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Nitrous oxide in the North Atlantic Ocean

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Abstract

In order to investigate the role of the North Atlantic Ocean as a source of atmospheric nitrous oxide and to decipher the major formation pathways of nitrous oxide, measurements of dissolved nitrous oxide were made during three cruises in the tropical, subtropical and subpolar North Atlantic in October/November 2002, March/April 2004, and May 2002, respectively. Nitrous oxide was close to equilibrium or slightly supersaturated in the surface layers suggesting that the North Atlantic acts as a weak source of nitrous oxide to the atmosphere. Depth profiles showed supersaturation throughout the water column with a distinct increasing trend from the subpolar to the tropical region. Lowest nitrous oxide concentrations, near equilibrium and with an average of 11.0±1.7 nmol L^{-1}, were found in the subpolar North Atlantic where the profiles showed no clear maxima. Highest values up to 37.3 nmol L^{-1} occurred in the tropical North Atlantic with clear maxima at approximately 400 m. A positive correlation of nitrous oxide with nitrate, as well as excess nitrous oxide with AOU, was only observed in the subtropical and tropical regions. Therefore, we conclude that the formation of nitrous oxide occurs in the tropical region rather than in the subpolar region of the North Atlantic and suggest nitrification is the dominant formation pathway in the subtropical and tropical regions.

1 Introduction

Nitrous oxide (N_2O) is an important atmospheric trace gas due to its influence on the Earth's climate. In the troposphere N_2O acts as a greenhouse gas whereas in the stratosphere it is involved in the depletion of ozone by providing NO-radicals (Prather et al., 2001). Since the beginning of the industrial revolution the global mean tropospheric N_2O mole fraction has risen rapidly from 270 ppb up to 314 ppb in 1998 (Prather et al., 2001). About 24% of the natural sources of atmospheric N_2O are contributed by the oceans (Prather et al., 2001; Seitzinger et al., 2000). Nitrous oxide is an important component of the oceanic nitrogen cycle, mainly formed by the microbial processes of nitrification and denitrification (Codispoti et al., 2001; Goreau et al., 1980): Nitrification is an aerobic two-step process in which ammonium is oxidized to nitrate ($NH_4^+ \rightarrow NH_2OH \rightarrow NO_2^- \rightarrow NO_3^-$) by two different groups of bacteria. In this process nitrous oxide is assumed to be a by-product, however until now the exact pathway for N_2O production remains unclear. In suboxic habitats nitrate can be reduced by denitrification to molecular nitrogen ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$), here nitrous oxide is an intermediate product. Especially at oxic/suboxic boundaries N_2O is produced by coupled nitrification and denitrification, due to the transfer of common intermediates (Yoshinari et al., 1997). Another possibility is aerobic denitrification, whereby under fully aerobic conditions organisms convert ammonia into nitrogen gas without the intermediary accumulation of nitrite (Robertson et al., 1988). All processes depend on oxygen concentrations, as well as the availability of substrates such as ammonium and nitrate. Many organisms are able to switch between different pathways depending on environmental conditions, and also the yield of N_2O during a process depends on environmental conditions (Goreau et al., 1980; Poth and Focht, 1985; Richardson, 2000). Positive correlations of N_2O with apparent oxygen utilization (AOU) or nitrate are interpreted as production of nitrous oxide by nitrification (Yoshinari, 1976; Cohen and Gordon, 1978; Yoshida et al., 1989). However, up to now the dominant production pathway for N_2O on the global scale and the contribution of different pathways still remains unclear (Codispoti et al., 2001; Popp et al., 2002).

Information on the vertical N_2O distribution in the North Atlantic is sparse, only a few profiles are available. The first vertical profiles for the North Atlantic were published by Junge and Hahn (1971) and Yoshinari (1976), additional data were collected by Butler et al. (1995), and recently data from a transect at 7°30′ N were reported by Oudot et al. (2002). In this paper we present a comprehensive set of 73 vertical profiles of nitrous oxide from three trans-Atlantic cruises, covering the subpolar North Atlantic, the subtropical and the tropical North Atlantic. Based on these new data, we examine the regional differences of the N_2O distribution and its formation pathways.

2 Study area

2.1 Research cruises

Samples from the three cruises were collected over the period from May 2002 to April 2004 (see Fig. 1).

The first cruise (May/June 2002), started in Hamburg, Germany with the German research vessel “Gauss”. The cruise track followed the WOCE-A2 transect to Halifax, Canada. Depth profiles of N_2O were measured at 16 stations. The WOCE-A2 transect is located between 42° N and 49° N.

The subtropical North Atlantic was investigated during March/April 2004 onboard the research vessel “Meteor”. The cruise started in Fort de France, Martinique (French Antilles) in the western part of the Atlantic and ended in Lisbon (Portugal). Samples were taken at 37 stations. Most stations were co-located with stations where samples were taken during the Transient Tracers in the Ocean Program (TTO) in 1982.

The tropical North Atlantic samples were taken during the M55-SOLAS cruise (Wallace and Bange, 2004) in October/November 2002, again with the German research vessel “Meteor”. This cruise started in the western tropical North Atlantic in Willemstad, Curaçao (Netherlands Antilles) and followed a cruise track along 10–11° N to Douala (Cameroon). The track included a transect to the equator between 26° W and 23.5° W. N_2O profiles were taken at 20 stations.

2.2 Hydrography

Several water masses in the North Atlantic can be identified in the T-S-diagram based on data from the three cruises (see Fig. 2). The main Atlantic water masses were identified according to commonly used classification schemes (Tomczak, 1999; Alvarez et al., 2004; Aiken et al., 2000; Joyce et al., 2001; Poole and Tomczak, 1999).

The WOCE A2 transect (Gauss 384-1 cruise), is located at the boundary region between the subpolar gyre (Gordon, 1986) and the subtropical gyre (Krauss, 1996). This region is highly variable, characterized by the exchange of upper-ocean water between the gyres mainly via the North Atlantic Current, and the Labrador Current. One of the most important water masses here is the Labrador Sea Water (LSW). These water masses provide the major part of the North Atlantic Intermediate Water in combination with the outflow of Mediterranean Sea Water (MW), which is detected in the eastern basin of the subtropical Atlantic Ocean near the Strait of Gibraltar (Richardson et al., 2000) and the Antarctic Intermediate Water (AAIW) from the south (Lorbacher, 2000). Additional water masses of the southern hemisphere that penetrate into the North Atlantic are the South Atlantic Central Water (SACW) and the Antarctic Bottom Water (AABW). SACW flows northwards, and mixes with the North Atlantic Central Water (NACW) at approximately 15° N in the western and 20° N in the eastern basin (Poole and Tomczak, 1999; Aiken et al., 2000).

A typical freshwater influence was found during the Meteor 55 cruise in the western tropical North Atlantic. Water of the Amazon was detected in the surface water, identified by high temperatures and low salinity. These plumes of freshwater are transported northwards by the North Brazil Current and eastwards by the equatorial current system (Fratantoni and Glickson, 2002).

3 Material and methods

Water samples for N_2O analysis were collected in triplicate from various depths, taken with a 24-Niskin-bottle rosette, equipped with a CTD-sensor. The analytical method applied is a modification of the method described by (Bange et al., 2001). Bubble free samples were taken immediately following oxygen sampling 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 2 mM mercury chloride solution. Then 10 mL of sample was replaced with a helium headspace for each vial, and the samples were allowed to equilibrate 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). Gaschromatographic separation was performed at 190° C on a packed molecular sieve column (6 ft×1/8″ SS, 5A, mesh 80/100, Alltech GmbH, Germany). The N_2O was detected with an electron capture detector. A mixture of argon with 5% by volume methane 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 N_2O 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.

3.1 Calculations

N_2O water concentrations (C_{N2O}) were calculated as follows:

$$C_{\mathrm{N2O}}\left[\mathrm{nmol\ L^{-1}}\right] = \left(\beta x P V_{wp} + \frac{xP}{RTV_{hs}} \right) V_{wp} \tag{1}$$

where β stands for the Bunsen solubility in nmol L^{-1} atm^{-1} (Weiss and Price, 1980), x is the dry gas mole fraction of N_2O 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 (8.2054×10^{-2} L atm mol^{-1} K^{-1}) and T is the temperature during equilibration. The salinity was measured by the CTD-Sensor during water sample collection. The overall relative mean analytical error was estimated to be ±1.8%.

The excess N_2O (ΔN_2O) was calculated as the difference between the calculated N_2O equilibrium concentration and the measured concentration of N_2O as follows

$$\Delta N_2O[\mathrm{nmolL^{-1}}]=N_2O(\mathrm{observed})-N_2O(\mathrm{equilibrium}). \tag{2}$$

To calculate the N_2O equilibrium concentration we used three different atmospheric mole fractions. Between the mixed layer and the atmosphere, N_2O exchanges in about three weeks (Najjar, 1992), thus we calculated ΔN_2O in the mixed layer using the actual atmospheric N_2O value of 318 ppb measured during the "Meteor 55" cruise (Walter et al., 2004). Below the thermocline, exchange with the atmosphere is unlikely, thus, calculated N_2O equilibrium concentrations depend on the atmospheric N_2O mole fraction at the time of deep-water formation. However, the exact atmospheric mole fraction of N_2O during deep-water formation is unknown because of uncertainty in age determination of water masses. Generally, tropical Atlantic deep waters below 2000 m seem to be older than 200 years (Broecker and Peng, 2000). Therefore for depths >2000 m ΔN_2O was calculated with the tropospheric preindustrial value of 270 ppb (Flückiger et al., 1999). An average of the actual and the preindustrial atmospheric value (i.e., 294 ppb) was used for the depth range between the upper thermocline and 2000 m. The thermocline was defined as the depth where the temperature differs from the surface temperature by more than 0.5°C (Tomczak and Godfrey, 2001). For the subtropical and subpolar region we calculated ΔN_2O with these same mole fractions, although the age of water masses is different to the tropical Atlantic and therefore some values may be underestimated, whereas others may be overestimated. The resulting uncertainties of ΔN_2O are about 10–15%; however, our conclusions are not significantly affected by this uncertainty. The equilibrium values of dissolved oxygen (O_2) were calculated with the equation given by Weiss (1970).

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

$$\mathrm{AOU}[\mu\mathrm{mol\ L}^{-1}]=\mathrm{O_2(equilibrium)}-\mathrm{O_2(observed)}. \quad (3)$$

4 Results

4.1 Distribution of nitrous oxide in the North Atlantic

4.1.1 N_2O distribution along isopycnal levels

In the surface layer of the North Atlantic (Fig. 3a) N_2O concentrations were relatively uniform with 8.5 ±1.2 nmol L^{-1}. In the region of the Labrador Current N_2O concentrations were enhanced with an average of 11.6 ±0.9 nmol L^{-1}. During the "Meteor 55" cruise, a plume of Amazon Water had been identified in the western basin of the tropical North Atlantic (Körtzinger, 2003). In contrast to Oudot et al. (2002), who reported enhanced values in the plume of the Amazon River, we found no influence on N_2O concentrations (Walter et al., 2004).

Below the thermocline, N_2O concentrations were variable with respect to depths and regions. We found highest concentrations in the eastern basin of the tropical North Atlantic throughout the water column, with maximum concentrations on σ_θ surfaces between 26.3 and 27.1 (Figs. 3b–e). At the Midatlantic Ridge, located at approximately 40° W, a distinct boundary between the western and eastern Atlantic basins was observed (Figs. 3d–e). In the eastern subtropical North Atlantic, at approximately 1000 m (σ_θ27.6–27.7), a tongue of outflow water from the Mediterranean Sea was detected by higher values of salinity and temperature (Richardson et al., 2000). However, we found no apparent influence of the Mediterranean water on N_2O concentrations.

Like the surface layer, deep waters (Fig. 3f) showed nearly uniform N_2O concentrations, though with higher values of 13.3±1.6 nmol L^{-1}. However, a weak but distinct trend of decreasing concentrations from the tropics (13.1±1.3 nmol L^{-1}) to the subpolar North Atlantic (11.1±1.4 nmol L^{-1}) could be observed.

4.1.2 Vertical N_2 O distribution

The vertical distribution of N_2O showed characteristically different profiles in different regions of the North Atlantic (Figs. 4a–c), and between the western and eastern basins of these regions (Figs. 5a–c).

In the subpolar North Atlantic (Fig. 4a) vertical gradients of nitrous oxide were weak over the complete cruise track, with no clear or only a very weakly pronounced subsurface maximum. N_2O concentrations were near equilibrium (11.0±1.3 nmol L^{-1}) throughout the water column, with average concentrations of 8.6±1.4 nmol L^{-1} in the surface layer (σ_θ25.3–27.0) and 11.3±1.5 nmol L^{-1} below the thermocline down to the bottom (σ_θ26.2–27.7). No differences between the western and the eastern basin were found (Fig. 5a).

In contrast, N_2O distributions and profiles in both the subtropical and tropical North Atlantic showed strong variations with water depth (Figs. 4b–c, Figs. 5b–c). In both regions, the profiles generally had one distinct maximum. In the surface layer (σ_θ19.3–26.8) concentrations were uniform, increasing below the thermocline up to a maximum and decreasing down to approximately 2000 m (σ_θ22.1–27.8). Below 2000 m (σ_θ27.8–27.9) N_2O concentrations were nearly constant with depth in both basins.

In the subtropical North Atlantic (Fig. 4b) N_2O surface concentrations were 8.7±0.7 nmol L^{-1}, comparable to those in the subpolar North Atlantic. Maximum values were found at depths between 600 to 1000 m (σ_θ 26.7–27.7); values ranged from 14.0 in the eastern basin (#198) to 21.3 nmol L^{-1} in the western basin (#156). Below 2000 m (σ_θ>27.8), concentrations were nearly constant at 13.1±0.9 nmol L^{-1}. Profiles in the western subtropical North Atlantic showed distinct maxima, while in the eastern basin no clear maximum was expressed (Fig. 5b). From the western to the eastern basin maximum concentrations decreased slightly from 17.7±1.4 nmol L^{-1} to 15.1±0.7 nmol L^{-1}. East of the Midatlantic Ridge maxima were not clearly expressed and were broader. Additionally, maximum ΔN_2O values were lower in the eastern (5.5±0.6 nmol L^{-1}) than in the western basin (7.9±1.3 nmol L^{-1}).

In the tropical North Atlantic (Fig. 4c) surface concentrations, with an average of 7.4±1.1 nmol L^{-1}, were slightly lower than in the subtropical and subpolar North Atlantic. In contrast to the subtropical North Atlantic, maxima of N_2O concentrations were found at shallower depths of approximately 400 m (σ_θ26.8–27.1). The maximum values were higher in general, and ranged from 23.8 nmol L^{-1} in the western basin (#4) to 32.1 nmol L^{-1} in the eastern basin (#44). At station #36, located in the Guinea Dome area (Siedler et al., 1992; Snowden and Molinari, 2003), we observed the highest N_2O values of about 37.3 nmol L^{-1} at 400 m (σ_θ 27.0) (Fig. 4c). At the equatorial stations the N_2O maxima were found at shallower water depths (240 m to 280 m, σ_θ 26.6–27.0). Maximum values ranged from 22.3 nmol L^{-1} (#26) to 24.9 nmol L^{-1} (#24). Below 2000 m (σ_θ>27.8) concentrations in the tropical North Atlantic were similar to those in the subtropics with an average of 13.2 ±1.3 nmol L^{-1}. In both basins of the tropical North Atlantic profiles looked similar with sharp and clear maxima, however, concentrations throughout the water column increased from west to east (Fig. 5c). Below 2000 m (σ_θ>27.8) N_2O concentrations were about 2 nmol L^{-1} higher in the eastern than in the western basin, whereas the difference of the maximum values was even higher (approximately 8 nmol L^{-1}).

N_2O profiles of the subtropical and tropical North Atlantic are in good agreement, both in absolute concentrations and shape of profiles, with those measured during the Bromine Latitudinal Air/Sea Transect II (BLAST II) cruise in October/November 1994 (Butler et al., 1995, http://www.cmdl.noaa.gov/hats/ocean/blast2/blastii.html). Below 1500 m in the North Atlantic as far as 20° S, the mean N_2O concentration observed by Butler et al. (1995) was about 13.5±1.0 nmol L^{-1} (n=18) which is in good agreement with our measurements (12.6±1.5 nmol L^{-1}, n=449).

4.2 Comparison of nitrous oxide with other parameters

Parameters most relevant for comparison with nitrous oxide are those assumed to be directly in connection with production pathways of N_2O, like oxygen or the apparent oxygen utilization (AOU), and nitrate. In general, we found the excess of N_2O (ΔN_2O) positively correlated with AOU and nitrate (Fig. 6). However, in view of differences between the basins, these correlations might not be sufficient and need higher resolution. Therefore data were divided as shown in Fig. 7.

In Figs. 7a–f correlations between the excess of N_2O with AOU (Figs. 7a–c) and with NO_3^- (Figs. 7d–f) are divided for all data of the respective regions.

Since a multiple regression analysis turned out to be not applicable due to the co-linearity between the independent variables nitrate and AOU, we applied simple regression analysis for the isopycnal levels below the thermocline (see Table 1). Above the thermocline in the surface layer no correlations were found.

In the subpolar North Atlantic (Figs. 7a, d) ΔN_2O is low, with values near zero. There were no significant correlations found with AOU (Fig. 7a) or nitrate (Fig. 7d; see Table 1).

In the subtropical North Atlantic (Figs. 7b, e) ΔN_2O was also low with values ranging from 0 to 10 nmol L^{-1}. In contrast to the subpolar North Atlantic we found significant correlations between ΔN_2O, AOU (Fig. 7b) and nitrate (Fig. 7e; see Table 1), especially at depths down to the N_2O maxima (ca. 1000 m; σ_θ<27.7; see regression lines in Figs. 7b, e). Below 1000 m (σ_θ27.7) ΔN_2O did not correlate with AOU or NO_3^- (circled data in Figs. 7b, e).

In the tropical North Atlantic (Figs. 7c, f) correlations between ΔN_2O, AOU (Fig. 7c) and nitrate (Fig. 7f) were more pronounced. We observed different ΔN_2O/AOU ratios at depths down to ΔN_2O maxima and below the ΔN_2O maxima down to the bottom. From the surface layer down to 500 m (σ_θ<27.1; see regression line a) the slope of the regression line (ΔN_2O/AOU) was approximately 20 % lower than at depths below 500 m (σ_θ>27.1; see regression line b), what implies that the yield of N_2O at equal AOU is lower at shallower depths.

5 Discussion

Based on our results, we were able to assign measured N_2O concentrations to the water masses as shown in Fig. 2a (see Fig. 8). In the following we discuss distributions and possible origins of nitrous oxide at different depths with regard to these water masses.

5.1 N_2O in the surface layer of the North Atlantic

In the surface layer of the North Atlantic the distribution of N_2O was relatively uniform, with concentrations near equilibrium. This is in line with the assumption that denitrification and nitrification as sources of nitrous oxide in the surface layer seem to be negligible due to the high oxygen concentrations and light inhibition of nitrification (Horrigan et al., 1981). Thus, correlations between ΔN_2O, AOU and nitrate were nonexistent. Accordingly, we suggest that the N_2O distribution in the surface layer is most likely driven by solubility and mixing effects. This is also applicable for the enhanced N_2O concentrations found in the Labrador Current. The ΔN_2O concentrations, which are corrected for temperature, showed no enhanced values in this region. Thus, higher N_2O concentrations in the Labrador Current are likely caused by the solubility effect as well. In the warmer surface layer of the tropical North Atlantic ΔN_2O values were up to 4 nmol L^{-1}, indicating the tropical North Atlantic acts as a weak source for atmospheric N_2O (Walter et al., 2004).

5.2 N_2O below the surface layer down to 2000 m

Variations of N_2O vertical profiles reflected effects of water mass ventilation and subsurface N_2O production history. In the subpolar North Atlantic we assume that the hydrographic setting (such as convection processes during deep water formation and vertical mixing) is responsible for the observed concentrations and distributions of N_2O and ΔN_2O. The most important feature in the subpolar North Atlantic is the formation of deep water in winter in the Labrador and Irminger Seas as part of the North Atlantic circulation in 500 to 2000 m (Rhein, 2000), which carries the atmospheric N_2O imprint to depth. Labrador Sea Water spreads rapidly east- and southwards (Rhein, 2000) and thus causes the uniform distribution of N_2O within the subpolar North Atlantic. Although the productivity of phytoplankton is relatively high in the subpolar North Atlantic, we assume low biological production of N_2O because of two factors: 1) high oxygen concentrations and 2) low temperatures. The yield of N_2O depends on oxygen concentration (Goreau et al., 1980; Poth and Focht, 1985; Richardson, 2000; Codispoti et al., 1992), whereas high oxygen concentrations weaken the production of N_2O. Furthermore the low temperatures of the North Atlantic might have been crucial as well. The temperature dependence of both nitrification rates and enzyme activities is controversially discussed (Berounsky and Nixon, 1990; Vouve et al., 2000; Barnard et al., 2005; Herbert, 1999; Rheinheimer, 1964; Hansen et al., 1981; Rysgaard et al., 1996), however growth rates and biological production of bacteria clearly depend on the prevailing temperatures (Bock and Wagner, 2001; Hoppe et al., 2002). Thus, N_2O production might not be limited directly by temperature but indirectly by the limited abundance of N_2O producing bacteria.

In the subtropical North Atlantic concentrations of N_2O and ΔN_2O were distinctly higher compared to the subpolar North Atlantic. Profiles differed clearly between the western and eastern basin. N_2O profiles in the western basin showed clearly expressed N_2O maxima between 600 to 1000 m. This pattern was not observable east of the Midatlantic Ridge where N_2O and ΔN_2O concentrations were lower than in the western basin, and no peak maxima were observed. Hydrographic processes likely explain the shape of profiles, especially the advection of Labrador Sea Water (LSW) into the eastern basin. LSW with low N_2O concentrations is transported either along the eastern continental slope of America or across the Charlie-Gibbs-Fracture-Zone (Bower et al., 2002). It flows into the eastern subtropical basin at 500–2000 m (Rhein, 2000; Alvarez et al., 2004), and spreads north- and southwards (Bower et al., 2002; Rhein, 2000). In the western basin N_2O concentrations and profiles are in agreement with profiles published by Yoshinari (1976), who also found maximum values in water masses with lower oxygen concentrations. These were identified as Antarctic Intermediate Water (AAIW), which flows northwards. We assume the AAIW transports N_2O from the south to the subpolar North Atlantic. At depths shallower than 1000 m (σ_θ<27.7) ΔN_2O was significantly correlated with oxygen utilization and nitrate concentrations (Figs. 7b, e; Table 1), indicating nitrification has contributed to measured N_2O concentrations.

In the tropical North Atlantic the N_2O profiles and the observed trend along the West-East transect are in overall agreement with recently published data from a transect along 7.5° N (Oudot et al., 2002) and a previous study in the Guinea Dome area (Oudot et al., 1990). Although the overall pattern is the same, we observed generally lower N_2O concentrations than Oudot et al. (2002). This might be a result of a calibration disagreement, supported by measured atmospheric N_2O values of 316 ppb in 1993. For example, we found a peak N_2O concentration of up to 37.3 nmol L^{-1} in South Atlantic Central Water (SACW) of the eastern basin, whereas Oudot et al. (2002) reported values of up to 60 nmol kg^{-1}. Oudot et al. (2002) assumed enhanced biological activity and remineralization of organic matter in upwelling ecosystems to be responsible for these higher values in the east. However, upwelling in this area is a temporary event (Voituriez et al., 1982; Siedler et al., 1992), and during our cruise no upwelling was observed.

Despite the fact that upwelling might have a long-term large-scale effect, we suppose additional reasons for the higher N_2O concentrations in the eastern basin. The productivity in the eastern basin is fueled not only by coastal upwelling (Signorini et al., 1999) but also by dust deposition off the West African coast (Mills et al., 2004). Moreover, nutrient input by major tropical rivers such as the Senegal, Gambia and Niger (Perry et al., 1996) contribute to enhanced production off the West African coast, indicated by enhanced chlorophyll a concentrations (for the 2002 seasonal cycle of chlorophyll a see monthly data set of Sea-viewing Wide Field-of-view Sensor (SeaWiFS: http://earthobservatory.nasa.gov/Observatory/Datasets/chlor.seawifs.html).

Enhanced productivity leads to a high export production (Antia et al., 2001). Subsequently lowered O_2 concentrations in the eastern intermediate layers due to the demineralization of organic matter support the production of N_2O. Therefore, enhanced N_2O concentrations in the eastern basin at this time of year (October/November 2002) might be a residual signal of past high production episode (Signorini et al., 1999).

Upwelling events, indicated by lower sea surface temperatures, were only found at the equator. Surface N_2O concentration and sea surface temperature were positively correlated (Walter et al., 2004), and the comparably shallow N_2O maxima along the equator were caused by upwelling.

Due to the occurrence of linear relationships between ΔN_2O and AOU and between N_2O and nitrate we conclude that nitrification might be the major pathway of N_2O formation in the tropical Atlantic Ocean (Yoshida et al., 1989). Like N_2O, ΔN_2O showed an increasing trend from West to East indicating that nitrification is more pronounced in the eastern than the western basin of the tropical Atlantic.

5.3 N_2 O in deep waters >2000 m (σ_θ>27.8)

Because the deep ocean contains high nitrate concentrations, nitrification was assumed to be responsible for N_2O production (Zehr and Ward, 2002; Bange and Andreae, 1999). Due to the low ΔN_2O in deep waters and insufficient correlations with nitrate and AOU, we assume N_2O at these depths probably originates from deep water formation and mixing processes of southern and northern hemisphere water masses. N_2O profiles from a cruise into the Antarctic circumpolar current (2° E/49.5° S) (Walter et al., 2005) and BLAST II data east of Patagonia reveal distinctly higher N_2O concentrations in the deep waters of the southern hemisphere, with values of approximately 17 nmol L^{-1}. Northwards transport within Antarctic Bottom Water could lead to enhanced N_2O concentrations in the deep water of the North Atlantic by mixing and diffusion process.

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6 Conclusions

N_2O concentrations in the North Atlantic showed characteristic variations in the vertical and horizontal distributions. In general, distribution of N_2O can be explained by a combination of biological and hydrographic reasons. The main conclusions of the present study are

- Production of N_2O by nitrification occurs mainly in the tropical North Atlantic, especially in the eastern basin. Maximum values were found in the Antarctic Intermediate Water (AAIW) in the western basin, and in the South Atlantic Central Water (SACW) in the eastern basin.
- Vertical N_2O distribution and shape of profiles in the subtropical North Atlantic originate from production by nitrification and advection of AAIW from the south into the western subtropical North Atlantic, respectively advection of LSW from the north in the eastern subtropical North Atlantic.
- In the subpolar North Atlantic mainly mixing processes may control the distribution of N_2O, particularly the deep water formation in the Labrador Sea. Production seems to be negligible.
- Tropical and subtropical regions showed supersaturation throughout the water column, thus the tropical and subtropical North Atlantic act as a source of atmospheric N_2O.
- Outflow water of the Amazon or the Mediterranean Sea does not affect the N_2O concentration.

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Table 1. Regression analyses between ΔN_2O and AOU, and ΔN_2O and NO_3^- at different isopycnal levels. Bold numbers mean relationships with significance levels of $p<0.001$ and $R^2>0.5$. The coefficients a and b mean slope and intercept.

			ΔN_2O/AOU			$\Delta N_2O/NO_3^-$		
region	sigma	n	a	b	R^2	a	b	R^2
subpolar	thermocline–26.0	–	–	–	–	–	–	–
	26.1–26.5	–	–	–	–	–	–	–
	26.6–27.0	13	0.045	−0.209	0.21	0.205	−0.882	0.09
	27.1–27.5	49	0.028	−0.452	0.23	0.159	−1.087	0.14
	27.6–27.9	179	0.022	−1.714	0.07	0.164	−3.240	0.03
subtropical	thermocline–26.0	–	–	–	–	–	–	–
	26.1–26.5	45	**0.038**	**1.307**	**0.58**	**0.297**	**1.337**	**0.51**
	26.6–27.0	106	**0.065**	**0.397**	**0.75**	**0.390**	**0.186**	**0.68**
	27.1–27.5	121	**0.055**	**0.426**	**0.67**	**0.312**	**−0.052**	**0.60**
	27.6–27.9	355	0.069	−3.083	0.38	−0.126	4.579	0.02
tropical	thermocline–26.0	34	**0.080**	**3.783**	**0.72**	**0.599**	**4.681**	**0.61**
	26.1–26.5	39	**0.099**	**−1.421**	**0.83**	**0.777**	**−3.212**	**0.81**
	26.6–27.0	98	0.107	−3.112	0.49	0.376	6.068	0.20
	27.1–27.5	63	0.114	−10.638	0.43	1.289	−35.05	0.42
	27.6–27.9	69	**0.075**	**−4.853**	**0.67**	**0.619**	**−11.83**	**0.66**

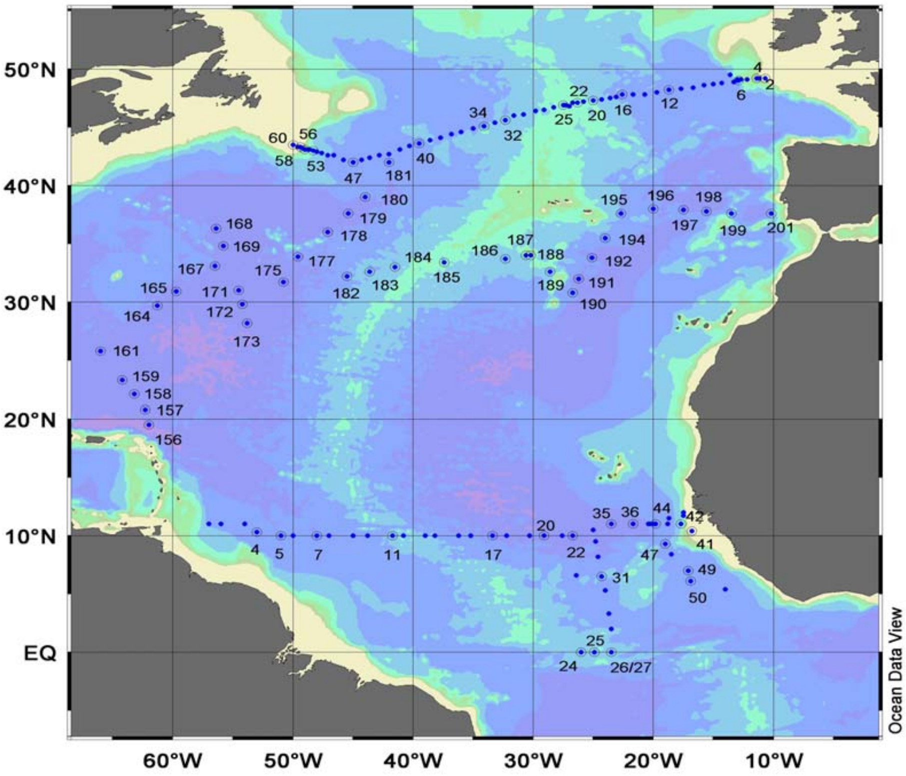

Fig. 1. Cruise tracks for "Gauss 384-1" (subpolar North Atlantic, 16 May to 14 June 2002), "Meteor 60-5" (subtropical North Atlantic, 9 March to 14 April 2004) and "Meteor 55" (tropical North Atlantic, 13 October to 16 November 2002). Numbers are given for stations where N_2O profiles were measured.

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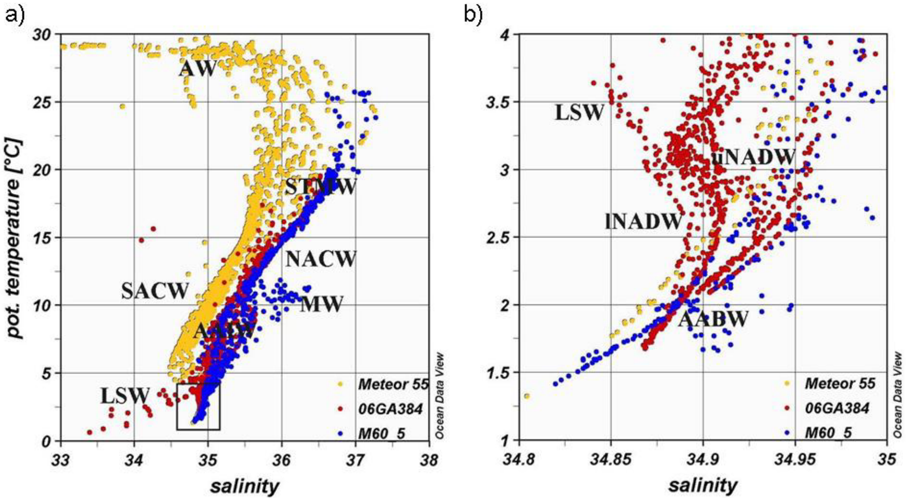

Fig. 2. T-S-diagram of the North Atlantic; **(a)** T-S-diagram with data from all three cruises; **(b)** T-S-diagram in (a) framed by box.; AW: Amazon Water; STMW: Subtropical Mode Water; MW: Mediterranean Water; SACW: South Atlantic Central Water; NACW: North Atlantic Central Water; AAIW: Antarctic Intermediate Water, AABW: Antarctic Bottom Water; lNADW: lower North Atlantic Deep Water; uNADW: upper North Atlantic Deep Water; LSW: Labrador Sea Water.

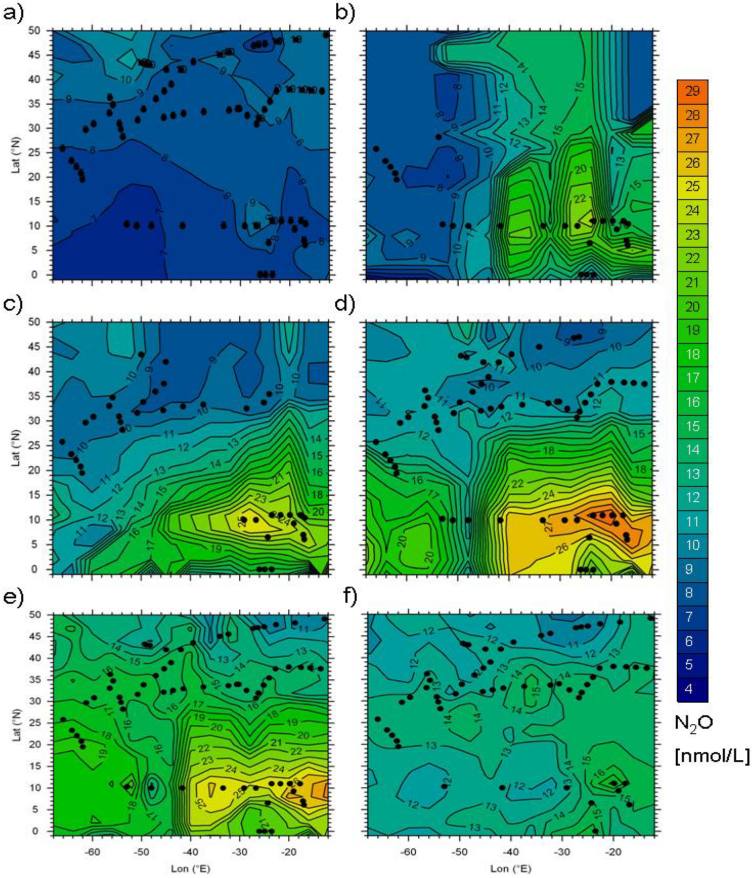

Fig. 3. Distribution of N_2O in the North Atlantic along isopycnal levels σ_θ[kg m^{-3}]. Dots indicate stations with available data for the isopycnal levels. **(a)** surface–thermocline; **(b)** thermocline–26.0; **(c)** 26.1–26.5; **(d)** 26.6–27.0; **(e)** 27.1–27.5; **(f)** 27.6–27.93.

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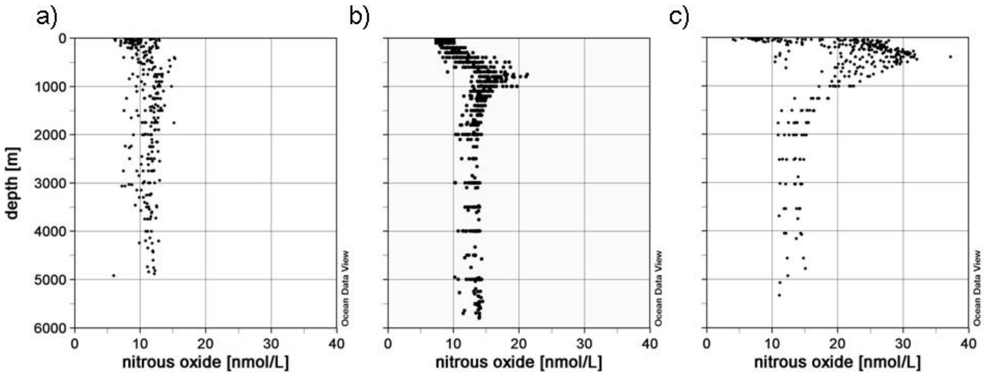

Fig. 4. N_2O concentration in the North Atlantic plotted against depth. **(a)** subpolar, **(b)** subtropical, **(c)** tropical North Atlantic.

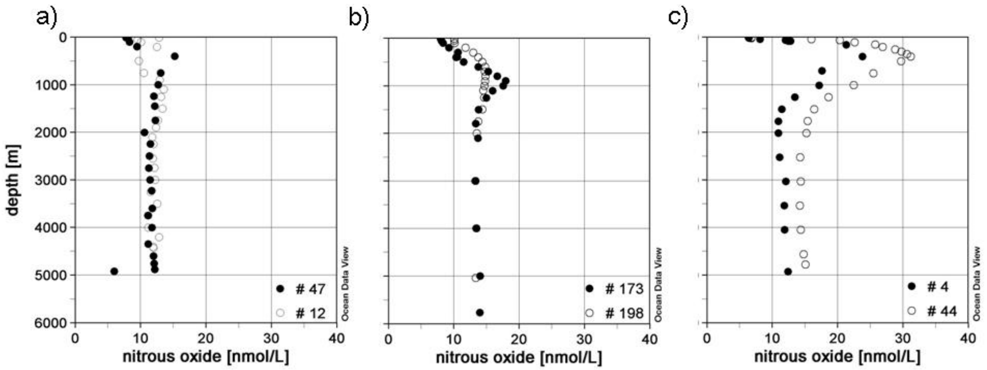

Fig. 5. Selected vertical N_2O profiles in the western basin (filled symbols) and the eastern basin (open symbols) in the North Atlantic. Stations were indicated by numbers. **(a)** subpolar, **(b)** subtropical, **(c)** tropical North Atlantic.

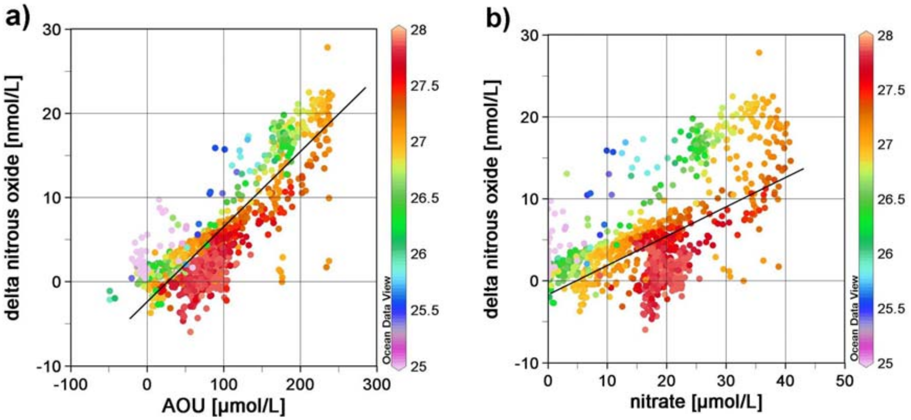

Fig. 6. ΔN_2O in comparison with AOU **(a)** and nitrate **(b)** for the North Atlantic, sigma σ_θ is colour coded in kg m^{-3}.
$y(\Delta N_2O)=0.089x(AOU)–3.245$, $R^2=0.714$
$y(\Delta N_2O)=0.331x(NO_3^-)-1.263$, $R^2=0.322$.

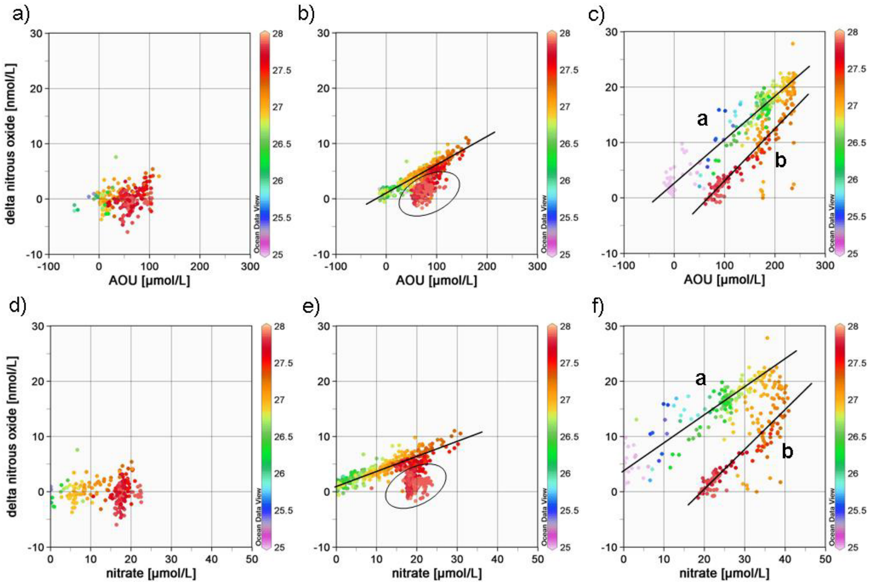

Fig. 7. ΔN_2O in comparison with AOU **(a–c)** and nitrate **(d–f)**, sigma σ_θ is colour coded in kg m^{-3}.
(a) and (d) subpolar North Atlantic
(b) and (e) subtropical North Atlantic;
y $(\Delta N_2O)=0.0473x(AOU)+1.1409$, $R^2=0.86$ for $\sigma_\theta < 27.7$(~ <1000 m);
y $(\Delta N_2O)=0.2497x(NO_3^-)+1.1776$, $R^2=0.80$ for $\sigma_\theta < 27.7$(~ <1000 m);
circled data represent $\sigma_\theta > 27.7$(~>1000 m)
(c) and (f) tropical North Atlantic;
line a: y $(\Delta N_2O)=0.0785x(AOU)+2.4381$, $R^2=0.87$ for $\sigma_\theta < 27.1$(~<500 m);
line b: y $(\Delta N_2O)=0.0942x(AOU)-6.6675$, $R^2=0.81$ for $\sigma_\theta > 27.1$(~>500 m);
line a: y $(\Delta N_2O)=-0.4848x(NO_3^-)+3.1756$, $R^2=0.79$ for $\sigma < 27.1$(~<500 m);
line b: y $(\Delta N_2O)=0.7379x(NO_3^-)-14.665$, $R^2=0.79$ for $\sigma > 27.1$ (~>500 m).

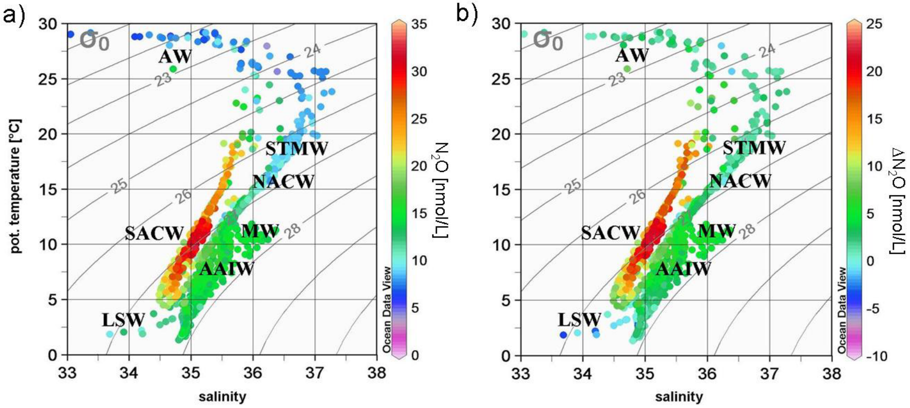

Fig. 8. N_2O concentration **(a)** and ΔN_2O **(b)** distributed in a T-S-diagram, the N_2O and ΔN_2O concentrations are colour coded in $\mathrm{nmol\,L^{-1}}$. AW: Amazon Water; STMW: Subtropical Mode Water; MW: Mediterranean Water; SACW: South Atlantic Central Water; NACW: North Atlantic Central Water; AAIW: Antarctic Intermediate Water; LSW: Labrador Sea Water.