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Distribution of N₂O in the Baltic Sea during transition from anoxic to oxic conditions

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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 (N₂O), we measured dissolved and atmospheric N₂O 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 N₂O concentrations: Shallow stations in the Kiel Bight and Pomeranian Bight were well-ventilated with uniform N₂O 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 (O₂) or declining hydrogen sulphide (H₂S) concentrations, thus, affecting the conditions for the production of N₂O. Pattern of N₂O profiles and correlations with parameters like oxygen and nitrate differed between the basins. Because of the positive correlation between Δ N₂O and AOU in oxic waters the dominant production pathway seems to be nitrification rather than denitrification.

Advection of N₂O by North Sea Water was found to be of minor importance. A rough budget revealed a significant surplus of in situ produced N₂O after the inflow. However, due to the permanent halocline, it can be assumed that the N₂O produced does not reach the atmosphere. Hydrographic

aspects therefore are decisive factors determining the final release of N₂O produced to the atmosphere.

1 Introduction

1.1 Nitrous oxide

Nitrous oxide (N₂O) 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).

N₂O 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, N₂O 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 N₂O as an intermediate (Cohen and Gordon, 1978). N₂O 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 N₂O during nitrifier-denitrification or aerobic denitrification (Wrage et al., 2001). Both processes enable nitrifiers to oxidize NH₄⁺ to NO₂⁻, followed by the reduction of NO₂⁻ to N₂O or N₂ (Robertson and Kuenen, 1984; Robertson et al., 1988; Richardson, 2000). In anoxic habitats N₂O is used, instead of oxygen, as an electron acceptor (Elkins et al., 1978; Cohen and Gordon, 1978).

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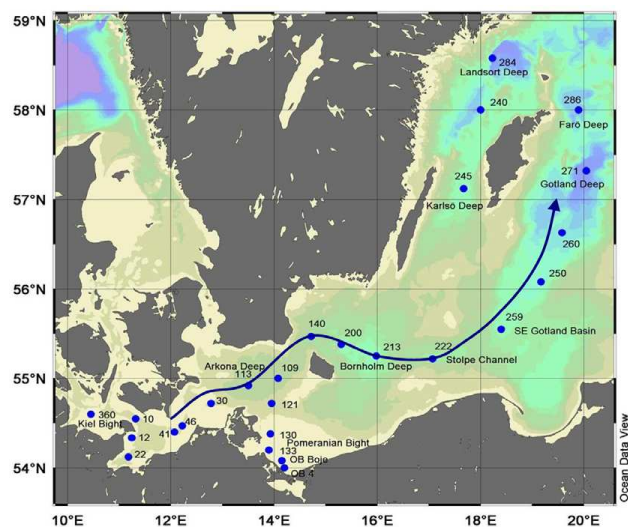


Fig. 1. Map of the western, southern and central Baltic Sea with locations of the stations. The stations were grouped as follows: well-mixed stations are number 10, 12, 22, 30, 41, 46, 121, 130, 133, 360, OB Boje and OB 4; the Arkona Basin is represented by station 109 and 113; the Bornholm Basin is represented by station 140, 200, 213 and 222; in the eastern Gotland Basin station 250, 259, 260, 271 and 286 were grouped; and the western Gotland Basin is represented by station 240, 245 and 284. The arrow indicates the main flow direction of North Sea Water.

The yield of N₂O during these processes strongly depends on the concentration of dissolved oxygen and nitrate (Brettar and Rheinheimer, 1991; Goreau et al., 1980; Vollaek and Zumft, 2001; Wetzel, 1983), with maximal N₂O accumulation at the interface between oxic and suboxic layers, a general depletion within the core of suboxic water column, and invariably near-zero values in anoxic waters (Codispoti et al., 2005). Positive correlations between N₂O and oxygen or nitrate are commonly interpreted as an indication of N₂O production by nitrification (Yoshinari, 1976; Yoshida et al., 1989; Cohen and Gordon, 1978). In contrast, production by denitrification is inferred by missing correlations (Elkins et al., 1978; Cohen and Gordon, 1978). However, up to now the dominant production pathway for N₂O on the global scale remains unclear and is discussed controversially (Codispoti et al., 2001; Popp et al., 2002; Yamagishi et al., 2005).

Oceans account for more than 25% of total natural emissions of N₂O to the atmosphere, and contribute significantly to the global N₂O budget (Prather et al., 2001; Seitzinger et al., 2000). Particularly coastal regions, including estuarine and upwelling regions, play a major role for the formation and release of N₂O to the atmosphere (Bange et al., 1996; Naqvi et al., 2000; Seitzinger et al., 2000). The first study of N₂O in the Baltic Sea was carried out by Rönner (1983) who found the region to be a source of atmospheric N₂O. In contrast to open ocean areas coastal regions are expected to be more influenced by conversion processes in sediments or

by riverine inputs. In the Bodden waters and Danish fjords of the Baltic Sea enhanced N₂O concentrations were correlated with seasonal riverine input (Jørgensen and Sørensen, 1985; Dahlke et al., 2000). Additionally, denitrification processes in sediments were shown to contribute to the release of N₂O in Danish fjords (Jørgensen and Sørensen, 1985).

1.2 Study area

The Baltic Sea is an adjacent sea of the Atlantic Ocean and part of the European continental shelf. It consists of a series of basins (Arkona, Bornholm, and Gotland Basin; see Fig. 1), with restricted horizontal and vertical water exchange due to shallow sills and a clear salinity induced stratification of water masses.

In January 2003 a major inflow of cold, highly saline and oxygen-rich North Sea Water was observed. It was the most important inflow event since 1993 and terminated the ongoing stagnation period in the central Baltic Sea (Feistel et al., 2003; Nausch et al., 2003). This inflow event was preceded by a minor inflow of warmer and less oxygenated water in August 2002. Due to the inflow of North Sea Water oxygen conditions changed from anoxic to oxic in most parts of the Baltic Sea. From the inflow in January 2003 until our cruise in October 2003 water renewal was already detectable at the Farö Deep (station 286), however the western Gotland Basin was still unventilated (Feistel et al., 2003; Nausch et al., 2003).

Due to the fact that N₂O production strongly depends on environmental conditions such as oxygen concentration (e.g., Naqvi et al., 2000) any natural or anthropogenic-induced shifts of coastal ecosystems will affect the formation and subsequent release of N₂O to the atmosphere. In this context the inflow of North Sea Water into the Baltic Sea offered a very good opportunity to investigate naturally changing environmental conditions with regard to the production of N₂O.

1.3 Description of water masses

We refer to four different water masses, characterized by temperature, salinity and oxygen concentrations (Fig. 2). We followed the description of the “Institut für Ostseeforschung” (IOW) cruise reports (Nausch, 2003a; Nagel, 2003; Feistel, 2003; Nausch, 2003b, c; Wasmund, 2003) and the hydrographic-chemical report of the Baltic Sea in 2003 (Nausch et al., 2004). These water masses were characteristic for the time period after the inflow event in summer and autumn 2003.

The Surface Water layer (*sw*) was characterized by uniform temperature and salinity, in combination with high oxygen concentrations. Below this layer, rapidly decreasing temperatures indicated Winter Water (*ww*), which is formed annually during convection in winter. Salinity and oxygen concentrations were still uniform. The “old” Bottom Water (*bw*) was visible by increasing temperature and simultaneously in-

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 (H₂S). 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 N₂O 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 N₂O 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 N₂O 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⁻¹. For the two-point calibration procedure we used standard gas mixtures with 311.8 ± 0.2 ppb and 346.5 ± 0.2 ppb N₂O 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.

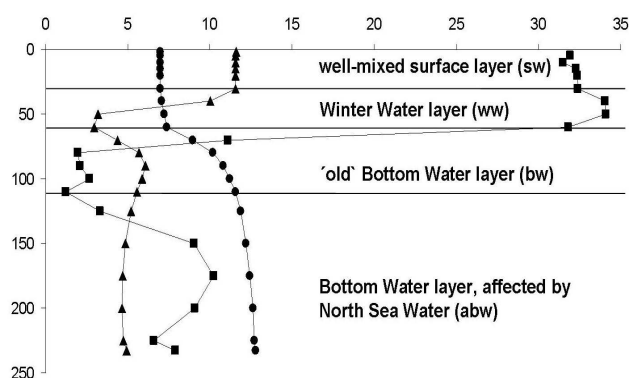


Fig. 2. Characterization of different water masses in the Baltic Sea, for example at station 271 in the Eastern Gotland Basin (triangles: temperature (°C), circles: salinity, squares: oxygen ($\mu\text{mol } 10^1 \text{ L}^{-1}$)).

2.1 Calculations

N₂O 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 β 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 N₂O 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 N₂O ($\Delta\text{N}_2\text{O}$) was calculated as the difference between the calculated N₂O equilibrium concentration and the measured concentration of N₂O 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 N₂O 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 ± 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

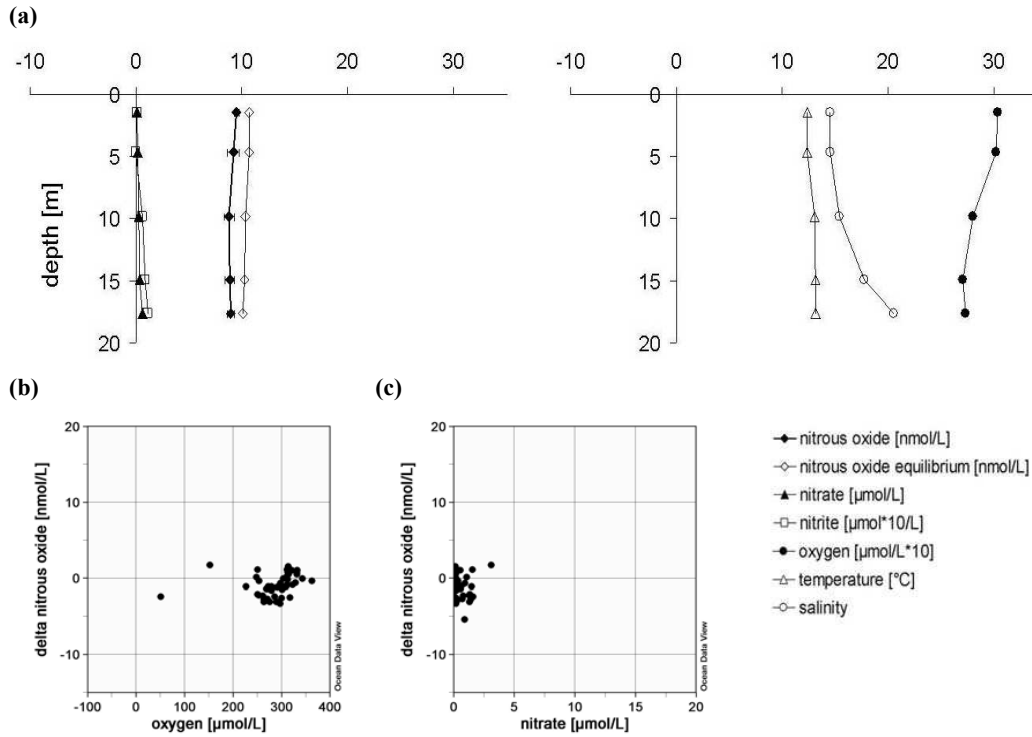


Fig. 3. Well mixed basins; (a) left plot with profiles of N₂O, calculated N₂O equilibrium concentration, NO₃⁻, NO₂⁻ at station 41 in the Mecklenburg Bight and right plot with profiles of temperature, salinity and oxygen at station 41 in the Mecklenburg Bight; (b) ΔN₂O plotted against oxygen at all stations <30 m; c) ΔN₂O plotted against NO₃⁻ 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 (O₂) were calculated with the equation given by Weiss (1970). The concentration of H₂S is expressed as the negative oxygen equivalent (1 μmol L⁻¹ H₂S = -2.00 μmol L⁻¹ O₂). Dissolved nutrients and CTD data were provided by the participating working groups. Concentrations of the dissolved inorganic nitrogen compounds nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺), and oxygen (O₂) were determined using standard methods (Grasshoff et al., 1983).

The N₂O 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 N₂O concentration in any given basin from the upper part of the halocline to the bottom (nmol L⁻¹), $n_{\text{N}_2\text{O}}$ is the molecular weight of N₂O (44 g mol⁻¹) and V is the water volume of each basin (km³).

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.

The N₂O 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 N₂O content of the basins before and after the inflow event in tonnes, d_{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_{basin} is the calculated volume of the basins (km³), n is the molecular weight of N₂O (44 g mol⁻¹), and $r_{\text{N}_2\text{O}}$ is the assumed N₂O release factor of 0.003 (0.3%) over continental shelves during nitrification (Seitzinger and Kroeze, 1998).

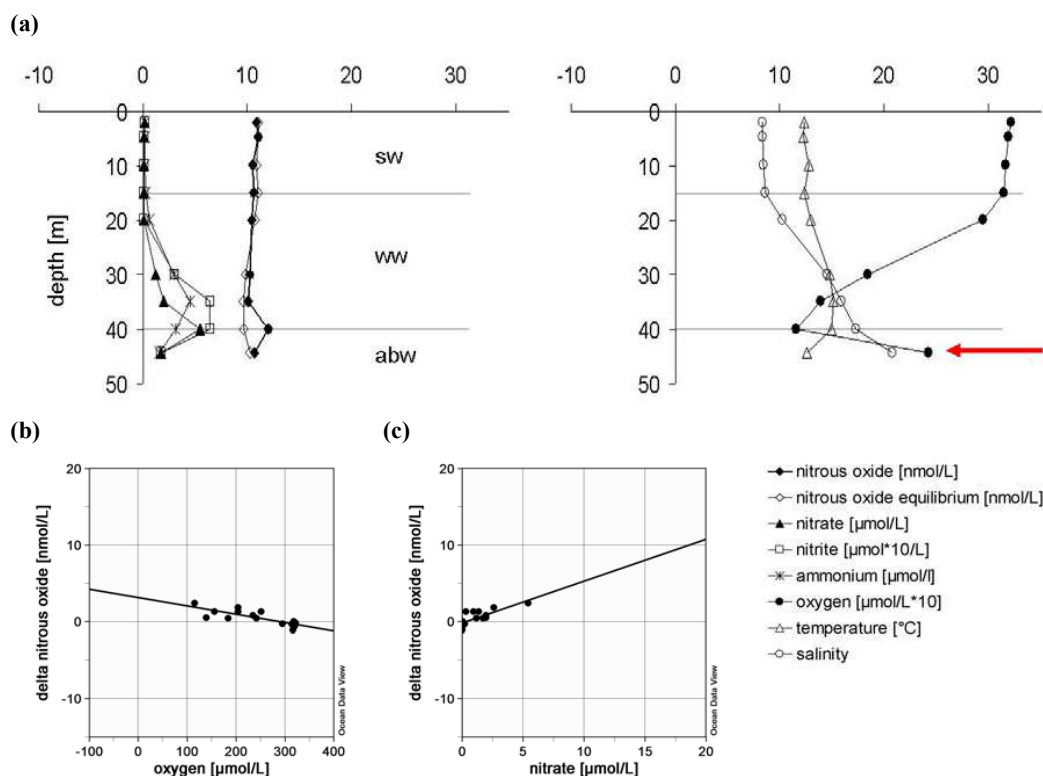


Fig. 4. Arkona Basin; (a) station 113 (Arkona Deep): left plot with profiles of N₂O, N₂O equilibrium concentration, NO₃⁻, NO₂⁻, right plot with profiles of temperature, salinity and oxygen, the arrow indicate the influence of North Sea Water; abbreviations see Fig. 2.; (b) ΔN₂O plotted against oxygen (at all stations in the Arkona Basin, $y = -0.011x + 3.132$, $R^2 = 0.67$; $n = 18$); (c) ΔN₂O plotted against NO₃⁻ (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 N₂O 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 N₂O 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 ΔN₂O and other parameters like O₂ and NO₃⁻ (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 H₂S 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 H₂S concentrations were uniform.

3.2.1 Arkona Basin

In the Arkona Basin (stations 109 and 113 (Fig. 4a)), N₂O concentrations were constant and near equilibrium

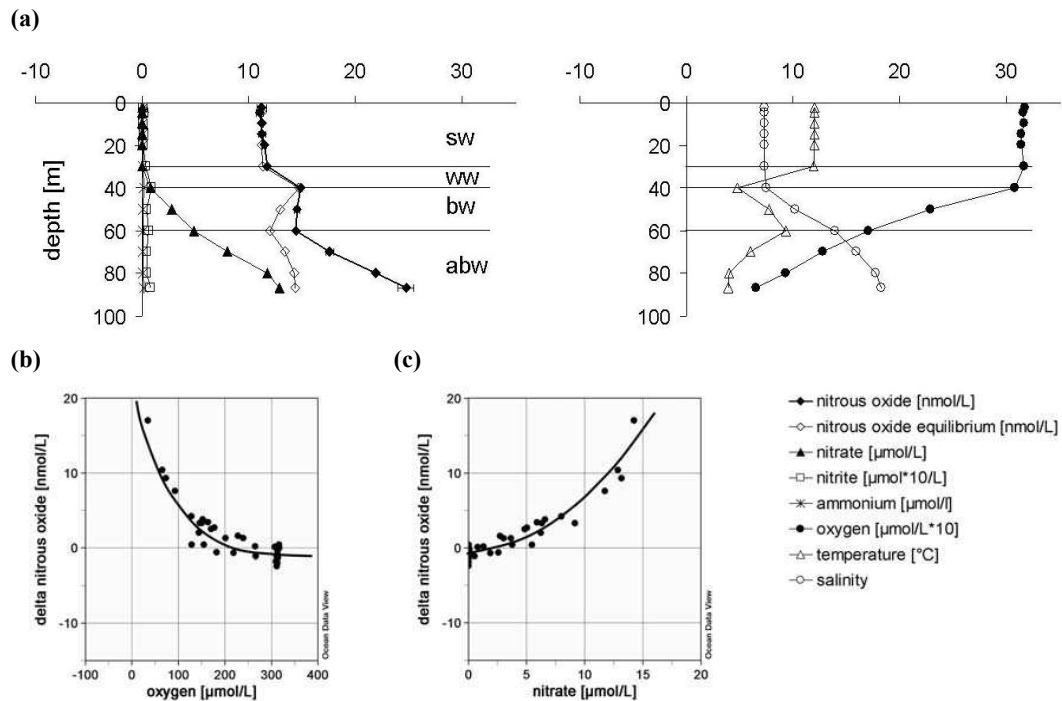


Fig. 5. Central Bornholm Basin; (a) station 213 (Bornholm Deep): left plot with profiles of N₂O, N₂O equilibrium concentration, NO₂⁻, NO₃⁻, right plot with profiles of temperature, salinity and oxygen, abbreviations see Fig. 2; (b) Δ N₂O plotted against oxygen (at all stations in the Bornholm Basin, $y=0.0003x^2-0.1531x+19.517$, $R^2=0.88$; $n=32$); (c) Δ N₂O plotted against NO₃⁻ (at all stations in the Bornholm Basin, $y=0.0585x^2+0.1438x-0.6155$, $R^2=0.90$; $n=32$).

(10.9 ± 0.7 nmol L⁻¹) throughout the water column. In the Winter Water below the thermocline at 15 m O₂ concentrations decreased, associated with increasing NO₂⁻, NO₃⁻ and NH₄⁺. Δ N₂O was slightly negatively correlated with O₂ (Fig. 4b), and positively correlated with NO₃⁻ (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 N₂O concentration.

3.2.2 Bornholm Basin

In the Bornholm Basin (Fig. 5, stations 140, 200, 213 and 222), N₂O 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 N₂O and Δ N₂O were comparable to the Arkona Basin. At station 222 (outflow, not shown) N₂O concentrations in the surface layer were uniformly near equilibrium at approximately 10 nmol L⁻¹, below the surface layer concentrations were uniformly around 15.4 nmol L⁻¹. In the central Bornholm Basin, at station 200 (not shown) and 213 (Fig. 5a) N₂O concentrations increased rapidly within the layer affected by North Sea Water (abw, below 60 m), with N₂O values up to 31.3 nmol L⁻¹ (station 200). These were the highest values measured during the entire cruise. In water

masses above, N₂O was near equilibrium, with slightly enhanced Δ N₂O values in the “old” Bottom Water (*bw*, 40–60 m). In the Bornholm Basin Δ N₂O was clearly negatively correlated with oxygen and positively with NO₃⁻ (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, N₂O 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 N₂O values at approximately 20 nmol L⁻¹ and positive Δ N₂O. 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 H₂S concentrations down to the bottom. Throughout the Bottom Water N₂O 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 N₂O concentrations was observed at depths between 90 and 110 m (see arrows in Fig. 6a), combined with a local minimum in NO₃⁻ values.

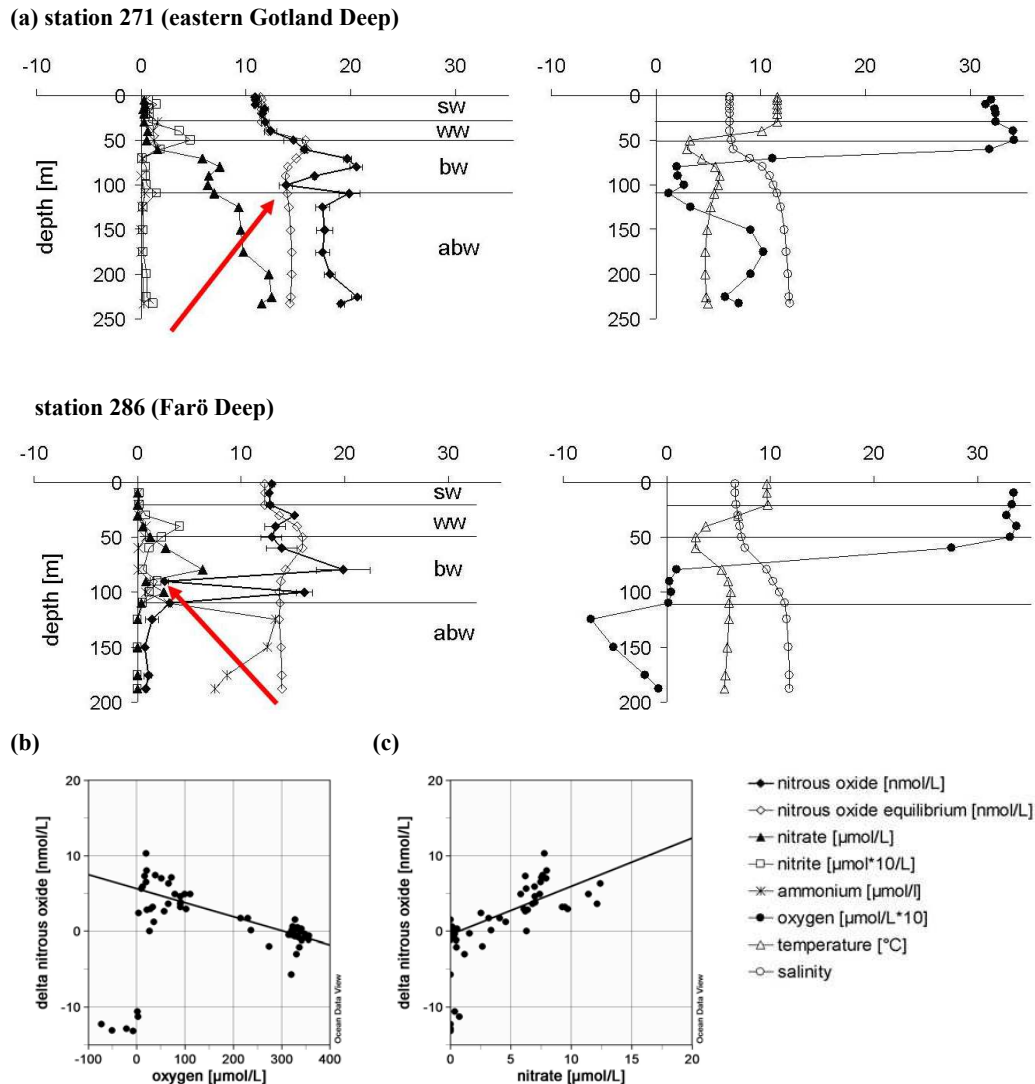


Fig. 6. Eastern Gotland Basin; (a) station 271 (Gotland Deep, upper plots) and 286 (Farö Deep, lower plots): left plots with profiles of N₂O, N₂O equilibrium concentration, NO₃⁻, NO₂⁻; right plots with profiles of temperature, salinity and oxygen, abbreviations see Fig. 2; (b) $\Delta\text{N}_2\text{O}$ plotted against oxygen (at all stations in the Eastern Gotland Basin, $y = -0.019x + 5.625$, $R^2 = 0.67$; $n = 62$ (except for $\text{O}_2 < 3 \mu\text{mol L}^{-1}$)); (c) $\Delta\text{N}_2\text{O}$ plotted against NO₃⁻ (at all stations in the Eastern Gotland Basin, $y = 0.639x - 0.459$, $R^2 = 0.62$; $n = 62$ (except for $\text{O}_2 < 3 \mu\text{mol L}^{-1}$)); H₂S 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, $\Delta\text{N}_2\text{O}$ was linearly correlated with O₂ and NO₃⁻ (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. N₂O 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 N₂O concentrations dropped sharply at the oxidic/anoxic interface and re-

mained near zero in the anoxic deep waters. $\Delta\text{N}_2\text{O}$ values were negative and were not correlated with NO₃⁻ (Fig. 7c). $\Delta\text{N}_2\text{O}$ 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

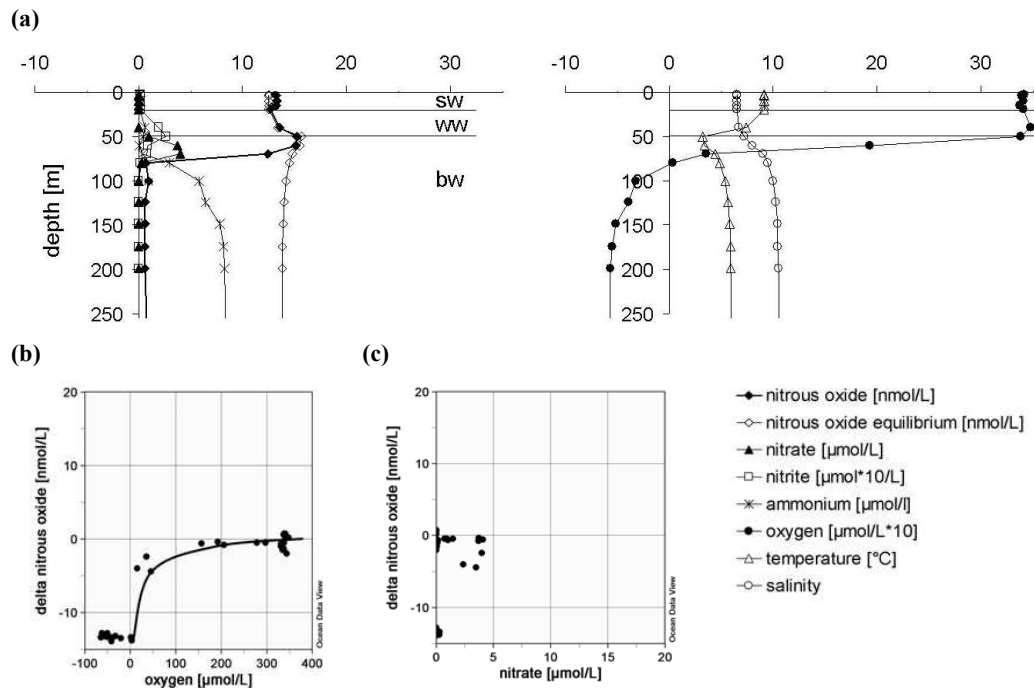


Fig. 7. Western Gotland Basin; (a) station 284 (Landsort Deep): left plot with profiles of N₂O, N₂O equilibrium concentration, NO₃⁻, NO₂⁻, right plot with profiles of temperature, salinity and oxygen, abbreviations see Fig. 2; (b) Δ N₂O plotted against oxygen (at all stations in the Western Gotland Basin; $y=2.2467 \ln(x)-13.322$, $R^2=0.86$; $n=29$ (with exception of $O_2 < 0 \mu\text{mol L}^{-1}$)); (c) Δ N₂O plotted against NO₃⁻ (at all stations in the Western Gotland Basin); H₂S 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 N₂O, our measured N₂O concentrations reflect the continuum of unaffected and changing oxygen conditions quite well. In oxic and well mixed waters, vertical N₂O 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 N₂O concentrations near zero (Fig. 7a). Therefore, in both cases no correlations between N₂O 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 N₂O distributions that were clearly correlated with oxygen and nitrate (Fig. 5b–c, Fig. 6b–c).

These vertical N₂O distributions are in general agreement with the few previously published N₂O 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: N₂O 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 N₂O 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 N₂O profiles from the then anoxic Gotland Deep, reported by Rönner and Sörensson (1985) is comparable to our N₂O 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 N₂O in the different basins.

5 Hydrographic aspects

In surface layers and well-mixed water bodies of shallow stations, observed N₂O concentrations were near the equilibrium due to exchange with the atmosphere. In the Winter Water N₂O 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 N₂O distribution. This water mass is formed during winter convection, when N₂O 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 N₂O solubility during formation of the Winter Water are the reason for the enhanced N₂O concentrations in this layer.

N₂O in the deep water of the Baltic Sea might be affected by the inflow of North Sea Water. Intrusion of N₂O 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, N₂O concentrations did not increase and remained close to equilibrium (Fig. 4a–b). These results point to small supply of N₂O by North Sea Water, and are supported by measurements of Law and Owens (1990). They found N₂O concentrations close to equilibrium up to approximately 10 nmol L⁻¹ in the North Sea. Thus, the enhanced N₂O 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 N₂O 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 N₂O 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 H₂S containing bottom waters N₂O concentrations were constantly near zero, and therefore no correlation with either O₂ or NO₃⁻ was found. The N₂O production by nitrification and denitrification might probably be inhibited by the presence of H₂S (Joye and Hollibaugh, 1995; Knowles, 1982; Sørensen et al., 1980), and while changing to anoxic conditions, N₂O 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 N₂O (up to 1.7 nmol L⁻¹) in the anoxic water masses, which may have been residuals of a previous production process during oxic conditions.

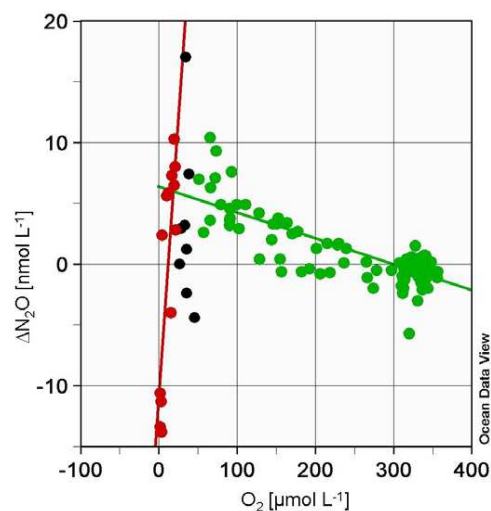


Fig. 8. Correlation between $\Delta\text{N}_2\text{O}$ and O_2 in the Baltic Sea. Correlations were calculated for oxic waters with O_2 concentrations $>50 \mu\text{mol L}^{-1}$ (green coloured, $y=-0.019x+5.41$, $R^2=-0.70$; $n=183$) and $<20 \mu\text{mol L}^{-1}$ (red coloured, $y=1.038x-11.36$, $R^2=0.81$; $n=12$). 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 N₂O is expected to be mainly produced by denitrification processes (Codispoti et al., 2001), usually indicated by decreasing NO₃⁻ concentrations and a secondary NO₂⁻ 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 N₂O was observed, rather a local minimum of N₂O was found (Fig. 6a, indicated by arrows). Naqui and Noronha (1991) reported that minima of nitrate correlated to minima of N₂O 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 N₂O was not found either. Thus, the observed N₂O profiles might reflect previous redox transformations in the water column.

The local minimum of N₂O 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 N₂O is a previous signal of former anoxic bottom water, pushed up by the small inflow event in August 2002. The restriction of

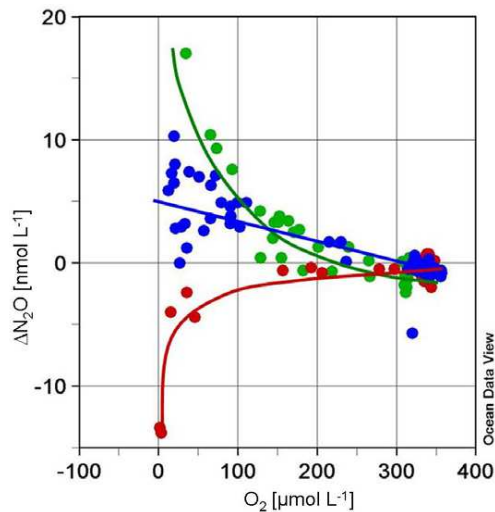


Fig. 9. Correlation between $\Delta\text{N}_2\text{O}$ and O_2 in the Baltic Sea; Correlations were calculated for the Bornholm Basin (stations 140, 200, 213, 222, green coloured, $y = -6.83 \ln(x) + 37.88$, $R^2 = 0.86$; $n = 40$), the eastern Gotland Basin (station 259, 250, 260, 271, blue coloured, $y = -0.02x + 5.88$, $R^2 = 0.70$; $n = 54$) 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 N₂O production.

5.1.3 Correlation between N₂O and O₂

At O₂ concentrations $> 50 \mu\text{mol L}^{-1}$ $\Delta\text{N}_2\text{O}$ is clearly negatively correlated with O₂, indicating production by nitrification (see Fig. 8, green data points). At O₂ concentrations $< 20 \mu\text{mol L}^{-1}$ $\Delta\text{N}_2\text{O}$ and O₂ 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 N₂O 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 N₂O seemed to be degraded; probably used as an electron acceptor instead of oxygen and thereby reduced to N₂ (Elkins et al., 1978; Cohen and Gordon, 1978).

These findings suggest a change in N₂O converting processes either by different bacteria species or different processes. Bauer (2003) investigated NH₄⁺ oxidizing bacte-

ria in the eastern Gotland Basin, and found similar bacterial communities at different depths; their nitrification activities however depended on O₂ 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 N₂O during these processes is probably controlled particularly by the O₂ 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 H₂S 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 O₂ were regionally different and not always linear (Figs. 5b–c, 6b–c, 7a, 9). Particularly in the Bornholm Basin, N₂O and oxygen as well as N₂O 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 N₂O. 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 N₂O accumulation. For various communities of NH₄⁺ oxidizing bacteria different lag times after switching from anoxic to oxic incubations have been shown and the production of N₂O might not have started immediately after the ventilation

Table 1. Estimated N₂O 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 ₂ O conc. below the halocline (nmol L ⁻¹)	Water volume (km ³)	N ₂ O content before the inflow event (tonnes)	N ₂ 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	64 ± 23	1194 ± 256
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% N₂O release during nitrification (Seitzinger and Kroeze, 1998).

	Δ <i>m</i> _{N₂O} (tonnes)	<i>d</i> _{basin} (day)	Water volume (km ³)	N ₂ O net production rate (nmol L ⁻¹ d ⁻¹)	net nitrification rate (nmol L ⁻¹ d ⁻¹)
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 N₂O at the oxic-anoxic interface was found. We suspect that the correlation between ΔN₂O and O₂ 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 N₂O inventories before and after the North Sea Water inflow event

The North Sea Water inflow consisted of a water volume of 200 km³ (Feistel and Nausch, 2003). With an assumed N₂O concentration of 10±2 nmol L⁻¹ (Law and Owens, 1990), the North Sea Water transported approximately 88±18 tonnes N₂O 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, N₂O concentrations near zero similar to measured profiles in the western Gotland Basin in October 2003 (Fig. 7a) can be assumed. The mean N₂O concentration in the western Gotland Basin was 0.97±0.34 nmol L⁻¹. On the basis of these values the calculated N₂O 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 N₂O contents of the Bornholm Basin and the eastern Gotland Basin, calculated with the mean of measured N₂O 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 N₂O.

The estimated N₂O content in the stratified basins showed distinctly higher values after the inflow of the North Sea Water than before. The N₂O concentration in the North Sea Water was assumed to be near equilibrium, so there was no significant advection of N₂O from the North Sea. Thus, the observed elevated N₂O concentrations in the Baltic Sea basins probably resulted from a stimulation of N₂O production by the inflow, most likely by advection of oxygen (see Table 1).

Although more than 1000 tonnes of N₂O were produced, it is questionable whether the North Sea Water inflow makes the Baltic Sea a source of atmospheric N₂O. Due to the strong salinity stratification, it can be assumed that the N₂O produced stays below the permanent halocline, and therefore it will not reach the atmosphere. Commonly N₂O budgets are modeled as a function of nitrification and denitrification. For example, Seitzinger and Kroeze (1998) modelled the distribution of N₂O production, based on the input of nitrogen compounds into estuaries by rivers. However, estimations of global N₂O 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 N₂O emissions.

Based on the calculated N₂O 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 N₂O production mainly in oxic water masses below the Winter Water layer.
- We found no indication for advection of N₂O by North Sea Water; however, the environmental conditions for N₂O production were clearly changed due to the North Sea Water inflow.
- The inflow leads to a stimulation of N₂O production below the permanent halocline, but due to the halocline, the Baltic Sea is not a significant source of N₂O to the atmosphere.
- There was no indication for an accumulation of N₂O 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.

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