Nitrous oxide measurements during EIFEX, the European Iron Fertilization Experiment in the subpolar South Atlantic Ocean

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[1] We measured the vertical water column distribution of nitrous oxide (N_2O) during the European Iron Fertilization Experiment (EIFEX) in the subpolar South Atlantic Ocean during February/March 2004 (R/V *Polarstern* cruise ANT XXI/3). Despite a huge build-up and sedimentation of a phytoplankton bloom, a comparison of the N_2O concentrations within the fertilized patch with concentrations measured outside the fertilized patch revealed no N_2O accumulation within 33 days. This is in contrast to a previous study in the Southern Ocean, where enhanced N_2O accumulation occurred in the pycnocline. Thus, we conclude that Fe fertilization does not necessarily trigger additional N_2O formation and we caution that a predicted radiative offset due to a Fe-induced additional release of oceanic N_2O might be overestimated. Rapid sedimentation events during EIFEX might have hindered the build-up of N_2O and suggest, that not only the production of phytoplankton biomass but also its pathway in the water column needs to be considered if N_2O radiative offset is modeled. **Citation:** Walter, S., I. Peeken, K. Lochte, A. Webb, and H. W. Bange (2005), Nitrous oxide measurements during EIFEX, the European Iron Fertilization Experiment in the subpolar South Atlantic Ocean, *Geophys. Res. Lett.*, *32*, L23613, doi:10.1029/2005GL024619.

1. Introduction

[2] Inspired by the iron (Fe) limitation hypothesis [*Martin et al.*, 1991], several Fe fertilization experiments have been performed in high nutrient-low chlorophyll (HNLC) regions such as the Southern Ocean, and the subarctic and equatorial Pacific Ocean [see, e.g., *Boyd*, 2004, 2002]. *Fuhrman and Capone* [1991] pointed out that stimulating ocean productivity by Fe addition might result in an enhanced formation of nitrous oxide (N_2O). This point is especially important in view of the fact that N_2O is an atmospheric trace gas with a high global warming potential [*Jain et al.*, 2000]. Thus, enhanced N_2O formation by Fe addition might counteract the climatic benefits of a drawdown of atmospheric carbon dioxide (CO_2).

[3] *Fuhrman and Capone* [1991] argued that enhanced productivity will lead to an enhanced nitrogen export from the euphotic zone, which in turn would result in additional N_2O formation via enhanced nitrification ($NH_4^+ \rightarrow$ $NH_2OH \rightarrow NO_2^- \rightarrow NO_3^-$). N_2O formed via nitrification is thought to be dominating in the oxic part of the world's oceans [see, e.g., *Nevison et al.*, 2003]. The idea of a link between Fe fertilization and enhanced N_2O formation was supported by the study of *Law and Ling* [2001], who found a small but significant N_2O accumulation in the pycnocline during the Southern Ocean Iron Enrichment Experiment (SOIREE) in the Australasian sector of the Southern Ocean (61°S, 140°E) in February 1999. Recently, *Jin and Gruber* [2003] predicted the long-term effect of Fe fertilization on oceanic N_2O emissions on a global scale with a coupled physical-biogeochemical model. Based on their model results they concluded that Fe fertilization-induced N_2O emissions could offset the radiative benefits of the CO_2 drawdown [*Jin and Gruber*, 2003].

[4] Here we present our measurements of N_2O during the European Iron Fertilization Experiment (EIFEX; R/V *Polarstern* cruise ANT XXI/3) in the subpolar South Atlantic Ocean from 9 February to 21 March 2004 [*Smetacek and cruise participants*, 2005].

2. The EIFEX Setting

[5] A mesoscale cyclonic eddy, embedded in a meander of the Antarctic Polar Front, was identified as suitable for the EIFEX study [*Strass et al.*, 2005]. The eddy was centered at 49.4°S 2.25°E and extended over an area of 60×100 km. First fertilization was performed on 12–13 February by releasing 6000 kg iron sulfate ($FeSO_4$) into the mixed layer over an area of 150 km^2. Since iron concentrations had been decreasing (P. Croot, personal communication, 2004), fertilization was repeated on 26–27 February by releasing 7000 kg $FeSO_4$ over an area of 400 km^2. All sampled stations were located inside the eddy; the stations within fertilized waters will be called in-stations and those from unfertilized waters out-stations (Table 1). Inside and outside the fertilized patch was determined by photosynthetic activity (Fv/Fm) performed by Fast-Repetition-Rate-Fluorescence (FastTracka, Chelsea, UK) [*Röttgers et al.*, 2005]. Fv/Fm is known to be a very sensitive parameter, which increases immediately after iron fertilization.

[6] The hydrographic settings of the sampling stations were not uniform: The in-stations' hydrographic properties did not show any variability. However, the out-station 514 showed, in comparison with the in-stations, enhanced potential water temperatures in the density (σ_t) range from 27.25 to 27.7 kg m^{-3} (corresponding to a approximate depth range from 200 to 400 m). The hydrographic properties of the out-stations 546 and 587 were almost identical to the in-stations. This implies that station 514 is not a representative out-station and was therefore excluded

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Table 1. N$_2$O Measurements During EIFEX[a]

Station Number	Latitude,°S	Longitude,°E	Date	Days After First/ Second Fertilization	Patch Class.	N$_2$O ML Conc.,[b] nmol L^{-1}	N$_2$O ML Sat.,[b] %
513	49.59	2.05	28 Feb 04	16/2	In	13.3 ± 0.1 (5)	102 ± 1 (5)
514	49.31	2.34	29 Feb 04	17/3	Out	13.5 ± 0.3 (3)	104 ± 2 (3)
544	49.36	1.87	07 Mar 04	24/10	In	13.8 ± 0.5 (3)	106 ± 4 (3)
546	49.47	2.09	10 Mar 04	27/13	Out	13.1 (2)	102 (2)
570	49.43	2.05	14 Mar 04	31/17	In	13.1 ± 0.3 (5)	102 ± 3 (5)
580	49.12	2.38	16 Mar 04	33/19	In	12.5 ± 0.2 (3)	97 ± 1 (3)
586	49.50	2.10	18 Mar 04	35/21	Out	13.1 ± 0.5 (4)	102 ± 4 (4)

[a]Class. stands for classification and indicates whether a profile was inside or outside of the fertilized patch. ML stands for mixed layer; here defined as the depth where the temperature differs from the surface temperature by more than 0.5°C. Conc. and Sat. stand for concentration and saturation, respectively.
[b]Given as average ± standard deviation. Number of depths used for averaging is given in parentheses.

from the comparison (see also discussion of N$_2$O data below).

3. Methods

[7] Triplicate water samples from various depths were taken from a 24 x 12 L-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 (O$_2$) 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 a saturated aqueous mercury chloride (HgCl$_2$) solution. The samples were stored in the dark at 4 °C until analysis in our home laboratory from June to August 2004. In a time series experiment we found that N$_2$O concentrations in samples treated as described above did not change significantly over 10 months (S. Walter, Nitrous oxide in the Atlantic Ocean, Ph.D. thesis, in preparation, University of Kiel, 2005). N$_2$O water concentrations (C$_w$) were calculated as follows:

$$C_w \left[\text{nmol L}^{-1} \right] = \left(\beta x' P V_{wp} + \frac{x'P}{RT} V_{hs} \right) / V_{wp}$$

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$_2$O in the headspace in ppb, P is the atmospheric pressure in atm (set to 1 atm), V$_{wp}$ and V$_{hs}$ stand for the volumes of the water (14 mL) and headspace phases (10 mL), respectively. R is the gas constant (8.2054 10^{-2} L atm mol^{-1} K^{-1}) and T is the temperature during equilibration.

[8] For calibration we used standard gas mixtures with 311.8 ± 0.2 ppb and 346.5 ± 0.2 ppb N$_2$O in synthetic air (DEUSTE Steininger GmbH, Mühlhausen, Germany). The standard mixtures have been calibrated against the NOAA (National Oceanic and Atmospheric Administration, Boulder, Colorado) standard scale in the laboratories of the Air Chemistry Division of the Max Planck Institute for Chemistry, Mainz, Germany. The standard deviation of the N$_2$O concentration (C$_w$) was approximated with (C$_{wmax}$ − C$_{wmin}$)/1.91, where C$_{wmin}$ and C$_{wmax}$ stand for the minimal and maximal N$_2$O concentrations of the triplicate samples, respectively. The factor 1.91 is derived from the statistical method by *David* [1951]. The overall mean analytical error was ±2.7% (±0.5 nmol L^{-1}).

[9] N$_2$O saturations (sat) in% (i.e., 100% = equilibrium) were calculated as sat = 100 C$_w$/C$_a$, where C$_a$ is the equilibrium concentration of dissolved N$_2$O based on the N$_2$O atmospheric dry mole fraction, water temperature, and salinity [*Weiss and Price*, 1980]. For calculating C$_a$ in the mixed layer an ambient air mole fraction of 317.8 ppb was applied, which is the average of the monthly mean N$_2$O dry mole fractions measured at the AGAGE (Advanced Global Atmospheric Gases Experiment [see *Prinn et al.*, 2000]) baseline monitoring station Cape Grim (Tasmania) during February and March 2004. AGAGE data are available from the anonymous ftp site cdiac.esd.ornl.edu (subdirectory/ pub/ale_gage_agage/agage/gc-md/monthly) at the Carbon Dioxide Information Analysis Center in Oak Ridge, Tennessee.

[10] Dissolved O$_2$, nitrate, and CTD data were provided by the participating working groups. Further details can be found in the cruise report by *Smetacek and cruise participants* [2005].

4. Results and Discussion

[11] An overview of the N$_2$O measurements during EIFEX is given in Table 1 and in Figure 1. Mixed layer N$_2$O saturations were comparable to surface saturations (∼103%) from the same region measured during the Ajax cruise leg 2 in Jan-Feb 1984 [*Weiss et al.*, 1992]. Moreover, the overall mean N$_2$O deep water (>2000 m) concentration of 17.5 ± 0.2 nmol L^{-1} is in good agreement with the N$_2$O deep water-water age relationship by *Bange and Andreae* [1999]. Both, the observed surface saturation and deep-water concentration support the view that the N$_2$O samples were not affected by the time lag between sampling and measurements.

[12] In agreement with the results from SOIREE [*Law and Ling*, 2001], we did not observe a difference in N$_2$O mixed layer saturations between in-stations and out-stations (Table 1), which implies that N$_2$O emissions were not significantly different either.

[13] The N$_2$O profiles showed a pronounced maximum between 500 and 750 m which was associated with the O$_2$ minimum and the nitrate maximum (Figure 1) indicating that nitrification was the main N$_2$O formation process. Our N$_2$O concentrations are comparable to N$_2$O measurements from the South Atlantic and Southern Oceans [*Butler et al.*, 1995; *Law and Ling*, 2001; *Rees et al.*, 1997].

[14] Following the approach by *Law and Ling* [2001], we fitted a polynomial to the N$_2$O-σ$_t$ data of stations 546 and 587 (Figure 2). Out-station 514 was excluded because it
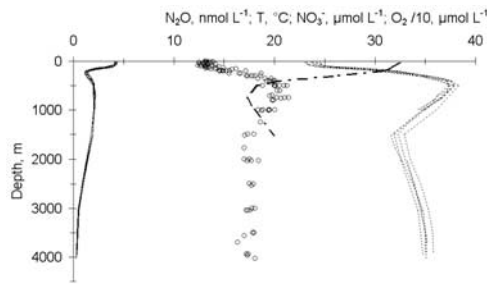
Figure 1. N₂O (open circles), water temperature (solid lines), NO₃⁻ (dashed lines), and O₂ (dashed dotted line) at the EIFEX stations listed in Table 1. O₂ data are only available for station 570 in the depth range from 0–1500 m. Please note that O₂ is given in μmol L⁻¹ divided by 10.

obviously was not representative as indicated by the data in Figure 2 (see also section EIFEX setting). A comparison of the N₂O concentrations of the in-stations with the polynomial fit based on the out stations revealed no significant differences (Figure 2). A third-order polynomial fit to the in-stations ($-52.766x^3 + 4320.7x^2 - 117{,}915x + 1{,}072{,}529$, $r^2 = 0.95$, $n = 67$, standard error of predicted N₂O = ± 0.63 nmol L⁻¹) was almost identical to the out-stations' fit ($-48.474x^3 + 3967.8x^2 - 108{,}241x + 984{,}148$, $r^2 = 0.96$, $n = 30$, standard error of predicted N₂O = ±0.56 nmol L⁻¹). Thus, we conclude that no significant changes in the N₂O concentrations occurred during EIFEX.

[15] Our conclusion is in contrast to the observation by *Law and Ling* [2001]. They found an accumulation of N₂O up to 0.9–1 nmol L⁻¹ in the pycnocline (60–80 m water depth) within 13 days during SOIREE. Adapting a N₂O accumulation rate of 0.08 nmol L⁻¹ d⁻¹ (=1 nmol L⁻¹/13 days), an increase of 2.6 nmol L⁻¹ (=0.08 nmol L⁻¹ × 33 days) would have been expected for a N₂O accumulation in the pycnocline in 100–200 m during EIFEX. This was not the case (Figure 2). It is possible that N₂O accumulation in the pycnocline was not detected because of insufficient analytical precision and/or coarse sampling of the depths profiles: A possible N₂O accumulation must have been low (<0.5 nmol L⁻¹ over the duration of the experiment as implied by our mean analytical error) or must have taken place in a narrow depth range of less than 40 m (i.e., the mean depth spacing of sampling from the surface to the pycnocline in about 200 m). Moreover, in contrast to EIFEX, Fe addition during SOIREE was performed four times within a week over a much smaller area (50 km² [*Law and Ling*, 2001]). Therefore, the observed N₂O accumulation in the pycnocline during SOIREE may have been a fast short-term response to the intensive short-term Fe fertilization. Because we started N₂O sampling 16 days after the first Fe addition (i.e., 2 days after the second Fe addition) we might have missed this short-term signal during EIFEX.

[16] During EIFEX chlorophyll *a* (chl *a*) standing stocks increased 3 fold until day 26, but remarkably decreased thereafter [*Peeken et al.*, 2005]. The main beneficiaries of the iron fertilization were diatoms in all size classes (L. Hoffmann et al., Different reactions of

Southern Ocean phytoplankton size classes to iron fertilisation, submitted to *Limnology and Oceanography*, 2005). Toward the end of the experiment, the diatom marker fucoxanthin and chl *a* could be followed down the water column to 4000 m and a low ratio of phaeopigments to chl *a* indicated the export of fresh material most likely originating from the iron fertilized patch [*Peeken et al.*, 2005]. An explanation for the absence of an increase of N₂O in the deep (e.g., in the O₂ minimum zone) might be the very rapid export of the fresh phytoplankton material to the deep ocean during EIFEX [*Peeken et al.*, 2005], which started about 23 days after the second Fe addition. Thus, we can argue that the rapid export of organic material during EIFEX might have been too rapid for the nitrifying bacteria in the deep ocean to adapt to and, thus, an additional build-up of N₂O in the deep could not take place. Nitrifying bacteria, especially ammonium-oxidizing bacteria (AOB), are known for lag phases up to several weeks after periods of low metabolic activities [*Schmidt et al.*, 1999].

[17] The responsible process for the N₂O accumulation during SOIREE [*Law and Ling*, 2001] and the proposed further increase of N₂O in prolonged iron fertilization experiments could not be identified. Thus, a possible link between N₂O accumulation and Fe fertilization remains to be not a simple cause-and-effect mechanisms and the
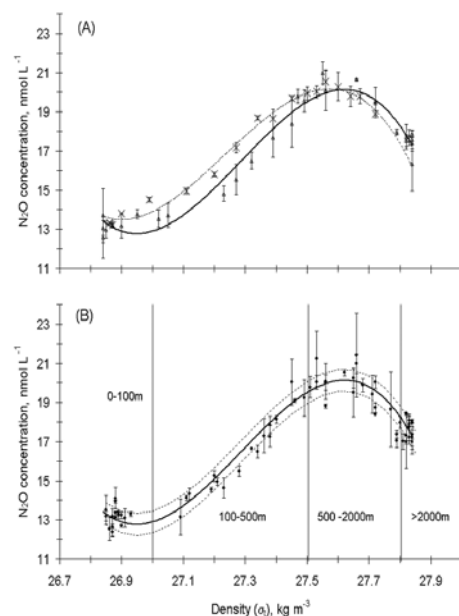
Figure 2. N₂O concentrations vs. density (σ_t) during EIFEX. (a) Out-stations: Triangles stand for stations 546 and 587 and crosses stand for station 514. The bold solid line represents a third-order polynomial fit based on stations 546 and 587 (see text for statistical details). The thin solid line represents a third-order polynomial fit based on station 514. (b) In-stations: 513, 544, 570, and 580 (symbols) compared with the polynomial fit based on out-stations 546 and 587 (bold line, see Figure 2a). The dashed lines indicate the standard error of the predicted N₂O. Depths intervals are indicated.

magnitude of a possible radiative offset still needs to be proven.

5. Conclusions

[18] We did not observe a N$_2$O accumulation during the in situ iron fertilization experiment EIFEX in the subpolar South Atlantic Ocean in February/March 2004. This is in contrast to previous measurement by *Law and Ling* [2001] in the Australasian sector of the Southern Ocean. We conclude that Fe fertilization does not necessarily trigger additional N$_2$O formation, which might depend on differences of the environmental conditions (e.g., the fate of the Fe-induced phytoplankton bloom). We caution, therefore, that predictions of a radiative offset caused by a Fe-induced additional release of oceanic N$_2$O [*Jin and Gruber*, 2003; *Law and Ling*, 2001] might be overestimated. In order to solve this problem further long-term experiments with particular emphasis on sedimentation processes are necessary to prove a link between Fe addition and enhancement of N$_2$O formation and the subsequent release of N$_2$O to the atmosphere.

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