271, western Gotland Basin: station 240, 245, 284. Station 286 is located in the northern part of the Gotland Basin and thus has not been taken into account.

Net nitrification rates ( $N$ ) were estimated for the Bornholm Basin and the eastern Gotland Basin.

$$N \left[ \text{nmol L}^{-1} \text{d}^{-1} \right] = \frac{\Delta m_{\text{N}_2\text{O}}}{d_{\text{basin}} * V_{\text{basin}} * n * 10^{-9} * r_{\text{N}_2\text{O}}} \quad (5)$$

where  $\Delta m_{\text{N}_2\text{O}}$  is the difference of calculated N<sub>2</sub>O content of the basins before and after the inflow event in tonnes,  $d_{\text{basin}}$  is the number of days from the first observation of the intrusion of North Sea Water until our measurements (assumed by data from the cruise reports of Nausch, 2003a; Nagel, 2003; Feistel, 2003; Nausch, 2003b; Wasmund, 2003; Nausch, 2003c).

$V_{\text{basin}}$  is the calculated volume of the basins (km<sup>3</sup>),  $n$  is the molecular weight of N<sub>2</sub>O (44 g mol<sup>-1</sup>), and  $r_{\text{N}_2\text{O}}$  is the assumed N<sub>2</sub>O release factor of 0.003 (0.3%) over continental shelves during nitrification (Seitzinger and Kroeze, 1998).



**Fig. 4.** Arkona Basin; (a) station 113 (Arkona Deep): left plot with profiles of N<sub>2</sub>O, N<sub>2</sub>O equilibrium concentration, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, right plot with profiles of temperature, salinity and oxygen, the arrow indicate the influence of North Sea Water; abbreviations see Fig. 2.; (b)  $\Delta$ N<sub>2</sub>O plotted against oxygen (at all stations in the Arkona Basin,  $y = -0.011x + 3.132$ ,  $R^2 = 0.67$ ;  $n = 18$ ); (c)  $\Delta$ N<sub>2</sub>O plotted against NO<sub>3</sub><sup>-</sup> (at all stations in the Arkona Basin,  $y = 0.546x - 0.807$ ,  $R^2 = 0.66$ ;  $n = 18$ ).

### 3 Results

In order to account for the hydrographic characteristics of the Baltic Sea and the direction of the inflow of North Sea Water, we present the results according to the following classifications: I) well-mixed stations such as the Kiel, Lübeck and Pomeranian Bights and II) clearly stratified basins such as the Arkona, the Bornholm, the western and the eastern Gotland Basin (see Figs. 1, 2). For each basin selected profiles and empirically-tested correlations between N<sub>2</sub>O and parameters such as oxygen and nitrate are shown.

#### 3.1 Well-mixed stations

At shallow stations, with depths <30 m (station 10, 12, 22, 30, 41, 46, 121, 130, 133, 360, OB Boje, OB 4, Fig. 1), water columns were well mixed, and profiles showed nearly uniform vertical distributions of all parameters (Fig. 3a). Concentrations of N<sub>2</sub>O were near equilibrium; however the Pomeranian Bight (station 130, 133, OB Boje, OB 4) showed enhanced saturation values ( $104.6 \pm 7.9\%$ ) in comparison with the bights to the west of it. In the Kiel Bight (station 360), and the Lübeck (station 22) and Mecklenburg

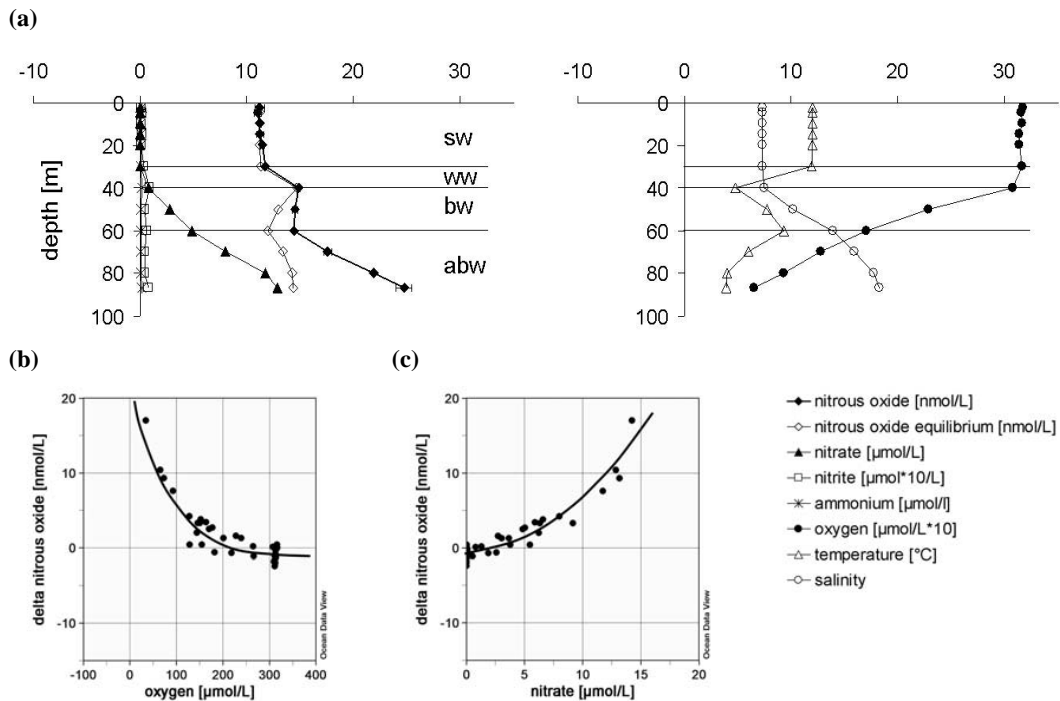
Bight (station 10, 12, 41, 46) the mean saturation value was  $79.3 \pm 10.7\%$ . No correlations were found between  $\Delta$ N<sub>2</sub>O and other parameters like O<sub>2</sub> and NO<sub>3</sub><sup>-</sup> (Fig. 3b–c).

#### 3.2 Stratified basins

Basins with water depths >30 m (Fig. 4–7) were clearly stratified into layers of well mixed Surface Water (*sw*), Winter (*ww*) and Bottom Water (*bw*) as described above. At several stations Bottom Water was affected by North Sea Water (*abw*), up to the Farö Deep in the northern part of the central Baltic Sea (Fig. 1, station 286) (Feistel et al., 2003). However, below 110 m the deep water of the Farö Deep was still anoxic, though with decreasing H<sub>2</sub>S concentrations from 125 m to the bottom (Fig. 6a, lower profiles). Stations in the western Gotland Basin such as the Landsort Deep (station 284, Fig. 7a) or the Karlsö Deep (station 245, not shown) were still unaffected by the inflow event, and so below 80 m H<sub>2</sub>S concentrations were uniform.

##### 3.2.1 Arkona Basin

In the Arkona Basin (stations 109 and 113 (Fig. 4a)), N<sub>2</sub>O concentrations were constant and near equilibrium



**Fig. 5.** Central Bornholm Basin; (a) station 213 (Bornholm Deep): left plot with profiles of N<sub>2</sub>O, N<sub>2</sub>O equilibrium concentration, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, right plot with profiles of temperature, salinity and oxygen, abbreviations see Fig. 2; (b) ΔN<sub>2</sub>O plotted against oxygen (at all stations in the Bornholm Basin,  $y=0.0003x^2-0.1531x+19.517$ ,  $R^2=0.88$ ;  $n=32$ ); (c) ΔN<sub>2</sub>O plotted against NO<sub>3</sub><sup>-</sup> (at all stations in the Bornholm Basin,  $y=0.0585x^2+0.1438x-0.6155$ ,  $R^2=0.90$ ;  $n=32$ ).

( $10.9\pm 0.7\text{ nmol L}^{-1}$ ) throughout the water column. In the Winter Water below the thermocline at 15 m O<sub>2</sub> concentrations decreased, associated with increasing NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. ΔN<sub>2</sub>O was slightly negatively correlated with O<sub>2</sub> (Fig. 4b), and positively correlated with NO<sub>3</sub><sup>-</sup> (Fig. 4c). At the bottom below 40 m inflowing North Sea Water (arrow in Fig. 4a) formed a 5 to 10 m thick oxygen enriched layer, however with no clear influence on the N<sub>2</sub>O concentration.

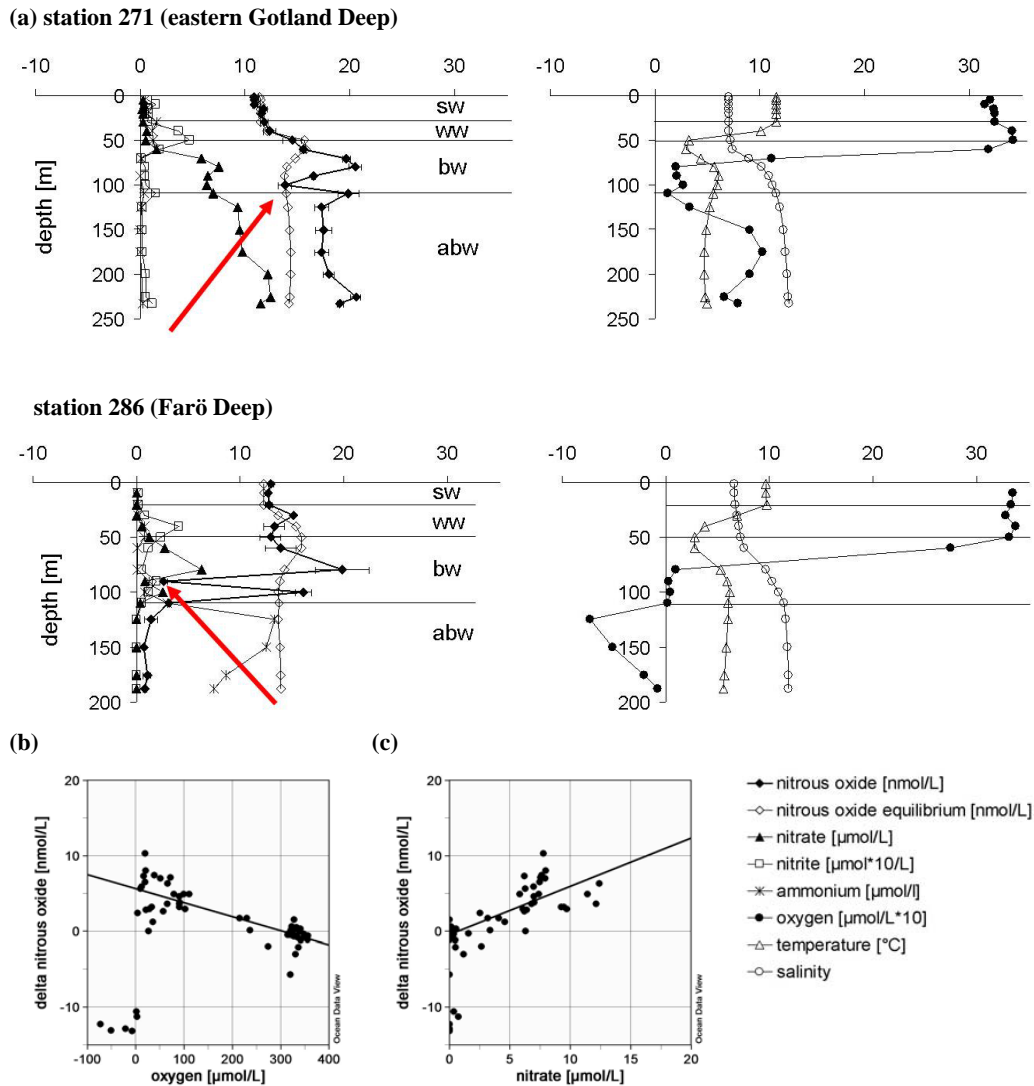
### 3.2.2 Bornholm Basin

In the Bornholm Basin (Fig. 5, stations 140, 200, 213 and 222), N<sub>2</sub>O profiles in the central basin (stations 200 (not shown) and 213 (Fig. 5a)) can be clearly distinguished from stations where water flows into and out of the basin. At station 140 (inflow, not shown) concentrations and distribution of N<sub>2</sub>O and ΔN<sub>2</sub>O were comparable to the Arkona Basin. At station 222 (outflow, not shown) N<sub>2</sub>O concentrations in the surface layer were uniformly near equilibrium at approximately 10 nmol L<sup>-1</sup>, below the surface layer concentrations were uniformly around 15.4 nmol L<sup>-1</sup>. In the central Bornholm Basin, at station 200 (not shown) and 213 (Fig. 5a) N<sub>2</sub>O concentrations increased rapidly within the layer affected by North Sea Water (abw, below 60 m), with N<sub>2</sub>O values up to 31.3 nmol L<sup>-1</sup> (station 200). These were the highest values measured during the entire cruise. In water

masses above, N<sub>2</sub>O was near equilibrium, with slightly enhanced ΔN<sub>2</sub>O values in the “old” Bottom Water (*bw*, 40–60 m). In the Bornholm Basin ΔN<sub>2</sub>O was clearly negatively correlated with oxygen and positively with NO<sub>3</sub><sup>-</sup> (Fig. 5b–c), but both correlations were nonlinear with polynomials providing the best fits.

### 3.2.3 Eastern Gotland Basin

The situation became more complex in the eastern Gotland basin (stations 259, 250, 260, 271 and 286). Profiles were not as homogeneous as in the Arkona or Bornholm Basin. Again, N<sub>2</sub>O concentrations were near equilibrium in the surface layer (*sw*, 0–20/30 m) and the Winter Water (*ww*, 20/30–60 m). At station 271 (Fig. 6a, upper profiles) the Bottom Water (*bw*) was well oxygenated, with N<sub>2</sub>O values at approximately 20 nmol L<sup>-1</sup> and positive ΔN<sub>2</sub>O. At station 286 (Fig. 6a, lower profiles) the Bottom Water (*bw*) was affected by the North Sea Water too, but was still anoxic. Inflow of North Sea Water was detectable by decreasing H<sub>2</sub>S concentrations down to the bottom. Throughout the Bottom Water N<sub>2</sub>O concentrations remained near zero. At station 250 (not shown), 271 (Fig. 6a, upper profiles) and 286 (Fig. 6a, lower profiles) a sharp local minimum of N<sub>2</sub>O concentrations was observed at depths between 90 and 110 m (see arrows in Fig. 6a), combined with a local minimum in NO<sub>3</sub><sup>-</sup> values.



**Fig. 6.** Eastern Gotland Basin; (a) station 271 (Gotland Deep, upper plots) and 286 (Farö Deep, lower plots): left plots with profiles of N<sub>2</sub>O, N<sub>2</sub>O equilibrium concentration, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>; right plots with profiles of temperature, salinity and oxygen, abbreviations see Fig. 2; (b) ΔN<sub>2</sub>O plotted against oxygen (at all stations in the Eastern Gotland Basin,  $y = -0.019x + 5.625$ ,  $R^2 = 0.67$ ;  $n = 62$  (except for  $O_2 < 3 \mu\text{mol L}^{-1}$ )); (c) ΔN<sub>2</sub>O plotted against NO<sub>3</sub><sup>-</sup> (at all stations in the Eastern Gotland Basin,  $y = 0.639x - 0.459$ ,  $R^2 = 0.62$ ;  $n = 62$  (except for  $O_2 < 3 \mu\text{mol L}^{-1}$ )); H<sub>2</sub>S is expressed by the negative oxygen equivalent ( $1 \mu\text{mol L}^{-1} \text{H}_2\text{S} = -2.00 \mu\text{mol L}^{-1} \text{O}_2$ ).

Except for the anoxic water masses, ΔN<sub>2</sub>O was linearly correlated with O<sub>2</sub> and NO<sub>3</sub><sup>-</sup> (Fig. 6b–c).

### 3.2.4 Western Gotland Basin

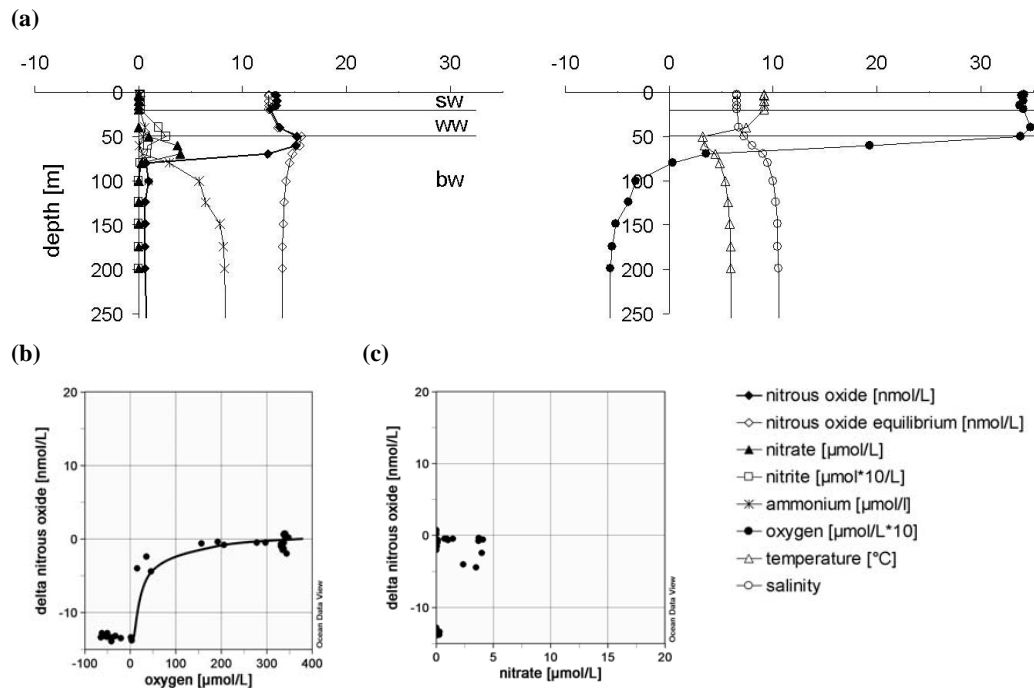
The western Gotland Basin with stations 284 (Fig. 7a), 245 and 240 revealed the “old” conditions, showing characteristics as yet unaffected by the latest intrusion of oxidic North Sea Water. N<sub>2</sub>O in the surface layer (sw, 0–20/40 m) and Winter Water (ww, 20/40–60 m) was near equilibrium. Below 50 m, oxygen concentrations decreased rapidly and N<sub>2</sub>O concentrations dropped sharply at the oxidic/anoxic interface and re-

mained near zero in the anoxic deep waters. ΔN<sub>2</sub>O values were negative and were not correlated with NO<sub>3</sub><sup>-</sup> (Fig. 7c). ΔN<sub>2</sub>O was logarithmically correlated with oxygen (Fig. 7b).

## 4 Discussion

Over the past two decades the previously frequent inflows of North Sea Water became rather rare (Feistel and Nausch, 2003), and oxygen levels in deep waters decreased. Thus, oxygen conditions in the Baltic Sea deep water cover a continuum from almost permanently oxidic (i.e. Arkona Basin) to





**Fig. 7.** Western Gotland Basin; (a) station 284 (Landsort Deep): left plot with profiles of N<sub>2</sub>O, N<sub>2</sub>O equilibrium concentration, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, right plot with profiles of temperature, salinity and oxygen, abbreviations see Fig. 2; (b)  $\Delta$ N<sub>2</sub>O plotted against oxygen (at all stations in the Western Gotland Basin;  $y=2.2467 \ln(x)-13.322$ ,  $R^2=0.86$ ;  $n=29$  (with exception of  $O_2 < 0 \mu\text{mol L}^{-1}$ )); (c)  $\Delta$ N<sub>2</sub>O plotted against NO<sub>3</sub><sup>-</sup> (at all stations in the Western Gotland Basin); H<sub>2</sub>S is expressed by the negative oxygen equivalent ( $1 \mu\text{mol L}^{-1} \text{H}_2\text{S} = -2.00 \mu\text{mol L}^{-1} \text{O}_2$ ).

almost permanently anoxic conditions (i.e. western Gotland Basin), with changes at non-regular intervals between anoxic and oxic conditions (i.e. Bornholm Basin, eastern Gotland Basin) (Feistel, 2003; Nausch, 2003a, b, c; Nagel, 2003; Wasmund, 2003).

The inflow event in January 2003 rapidly changed the environmental conditions of the deep basins. With respect to the oxygen dependent production of N<sub>2</sub>O, our measured N<sub>2</sub>O concentrations reflect the continuum of unaffected and changing oxygen conditions quite well. In oxic and well mixed waters, vertical N<sub>2</sub>O profiles were homogenous, with concentrations near equilibrium (Fig. 3a). Anoxic deep water layers, unaffected by North Sea Water (i.e. in the western Gotland Basin), had N<sub>2</sub>O concentrations near zero (Fig. 7a). Therefore, in both cases no correlations between N<sub>2</sub>O and either oxygen or nitrate were found (Fig. 3b–c, Fig. 7c). In contrast, stratified and recently ventilated water bodies in the Bornholm and eastern Gotland Basin revealed N<sub>2</sub>O distributions that were clearly correlated with oxygen and nitrate (Fig. 5b–c, Fig. 6b–c).

These vertical N<sub>2</sub>O distributions are in general agreement with the few previously published N<sub>2</sub>O profiles from the central Baltic Sea (Rönner, 1983; Rönner and Sörensson, 1985; Brettar and Rheinheimer, 1992). However, the past environmental settings of the deep central Baltic Sea basins were

different: N<sub>2</sub>O profiles from the central Baltic Sea reported by Rönner (1983) were obtained when oxic conditions prevailed during August–September 1977 after a strong inflow event in 1976/1977 (Schinke and Matthäus, 1998). These N<sub>2</sub>O profiles are comparable to our profiles, measured from the well oxygenated Bornholm Basin during October 2003 (Fig. 5a). Anoxic conditions were re-established in July 1979 and May–June 1980. The shape of the N<sub>2</sub>O profiles from the then anoxic Gotland Deep, reported by Rönner and Sörensson (1985) is comparable to our N<sub>2</sub>O profiles from the western Gotland Basin (e.g., the Landsort Deep, Fig. 7a). The same applied to observations by Brettar and Rheinheimer (1991) in August 1986 and July 1987 during the 1983–1993 stagnation periods (Schinke and Matthäus, 1998).

In the following sections we discuss the processes that may determine the observed distributions of N<sub>2</sub>O in the different basins.

## 5 Hydrographic aspects

In surface layers and well-mixed water bodies of shallow stations, observed N<sub>2</sub>O concentrations were near the equilibrium due to exchange with the atmosphere. In the Winter Water N<sub>2</sub>O concentrations were also near equilibrium, how-



ever with higher absolute values than in the surface layer (see Fig. 5a–7a). Mainly hydrographic aspects were here responsible for the observed N<sub>2</sub>O distribution. This water mass is formed during winter convection, when N<sub>2</sub>O concentrations were in equilibrium with the atmosphere and this signal is conserved during stratification of the upper layer in summer. The lower temperature and hence higher N<sub>2</sub>O solubility during formation of the Winter Water are the reason for the enhanced N<sub>2</sub>O concentrations in this layer.

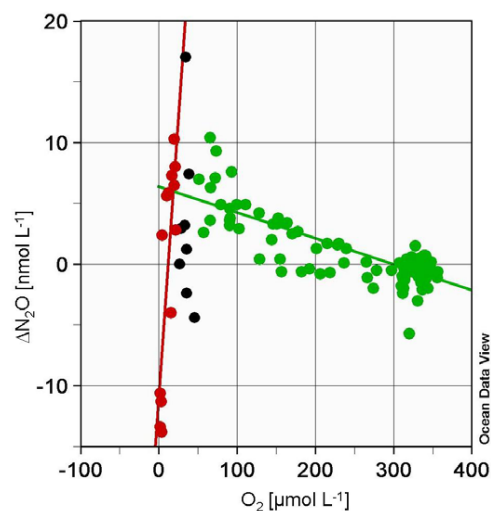
N<sub>2</sub>O in the deep water of the Baltic Sea might be affected by the inflow of North Sea Water. Intrusion of N<sub>2</sub>O by North Sea Water should be detectable at stratified stations, where the inflow of North Sea Water was clearly identified. In the Arkona Basin (station 109 and 113) this inflow was detectable at the bottom by lower temperature and higher oxygen concentrations; however, N<sub>2</sub>O concentrations did not increase and remained close to equilibrium (Fig. 4a–b). These results point to small supply of N<sub>2</sub>O by North Sea Water, and are supported by measurements of Law and Owens (1990). They found N<sub>2</sub>O concentrations close to equilibrium up to approximately 10 nmol L<sup>-1</sup> in the North Sea. Thus, the enhanced N<sub>2</sub>O values detected in layers affected by North Sea Water, for example in the Bornholm Basin (station 200 and 213), must originate from biological in situ production since the inflow, rather than advection.

## 5.1 Biological aspects

Previous studies demonstrated the existence of N<sub>2</sub>O producing bacteria and investigated the biological pathways, namely nitrification and denitrification in the Baltic Sea (Bauer, 2003; Brettar and Höfle, 1993; Brettar et al., 2001). Both processes are commonly inferred by correlations between N<sub>2</sub>O and oxygen or nitrate (Yoshinari, 1976; Yoshida et al., 1989; Cohen and Gordon, 1978; Butler et al., 1989).

### 5.1.1 Anoxic waters

In general, in anoxic and H<sub>2</sub>S containing bottom waters N<sub>2</sub>O concentrations were constantly near zero, and therefore no correlation with either O<sub>2</sub> or NO<sub>3</sub><sup>-</sup> was found. The N<sub>2</sub>O production by nitrification and denitrification might probably be inhibited by the presence of H<sub>2</sub>S (Joye and Hollibaugh, 1995; Knowles, 1982; Sørensen et al., 1980), and while changing to anoxic conditions, N<sub>2</sub>O can be consumed during denitrification as an electron acceptor instead of oxygen (Elkins et al., 1978; Cohen and Gordon, 1978). However, in contrast to other authors (Rönner et al., 1983; Brettar and Rheinheimer, 1992) we found low and uniformly distributed concentrations of N<sub>2</sub>O (up to 1.7 nmol L<sup>-1</sup>) in the anoxic water masses, which may have been residuals of a previous production process during oxic conditions.

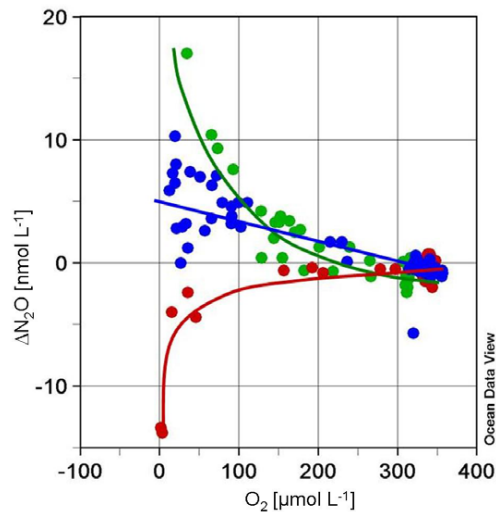


**Fig. 8.** Correlation between  $\Delta\text{N}_2\text{O}$  and  $\text{O}_2$  in the Baltic Sea. Correlations were calculated for oxic waters with  $\text{O}_2$  concentrations  $>50 \mu\text{mol L}^{-1}$  (green coloured,  $y=-0.019x+5.41$ ,  $R^2=-0.70$ ;  $n=183$ ) and  $<20 \mu\text{mol L}^{-1}$  (red coloured,  $y=1.038x-11.36$ ,  $R^2=0.81$ ;  $n=12$ ). These concentrations were empirically tested and gave the best fittings for both correlations.

### 5.1.2 Suboxic waters

In suboxic waters and at the boundary to anoxic water masses N<sub>2</sub>O is expected to be mainly produced by denitrification processes (Codispoti et al., 2001), usually indicated by decreasing NO<sub>3</sub><sup>-</sup> concentrations and a secondary NO<sub>2</sub><sup>-</sup> peak (Wrage et al., 2001; Kristiansen and Schaanning, 2002). These indicators for denitrification were found only at the Farö Deep (station 286, 90 m). However, no accumulation of N<sub>2</sub>O was observed, rather a local minimum of N<sub>2</sub>O was found (Fig. 6a, indicated by arrows). Naqui and Noronha (1991) reported that minima of nitrate correlated to minima of N<sub>2</sub>O are typical for most suboxic zones. Hannig et al. (2005) investigated denitrification associated microorganisms in the Gotland Basin (station 271 and 286) in October 2003. They did not find denitrification activities in suboxic water masses, but a high denitrifying potential restricted to a narrow depth range at the oxic-anoxic interface and the sulphidic zone. However, at these depths an accumulation of N<sub>2</sub>O was not found either. Thus, the observed N<sub>2</sub>O profiles might reflect previous redox transformations in the water column.

The local minimum of N<sub>2</sub>O was found not only at the Farö Deep, but also at the Gotland Deep (Fig. 6a, indicated by arrows) and at station 250 (profile not shown). A residual signal of the small inflow event in August 2002 could be observed at these depths between 90 and 110 m (Feistel et al., 2003). It is also possible that this minimum of N<sub>2</sub>O is a previous signal of former anoxic bottom water, pushed up by the small inflow event in August 2002. The restriction of



**Fig. 9.** Correlation between  $\Delta\text{N}_2\text{O}$  and  $\text{O}_2$  in the Baltic Sea; Correlations were calculated for the Bornholm Basin (stations 140, 200, 213, 222, green coloured,  $y = -6.83 \ln(x) + 37.88$ ,  $R^2 = 0.86$ ;  $n = 40$ ), the eastern Gotland Basin (station 259, 250, 260, 271, blue coloured,  $y = -0.02x + 5.88$ ,  $R^2 = 0.70$ ;  $n = 54$ ) and the western Gotland Basin (station 284, 240, 245, red coloured,  $y = 2.25 \ln(x) - 13.32$ ,  $R^2 = 0.86$ ;  $n = 29$ ). Anoxic data and station 286 were excluded. The correlations were empirically tested and gave the best fittings.

denitrification activity to a narrow depth range at anoxic-oxic boundaries was not only reported by Hannig et al. (2005) but also by Brettar et al. (2001). Therefore, the lack of denitrification signals seems to rule out denitrification as a major process responsible for N<sub>2</sub>O production.

### 5.1.3 Correlation between N<sub>2</sub>O and O<sub>2</sub>

At O<sub>2</sub> concentrations  $>50 \mu\text{mol L}^{-1}$   $\Delta\text{N}_2\text{O}$  is clearly negatively correlated with O<sub>2</sub>, indicating production by nitrification (see Fig. 8, green data points). At O<sub>2</sub> concentrations  $<20 \mu\text{mol L}^{-1}$   $\Delta\text{N}_2\text{O}$  and O<sub>2</sub> were significantly positively correlated (see Fig. 8, red data points), data between  $20 \mu\text{mol L}^{-1}$  and  $50 \mu\text{mol L}^{-1}$  were extremely scattered (see Fig. 8, black data points). Our results suggest a production of N<sub>2</sub>O during nitrification until an oxygen threshold of around  $20\text{--}50 \mu\text{mol L}^{-1}$ , although the exact threshold concentration cannot be established due to large scatter of the data. In the literature, threshold values of  $2 \mu\text{mol L}^{-1}$  for nitrification are reported (Carlucci and McNally, 1969; Gundersen et al., 1966). Below the threshold N<sub>2</sub>O seemed to be degraded; probably used as an electron acceptor instead of oxygen and thereby reduced to N<sub>2</sub> (Elkins et al., 1978; Cohen and Gordon, 1978).

These findings suggest a change in N<sub>2</sub>O converting processes either by different bacteria species or different processes. Bauer (2003) investigated NH<sub>4</sub><sup>+</sup> oxidizing bacte-

ria in the eastern Gotland Basin, and found similar bacterial communities at different depths; their nitrification activities however depended on O<sub>2</sub> concentrations. The oxygen sensitivity is species-specific and also enzyme-specific, with a broad range even between closely related species; therefore the scatter of data might reflect the variety of involved species and enzymes (Geets et al., 2006, Jiang and Bakken, 2000; Goreau et al., 1980; Wetzel, 1983; Robertson et al., 1988; Richardson, 2000). Particularly in environments with rapidly changing conditions it is advantageous for microorganisms to be able to switch between different metabolic pathways. For several nitrifiers the ability to switch between different processes such as “classical” nitrification, nitrifier-denitrification and aerobic denitrification has been shown (Wrage et al., 2001; Whittaker et al., 2000; Zart et al., 2000; Zehr and Ward, 2002). The change between aerobic and anaerobic metabolisms and thus the yield of N<sub>2</sub>O during these processes is probably controlled particularly by the O<sub>2</sub> concentration, although little is known about the detailed mechanisms (Baumann et al., 1996; John, 1977; Sørensen, 1987).

Alternatively, it is also possible to interpret the data from the hydrographical or temporal point of view. Figure 9 shows the same data set as shown in Fig. 8. This time the data set is grouped not according to the oxygen concentrations but to the affiliation to different basins. Station 286 was excluded due to its transitional character. At this station anoxic conditions in the deep waters were found similar to other stations in the western Gotland Basin, but H<sub>2</sub>S concentrations were decreasing towards the bottom. This indicates an early stage of ventilation, but still too weak to lead to oxic conditions.

In the stratified basins such as the Bornholm Basin, and the eastern and western Gotland Basin correlations of  $\Delta\text{N}_2\text{O}$  and O<sub>2</sub> were regionally different and not always linear (Figs. 5b–c, 6b–c, 7a, 9). Particularly in the Bornholm Basin, N<sub>2</sub>O and oxygen as well as N<sub>2</sub>O and nitrate showed significant non-linear relationships (Figs. 5b–c, 9). The Bornholm Basin, which was anoxic before the inflow (Schmidt, 2002), was ventilated by North Sea Water in January 2003, months before the northern part of the eastern Gotland Basin was affected by the inflow (Nausch, 2003a, Nausch et al., 2004). In October 2003 the oxygen conditions were already switching back to suboxic conditions (Nausch, 2003c; Wasmund, 2003), visible by decreasing oxygen concentrations compared to the beginning of the year. Accordingly the duration of elevated oxygen concentration in the respective basins may contribute to the observed differences in the accumulation of N<sub>2</sub>O. In the eastern Gotland Basin (Figs. 6b–c, 9) the anoxic conditions changed a few months after the Bornholm Basin: the Gotland Deep was ventilated by North Sea Water in May 2003 (Nausch, 2003b). Thus, there was less time for N<sub>2</sub>O accumulation. For various communities of NH<sub>4</sub><sup>+</sup> oxidizing bacteria different lag times after switching from anoxic to oxic incubations have been shown and the production of N<sub>2</sub>O might not have started immediately after the ventilation

**Table 1.** Estimated N<sub>2</sub>O content of single basins in the Baltic Sea below the halocline, before and after the inflow of North Sea Water in January 2003.

	mean N <sub>2</sub> O conc. below the halocline (nmol L <sup>-1</sup> )	Water volume (km <sup>3</sup> )	N <sub>2</sub> O content before the inflow event (tonnes)	N <sub>2</sub> O content after the inflow event (tonnes)
Bornholm Basin	>50 m 16.59±5.61	306	13±5	223±76
Eastern Gotland Basin	>70 m 18.46±3.43	1195	51±18	971±180
Σ		1501	<b>64 ± 23</b>	<b>1194 ± 256</b>
Western Gotland Basin	>70 m 0.97±0.34	657	28±10	28±10

**Table 2.** Estimated nitrification rates in the Bornholm Basin and the eastern Gotland Basin, based on the assumption of 0.3% N<sub>2</sub>O release during nitrification (Seitzinger and Kroeze, 1998).

	Δ <i>m</i> <sub>N<sub>2</sub>O</sub> (tonnes)	<i>d</i> <sub>basin</sub> (day)	Water volume (km <sup>3</sup> )	N <sub>2</sub> O net production rate (nmol L <sup>-1</sup> d <sup>-1</sup> )	net nitrification rate (nmol L <sup>-1</sup> d <sup>-1</sup> )
Bornholm Basin	210±81	265	306	0.059±0.023	19.62±7.57
Eastern Gotland Basin	920±198	167	1195	0.105±0.023	34.92±7.52

by North Sea Water (Geets et al., 2006; Bodelier et al., 1996). In the western Gotland Basin (Figs. 7b–c, 9) no ventilation by North Sea Water had occurred by October 2003, therefore degradation of N<sub>2</sub>O at the oxic-anoxic interface was found. We suspect that the correlation between ΔN<sub>2</sub>O and O<sub>2</sub> in the Bornholm Basin and the eastern Gotland Basin will become similar to that of the western Gotland Basin with time, when the conditions change to anoxic.

## 5.2 Estimated N<sub>2</sub>O inventories before and after the North Sea Water inflow event

The North Sea Water inflow consisted of a water volume of 200 km<sup>3</sup> (Feistel and Nausch, 2003). With an assumed N<sub>2</sub>O concentration of 10±2 nmol L<sup>-1</sup> (Law and Owens, 1990), the North Sea Water transported approximately 88±18 tonnes N<sub>2</sub>O into the Baltic Sea.

Before the North Sea Water inflow, the deep waters below the halocline were anoxic, not only in the western but also in the eastern Gotland Basin and the Bornholm Basin (Schmidt, 2002). Thus, N<sub>2</sub>O concentrations near zero similar to measured profiles in the western Gotland Basin in October 2003 (Fig. 7a) can be assumed. The mean N<sub>2</sub>O concentration in the western Gotland Basin was 0.97±0.34 nmol L<sup>-1</sup>. On the basis of these values the calculated N<sub>2</sub>O content of the Bornholm Basin and the eastern Gotland Basin was approximately 13±5 and 51±18 tonnes before the inflow (see Table 1).

After the inflow event the Bornholm Basin and the eastern Gotland Basin were clearly influenced by the North Sea Wa-

ter, whereas the western Gotland Basin was still unaffected (Nausch, 2003a; Nagel, 2003; Feistel, 2003; Nausch, 2003b; Wasmund, 2003; Nausch, 2003c). Based on these assumptions, the N<sub>2</sub>O contents of the Bornholm Basin and the eastern Gotland Basin, calculated with the mean of measured N<sub>2</sub>O concentrations below the halocline in these basins, were about 223±76 and 971±180 tonnes, respectively (Table 1). Thus, the North Sea Water led to a net production of 1130±233 tonnes N<sub>2</sub>O.

The estimated N<sub>2</sub>O content in the stratified basins showed distinctly higher values after the inflow of the North Sea Water than before. The N<sub>2</sub>O concentration in the North Sea Water was assumed to be near equilibrium, so there was no significant advection of N<sub>2</sub>O from the North Sea. Thus, the observed elevated N<sub>2</sub>O concentrations in the Baltic Sea basins probably resulted from a stimulation of N<sub>2</sub>O production by the inflow, most likely by advection of oxygen (see Table 1).

Although more than 1000 tonnes of N<sub>2</sub>O were produced, it is questionable whether the North Sea Water inflow makes the Baltic Sea a source of atmospheric N<sub>2</sub>O. Due to the strong salinity stratification, it can be assumed that the N<sub>2</sub>O produced stays below the permanent halocline, and therefore it will not reach the atmosphere. Commonly N<sub>2</sub>O budgets are modeled as a function of nitrification and denitrification. For example, Seitzinger and Kroeze (1998) modelled the distribution of N<sub>2</sub>O production, based on the input of nitrogen compounds into estuaries by rivers. However, estimations of global N<sub>2</sub>O emissions do not or only to a small extent

take into account the hydrographic aspects. The stratification of the water column probably leads to a reduced release of calculated amounts, and accordingly to an overestimation of N<sub>2</sub>O emissions.

Based on the calculated N<sub>2</sub>O content of the basins and the assumption of nitrification as the main production pathway net-nitrification rates were estimated (Table 2). These nitrification rates are in good agreement with previously published rates for the Baltic Sea (Enoksson, 1986; Bauer 2003). For the eastern Gotland Basin, Bauer (2003) calculated mean nitrification rates of  $21.6 \pm 11.1 \text{ nmol L}^{-1}$  at 60 m depth, and  $44.3 \pm 33.1 \text{ nmol L}^{-1}$  at 100 m depth.

These nitrification rates are low compared to rates published from other oceanic areas (e.g. Bianchi et al., 1999).

## 6 Summary

In January 2003 a major inflow of cold, highly saline and oxygen-rich North Sea Water was observed, terminating the ongoing stagnation period in parts of the central Baltic Sea.

- In agreement with previous studies, we found N<sub>2</sub>O production mainly in oxic water masses below the Winter Water layer.
- We found no indication for advection of N<sub>2</sub>O by North Sea Water; however, the environmental conditions for N<sub>2</sub>O production were clearly changed due to the North Sea Water inflow.
- The inflow leads to a stimulation of N<sub>2</sub>O production below the permanent halocline, but due to the halocline, the Baltic Sea is not a significant source of N<sub>2</sub>O to the atmosphere.
- There was no indication for an accumulation of N<sub>2</sub>O during denitrification. In oxic and suboxic water masses nitrification seems to be the main production pathway. The occurrence of nitrifier-denitrification and aerobic denitrification is possible, but needs further investigations.

**Acknowledgements.** We thank the officers and crew of R/V Gauss for their excellent support. We especially thank R. Hoffmann (MPI for Chemistry, Mainz) for the calibration of the standard gas mixtures, and the colleagues from the IOW for providing the CTD data and the nutrients. We thank Maren Voss, Wajih Naqvi, and Günther Uher for their comments which helped to improve the manuscript considerably. The study was financially supported by the Deutsche Forschungsgemeinschaft through grant WA1434/1. The German part of the HELCOM COMBINE program is conducted by the Leibniz Institut für Ostseeforschung Warnemünde on behalf of the Bundesamt für Seeschifffahrt und Hydrographie, Hamburg and is funded by the Bundesministerium für Verkehr, Bau und Stadtentwicklung, Berlin.

Edited by: S. W. A. Naqvi

## References

- Bange, H. W., Rapsomanikis, S., and Andreae, M. O.: Nitrous oxide in coastal waters, *Global Biogeochem. Cycles*, 10(1), 197–207, 1996.
- Bange, H. W., Rapsomanikis, S., and Andreae, M. O.: Nitrous oxide cycling in the Arabian Sea, *J. Geophys. Res.-Oceans*, 106(C1), 1053–1065, 2001.
- Bauer, S.: Structure and function of nitrifying bacterial communities in the Eastern Gotland Basin (Central Baltic Sea), Rostock, Univ., Diss., 2003, H 2003 B 4373, 2003.
- Baumann, B., Snozzi, M., Zehnder, A. J. B., and van der Meer, J. R.: Dynamics of denitrification activity of *Paracoccus denitrificans* in continuous culture during aerobic-anaerobic changes, *J. Bacteriol.*, 178(15), 4367–4374, 1996.
- Bianchi, M., Fosset, C., and Conan, P.: Nitrification rates in the NW Mediterranean Sea, *Aquat. Microb. Ecol.*, 17(3), 267–278, 1999.
- Bodelier, P. L. E., Libochant, J. A., Blom, C. W. P., and Laanbroek, H. J.: Dynamics of nitrification and denitrification in root-oxygenated sediments and adaptation of ammonia-oxidizing bacteria to low-oxygen or anoxic habitats, *Appl. Environ. Microbiol.*, 62, 4100–4107, 1996.
- Brettar, I. and Höfle, M. G.: Nitrous oxide producing heterotrophic bacteria from the water column of the central Baltic: abundance and molecular identification, *Mar. Ecol. Prog. Ser.*, 94, 253–265, 1993.
- Brettar, I., Moore, E. R. B., and Höfle, M. G.: Phylogeny and abundance of novel denitrifying bacteria isolated from the water column of the central Baltic Sea, *Microb. Ecol.*, 42(3), 295–305, 2001.
- Brettar, I. and Rheinheimer, G.: Denitrification in the central Baltic: evidence for hydrogen sulfide oxidation as motor of denitrification at the oxic-anoxic interface, *Mar. Ecol. Prog. Ser.* 77(2–3), 157–169, 1991.
- Brettar, I. and Rheinheimer, G.: Influence of carbon availability on denitrification in the Central Baltic Sea, *Limnol. Oceanogr.*, 37(6), 1146–1163, 1992.
- Butler, J. H., Elkins, J. W., Thompson, T. M., and Egan, K. B.: Tropospheric and dissolved N<sub>2</sub>O of the West Pacific and East Indian Oceans during the El-Nino Southern Oscillation event of 1987, *J. Geophys. Res.-Atmos.*, 94(D12), 14 865–14 877, 1989.
- Carlucci, A. F. and McNally, P. M.: Nitrification by marine bacteria in low concentrations of substrate and oxygen, *Limnol. Oceanogr.*, 14, 736–739, 1969.
- Codispoti, L. A., Brandes, J. A., Christensen, J. P., Devol, A. H., Naqvi, S. W. A., Paerl, H. W., and Yoshinari, T.: The oceanic fixed nitrogen and nitrous oxide budgets: Moving targets as we enter the anthropocene?, *Sci. Mar.*, 65, 85–105, 2001.
- Codispoti, L. A., Yoshinari, T., and Devol, A. H.: Suboxic respiration in the oceanic water column, in *Respiration in aquatic ecosystems*, edited by: Del Giorgio, P. A. and Williams, P. J. I. B., pp. 225–247, Oxford University Press, Oxford, 2005.
- Cohen, Y. and Gordon, L. I.: Nitrous oxide in the oxygen minimum of the eastern tropical North Pacific: Evidence for its consumption during denitrification and possible mechanisms for its production, *Deep-Sea Res.*, 25(6), 509–524, 1978.
- Dahlke, S., Wolff, S., Meyer-Reil, L.-A., Bange, H. W., Ramesh, R., Rapsomanikis, S., and Andreae, M. O.: Bodden waters (southern Baltic Sea) as a source of methane and nitrous oxide, in *Proceedings in Marine Sciences, Volume 2: Muddy Coast Dynamics*

- and Resource Management, edited by: Flemming, B. W., Delafontaine, M. T., and Liebezeit, G., pp. 137–148, Elsevier Science, Amsterdam, 2000.
- Elkins, J. W., Wofsy, S. C., McElroy, M. B., Kolb, C. E., and Kaplan, W. A.: Aquatic sources and sinks for nitrous oxide, *Nature*, 275(5681), 602–606, 1978.
- Enoksson, V.: Nitrification rates in the Baltic Sea: Comparison of three isotope techniques, *Appl. Environ. Microbiol.*, 51(2), 244–250, 1986.
- Feistel, R.: IOW Cruise report 11/03/02, March 2003, <http://www.io-warnemuende.de/projects/monitoring/documents/cr110302.pdf>, 2003.
- Feistel, R., Nausch, G., Matthäus, W., and Hagen, E.: Temporal and spatial evolution of the Baltic deep water renewal in spring 2003, *Oceanol.*, 45(2), 623–642, 2003.
- Feistel, R. and Nausch, G.: Water exchange between the Baltic Sea and the North Sea and conditions in the deep basins, HELCOM indicator fact sheets / Baltic Marine Environment Protection Commission – Helsinki Commission, <http://www.helcom.fi/environment/indicators2003/inflow.html>, 2003.
- Geets, J., Boon, N., and Verstraete, W.: Strategies of aerobic ammonia-oxidizing bacteria for coping with nutrient and oxygen fluctuations, *FEMS Microbiol. Ecol.*, 58, 1–13, doi:10.1111/j.1574-6941.2006.00170.x, 2006.
- Goreau, T. J., Kaplan, W. A., Wofsy, S. C., McElroy, M. B., Valois, F. W., and Watson, S. W.: Production of nitrite and nitrous oxide by nitrifying bacteria at reduced concentrations of oxygen, *Appl. Environ. Microbiol.*, 40(3), 526–532, 1980.
- Grasshoff, K., Ehrhardt, M., and Kremling, K. (Eds.): *Methods of seawater analysis*, Verlag Chemie, Weinheim, pp. 419, 1983.
- Gundersen, K., Carlucci, A. F., and Boström, K.: Growth of some chemoautotrophic bacteria at different oxygen tensions, *Experientia*, 22, 229–230, 1966.
- Hannig, M., Braker, G., Lavik, G., Kuypers, M., Dippner, J. W., and Jürgens, K.: Structure and activity of denitrifying bacteria in the water column of the Gotland Basin (Baltic Sea), Abstract presented at the SPOT-ON conference 2005, Warnemünde, June 26–July 1, 2005.
- HELCOM: Third periodic assessment of the state of the marine environment of the Baltic Sea 1989–1993, *Balt. Sea Environ. Proc.* no. 64b, p. 75, <http://www.baltic.vtt.fi/balticinfo/index.html>, 1996.
- Jiang, Q. Q. and Bakken, L. R.: Nitrous oxide production and methane oxidation by different ammonia-oxidizing bacteria, *Appl. Environ. Microbiol.*, 65, 2679–2684, 2000.
- Jørgensen, B. B. and Sørensen, J.: Seasonal cycles of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> reduction in estuarine sediments: The significance of a NO<sub>3</sub><sup>-</sup> reduction maximum in spring, *Mar. Ecol. Prog. Ser.*, 24, 65–74, 1985.
- John, P.: Aerobic and anaerobic bacterial respiration monitored by electrodes, *J. Gen. Microbiol.*, 98, 231–238, 1977.
- Joye, S. B. and Hollibaugh, J. T.: Influence of sulfide inhibition of nitrification on nitrogen regeneration in sediments, *Science*, 270, 623–625, 1995.
- Knowles, R.: Denitrification, *Microbiol. Rev.*, 46, 43–70, 1982.
- Kristiansen, S. and Schaanning, M. T.: Denitrification in the water column of an intermittently anoxic fjord, *Hydrobiologia*, 469, 77–86, 2002.
- Law, C.S., and Owens, N.J.P.: Denitrification and nitrous oxide in the North Sea, *Neth. J. Sea Res.*, 25(1–2), 65–74, 1990.
- Meier, M. H. E.: Modelling the age of Baltic seawater masses: Quantification and steady state sensitivity experiments, *J. Geophys. Res.*, 110, C02006, doi:10.1029/2004JC002607, 2005.
- Nagel, K.: IOW Cruise report 11/03/01, February 2003 <http://www.io-warnemuende.de/projects/monitoring/documents/cr110301.pdf>, 2003.
- 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., Jayakumar, D. A., Narvekar, P. V., Naik, H., Sarma, V., D'Souza, W., Joseph, S., and George, M. D.: Increased marine production of N<sub>2</sub>O due to intensifying anoxia on the Indian continental shelf, *Nature*, 408(6810), 346–349, 2000.
- Nausch, G.: IOW Cruise Report 40/03/22, January 2003, <http://www.io-warnemuende.de/projects/monitoring/documents/cr400322.pdf>, 2003a.
- Nausch, G.: IOW Cruise Report 44/03/03, May 2003, <http://www.io-warnemuende.de/projects/monitoring/documents/cr440303.pdf>, 2003b.
- Nausch, G.: Cruise report 11/03/04, October 2003, <http://www.io-warnemuende.de/projects/monitoring/documents/cr110304.pdf>, 2003c.
- Nausch, G., Feistel, R., Lass, H.-U., Nagel, K., and Siegel, H.: Hydrographisch-chemische Zustandseinschätzung der Ostsee 2003, *Meereswissenschaftliche Berichte*, 59(1), 1–80, 2004.
- Nausch, G., Matthäus, W., and Feistel, R.: Hydrographic and hydrochemical conditions in the Gotland Deep area between 1992 and 2003, *Oceanologia*, 45(2), 557–569, 2003.
- Ostrom, N. E., Russ, M. E., Popp, B., Rust, T. M., and Karl, D. M.: Mechanisms of nitrous oxide production in the subtropical North Pacific based on determinations of the isotopic abundances of nitrous oxide and di-nitrogen, *Chemosphere: Global Change Science*, 2(3–4), 281–290, 2000.
- Popp, B. N., Westley, M. B., Toyoda, S., Miwa, T., Dore, J. E., Yoshida, N., Rust, T. M., Sansone, F. J., Russ, M. E., Ostrom, N. E., and Ostrom, P. H.: Nitrogen and oxygen isotopomeric constraints on the origins and sea-to-air flux of N<sub>2</sub>O in the oligotrophic subtropical North Pacific gyre, *Global Biogeochem. Cycles*, 16(2), doi:10.1029/2001GB001806, 2002.
- Prather, M., Ehhalt, D., Dentener, F., Derwent, R., Dlugokencky, E., Holland, E., Isaksen, I., Katima, J., Kirchhoff, V., Matson, P., Midgley, P., and Wang, M.: Atmospheric chemistry and greenhouse gases, in *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., Van der Linden, P. J., Dai, X., Maskell, K., and Johnson, C. A., pp. 239–287, Cambridge University Press, Cambridge, UK, 2001.
- Richardson, D. J.: Bacterial respiration: A flexible process for a changing environment, *Microbiology*, 146, 551–571, 2000.
- Robertson, L. A. and Kuenen, J. G.: Aerobic denitrification - Old wine in new bottles, *Anton Leeuwenhoek J. Microbiol.*, 50(5–6), 525–544, 1984.
- Robertson, L. A., Vanniell, E. W. J., Torremans, R. A. M., and Kuenen, J. G.: Simultaneous nitrification and denitrification in aerobic chemostat cultures of *Thiosphaera pantotropha*, *Appl. Environ. Microbiol.*, 54(11), 2812–2818, 1988.
- Rönner, U.: Distribution, production and consumption of nitrous oxide in the Baltic Sea, *Geochim. Cosmochim. Acta*, 47, 2179–

- 2188, 1983.
- Rönner, U., Sörensson, F., and Holmhansen, O.: Nitrogen assimilation by phytoplankton in the Scotia Sea, *Polar Biol.*, 2(3), 137–147, 1983.
- Rönner, U. and Sörensson, F.: Denitrification rates in the low-oxygen waters of the stratified Baltic Proper, *Appl. Environ. Microbiol.*, 50, 801–806, 1985.
- Schinke, H. and Matthäus, W.: On the causes of major Baltic inflows – an analysis of long time series, *Continental Shelf Res.*, 18, 67–97, 1998.
- Schmidt, M.: IOW Cruise Report 11/02/03, October 2002, <http://www.io-warnemuende.de/projects/monitoring/documents/cr110203.pdf>, 2002.
- Seitzinger, S. P. and Kroeze, C.: Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems, *Global Biogeochem. Cycles*, 12(1), 93–113, 1998.
- Seitzinger, S. P., Kroeze, C., and Styles, R. V.: Global distribution of N<sub>2</sub>O emissions from aquatic systems: Natural emissions and anthropogenic effects, *Chemosphere: Global Science Change*, 2, 267–279, 2000.
- Sørensen, J.: Nitrate reduction in marine sediment: Pathways and interactions with iron and sulfur cycling, *Geomicrobiology J.*, 5(3–4), 401–422, 1987.
- Sørensen, J., Tiedje, J. M., and Firestone, R. B.: Inhibition by sulfide of nitric and nitrous oxide reduction by denitrifying *Pseudomonas fluorescens*, *Appl. Environ. Microbiol.*, 39(1), 105–108, 1980.
- Vollack, K. U. and Zumft, W. G.: Nitric oxide signaling and transcriptional control of denitrification genes in *Pseudomonas stutzeri*, *J. Bacteriol.*, 183(8), 2516–2526, 2001.
- Wasmund, N.: IOW Cruise Report 44/03/07, July-August 2003, <http://www.io-warnemuende.de/projects/monitoring/documents/cr440307.pdf>, 2003.
- Weiss, R. F.: The solubility of nitrogen, oxygen and argon in water and seawater, *Deep-Sea Res.*, 17, 721–735, 1970.
- Weiss, R. F. and Price, B. A.: Nitrous oxide solubility in water and seawater, *Mar. Chem.*, 8, 347–359, 1980.
- Wetzel, R. G.: *Limnology*, Saunders College Publishing, Philadelphia, Pa., 1983.
- Whittaker, M., Bergnam, D., Arciero, D. and Hooper, A. B.: Electron transfer during the oxidation of ammonia by the chemolithotrophic bacterium *Nitrosomonas europaea*, *Biochim. Biophys. Acta*, 1459, 346–355, 2000.
- WMO: Scientific assessment of ozone depletion: 2002, pp. 498, WMO (World Meteorological Organization), Geneva, 2003.
- Wrage, N., Velthof, G. L., van Beusichem, M. L., and Oenema, O.: Role of nitrifier denitrification in the production of nitrous oxide, *Soil Biol. Biochem.*, 33(12–13), 1723–1732, 2001.
- Yamagishi, H., Yoshida, N., Toyoda, S., Popp, B. N., Westley, M. B., and Watanabe, S.: Contributions of denitrification and mixing on the distribution of nitrous oxide in the North Pacific, *Geophys. Res. Lett.*, 32(2), LO4603, doi:10.1029/2004GLO21458, 2005.
- Yoshida, N., Morimoto, H., Hirano, M., Koike, I., Matsuo, S., Wada, E., Saino, T., and Hattori, A.: Nitrification rates and <sup>15</sup>N abundances of N<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> in the western North Pacific, *Nature*, 342, 895–897, 1989.
- Yoshinari, T.: Nitrous oxide in the sea, *Mar. Chem.*, 4, 189–202, 1976.
- Yoshinari, T., Altabet, M. A., Naqvi, S. W. A., Codispoti, L., Jayakumar, A., Kuhland, M., and Devol, A.: Nitrogen and oxygen isotopic composition of N<sub>2</sub>O from suboxic waters of the eastern tropical North Pacific and the Arabian Sea – Measurement by continuous-flow isotope-ratio monitoring, *Mar. Chem.*, 56(3–4), 253–264, 1997.
- Zart, D., Schmidt, I., and Bock, E.: Significance of gaseous NO for ammonia oxidation by *Nitrosomonas eutropha*, *Antonie van Leeuwenhoek*, 77, 49–55, 2000.
- Zehr, J. P. and Ward, B. B.: Nitrogen cycling in the ocean: New perspectives on processes and paradigms, *Appl. Environ. Microbiol.*, 68(3), 1015–1024, 2002.