GEOPHYSICAL RESEARCH LETTERS, VOL. 23, NO. 22, PAGES 3175-3178, NOVEMBER 1, 1996

Nitrous oxide emissions from the Arabian Sea

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Abstract. Dissolved and atmospheric nitrous oxide (N_2O) were measured on the legs 3 and 5 of the R/V *Meteor* cruise 32 in the Arabian Sea. A cruise track along 65°E was followed during both the intermonsoon (May 1995) and the southwest (SW) monsoon (July/August 1995) periods. During the second leg the coastal and open ocean upwelling regions off the Arabian Peninsula were also investigated. Mean N_2O saturations for the oceanic regions of the Arabian Sea were in the range of 99-103 % during the intermonsoon and 103-230 % during the SW monsoon. Computed annual emissions of 0.8-1.5 Tg N_2O for the Arabian Sea are considerably higher than previous estimates, indicating that the role of upwelling regions, such as the Arabian Sea, may be more important than previously assumed in global budgets of oceanic N_2O emissions.

Introduction

Nitrous oxide (N_2O) is an important atmospheric trace gas because it influences, directly and indirectly, the Earth's climate to a significant degree. In the troposphere, it acts as a greenhouse gas with a relatively long atmospheric lifetime [*Lashof and Ahuja*, 1990], whereas in the stratosphere it is the major source for NO radicals which are involved in one of the three main ozone reaction cycles [*Crutzen and Schmailzl*, 1983]. Recently published source estimates indicate that the world's oceans play a major, but not dominant role in the global budget of atmospheric nitrous oxide [*Khalil and Rasmussen*, 1992; *Bouwman et al.*, 1995]. Oligotrophic areas of the oceans are near equilibrium with the atmosphere [*Nevison et al.*, 1995]. Biologically productive regions (i.e., marginal seas, estuaries and coastal upwelling areas) which cover only about 20% of the world's ocean area appear to be responsible for ca. 60% of the oceanic N_2O emissions [*Bange et al.*, 1996a]. Upwelling regions, such as the eastern tropical Pacific and the Arabian Sea, are sites of large N_2O production due to denitrification and/or nitrification processes which occur at the boundaries of the oxygen depleted water masses [*Codispoti et al.*, 1992]. Since the studies of *Law and Owens* [1990] and *Naqvi and Noronha* [1991] it was speculated that the Arabian Sea, especially its upwelling-dominated northwestern part, represents a hot spot for N_2O emissions making a substantial contribution to the global budget of atmospheric N_2O. However, these flux estimates did not take into consideration the significant temporal and spatial variability of dissolved N_2O. Here we present our measurements of dissolved and atmospheric nitrous oxide in the Arabian Sea during the intermonsoon and southwest (SW) monsoon. Additionally, we present the first N_2O flux estimate from the Arabian Sea based on data from different seasons.

The two cruise legs were part of the Joint Global Ocean Flux Study (JGOFS) - German Arabian Sea Process Study and took place in May 1995 (leg M32/3) and July/August 1995 (leg M32/5) on the German Research Vessel Meteor. On the first leg, a cruise track from Muscat (Oman) to Victoria (Seychelles) along 65°E was followed (Figure 1a). Three drift studies at 18°N 65°E (10 days), 10°N 65°E (9 days), and 3°N 65°E (3 days) were carried out. The second leg from Victoria (Seychelles) to Muscat (Oman) followed 65°E northward to 14°30N 65E and a transect to the coast of Oman (Figure 1b). Oligotrophic waters in the central Arabian Sea were investigated (e.g., on stations D1, D2, and D3). Nutrient rich regions (e.g., coastal and open ocean upwelling waters) were sampled on the transect to the coast of Oman during leg M32/5.

Paper number 96GL03072.
0094-8534/96/96GL-03072$05.00

Methods

N_2O was determined with a gas chromatograph (GC) equipped with an electron capture detector (ECD). Further details of the analysis system are described in *Bange et al.* [1996b]. Seawater was pumped continuously from a depth of 7 m into a shower type equilibrator developed by R. F. Weiss (Scripps Institution of Oceanography (SIO), La Jolla, Ca.). During both legs, we found a mean water temperature increase between the sea chest and the equilibrator of 0.21±0.05°C. Concentrations and resulting saturation values were corrected for this difference [*Butler et al*, 1988]. A series of measurements of ambient and dissolved nitrous oxide followed by two standards was repeated every 100 min. Mixtures of N_2O in synthetic air were used to obtain two-point calibration curves. The mixtures used contained 300.5 ±0.1 and 349.6±0.2 ppb N_2O, respectively. These are gravimetrically prepared gas mixtures and have been calibrated in the laboratories of R. F. Weiss (SIO), against the SIO-1993 standard scale [*Weiss*, personal communication, 1996]. Because of the non-linear ECD response [*Butler and Elkins*, 1991], N_2O values in the range from 350 to 950 ppb, which is above the range covered by the calibration gases, may be overestimated by as much as 1.5% due to the linear regression applied [*Bange et al.*, unpublished data, 1996]. The precision, calculated as the ratio of the standard deviation of the atmospheric measurements and the mean atmospheric mixing ratio, was 0.7%. Unfortunately, nitrogen was used as the carrier gas during the second half of the first leg resulting in a precision of 1.6% during this period. The mean relative errors of the N_2O saturation and concentration were calculated to be 1.5% and 1.1%, respectively. Saturation values (expressed in %, i.e., 100% = equilibrium) were calculated by applying the solubility equation of *Weiss and Price* [1980]. Continuous time series of seawater temperature, salinity, wind speed, and atmospheric pressure were obtained from the ship's records.

Results and Discussion

Due to the seasonal northward shift of the Intertropical Convergence Zone, which is most pronounced during the SW monsoon, air masses sampled during the two legs were from the southern hemisphere. The average atmospheric N_2O dry mole

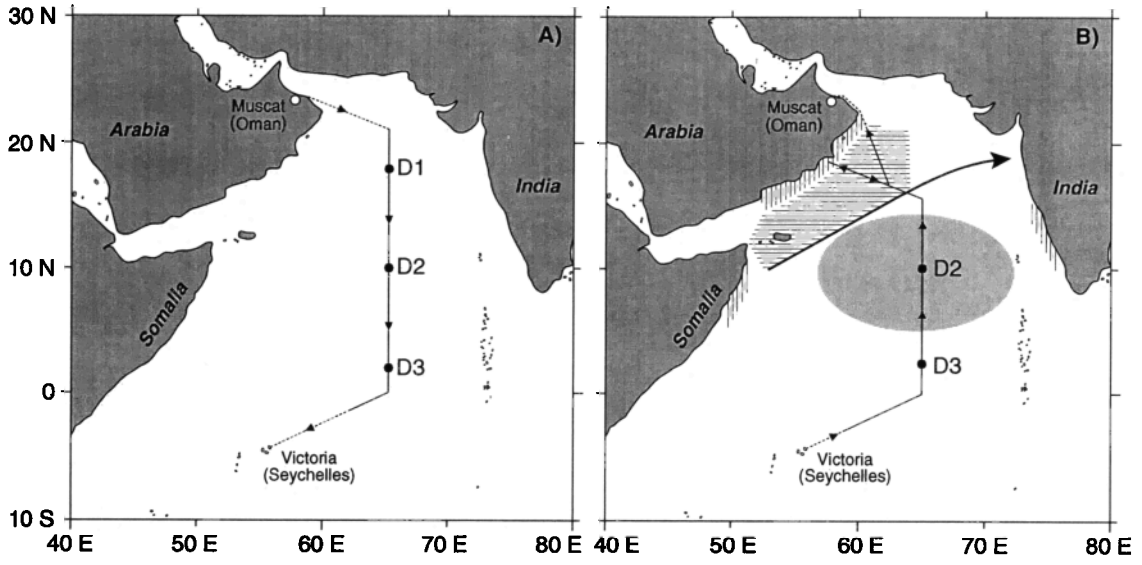

Figure 1. Cruise track of R/V *Meteor* cruise 32; the solid line indicates the parts of the cruise when N_2O was measured; the positions of stations D1, D2, and D3 are indicated: A) Leg 3 (May 1995); B) Leg 5 (July/August 1995); prominent features during the SW monsoon are also shown: areas of coastal upwelling (vertically hatched), area of occasional open ocean upwelling (horizontally hatched), and area with deepening of the mixed layer (gray shaded). The arrow indicates the axis of the Findlater Jet.

fractions were 307.5±4 ppb (May) and 309±2 ppb (July/August). They are only slightly lower than the southern hemispheric mean of 310 ppb (January 1995) [*Weiss*, personal communication, 1996]. Surface seawater N_2O concentrations in the central Arabian Sea ranged from 5.0 to 5.7 nmol L^{-1} (May 1995) and from 5.7 to 6.9 nmol L^{-1} (July 1995). Significantly higher concentrations of as much as 8.6 and 21.6 nmol L^{-1} were observed in the coastal and open ocean upwelling areas of Oman.

The equilibrated N_2O along 65°E during May and July 1995 is shown in Figure 2. The calculated mean saturation values for the central Arabian Sea indicate a modest, but significant trend towards higher saturation values during the SW monsoon (Table 1). This was confirmed by separate variance t-test statistics which indicated in all cases a significant seasonal difference at a confidence level of 99%. In July pronounced downwelling occurs on the southeastern side of the Findlater Jet, promoting deepening of the mixed layer down to the top of the oxygen minimum zone (OMZ). The OMZ usually extends from

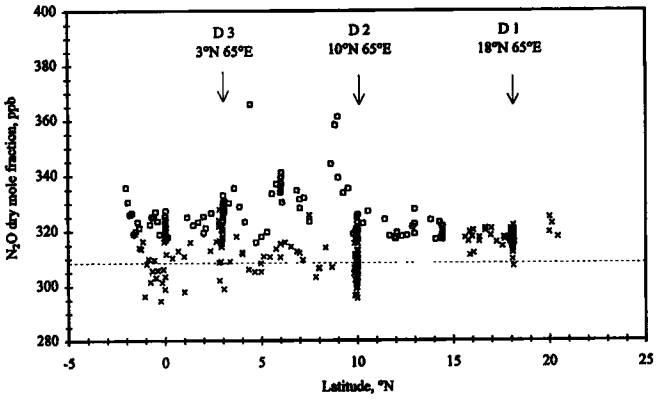

Figure 2. N_2O of equilibrated seawater along 65°E during May 1995 (crosses) and July 1995 (open squares). The stations D1, D2, and D3 are indicated. The dashed line indicates the mean atmospheric dry mole fraction of N_2O.

150 to 1000 m depth and is the site of intense denitrification exhibiting a sharp maximum of dissolved N_2O at ca. 150 m [*Naqvi and Noronha*, 1991]. Thus, the seasonal difference in surface N_2O concentrations of the central Arabian Sea may be explained by entrainment of N_2O from the OMZ or by advection of N_2O enriched water masses from the Arabian or Somali coast. The overall N_2O distribution along 65°E during the SW monsoon was characterized by marked spatial heterogeneity (Figure 2). The range of N_2O saturations along 65°E (94-118 %) is in reasonable agreement with data of *Weiss et al.* [1992] for a similar transect from 19.8-6.2°N along 64.5°E during the northeast (NE) monsoon 1977/78. Estimated N_2O saturation values from their data range between 101-124 % (avg. 108±3 %). N_2O saturation values reported by *Naqvi and Noronha* [1991] from 12 stations located mainly along 67°E from 21-12°N, sampled during the NE monsoon in December 1988, range from 90 to 258 % (with an average of 182±47 %). For a station at 18°N 65°E (which is identical with our station D1) the latter authors report a N_2O saturation of 140.5%. Recently, *Lal et al.* [1996] reported N_2O saturations from two studies in the central Arabian Sea. On a transect from 11-22°N, mainly along 64°E, they found mean N_2O saturations of 106±8 % (intermonsoon, Apr./May 1994) and 148±10 % (decline of the NE monsoon; Feb./Mar. 1995). The former value is in agreement with our results from the intermonsoon leg (Table 1). Summarizing the results from various N_2O measurements in the central Arabian Sea it is obvious that there are substantial differences which are probably caused by the enormous seasonal and inter-annual variability of the Arabian Sea.

Our measurements of equilibrated N_2O in the upwelling areas are illustrated by Figure 3. In the coastal upwelling area of Oman, from 58.3°E to 57.2°E, we calculated N_2O saturation values up to 308% (avg. 230%, Table 1). N_2O depth profiles from the coastal upwelling indicate that the high N_2O surface concentrations are mainly the result of upwelled N_2O enriched subsurface water masses [*Bange et al.*, unpublished data, 1996]. The average value of 187±40 % reported by *Law and Owens*

Table 1. Mean N_2O Surface Saturations (± 1 s.d.) During the Intermonsoon and SW Monsoon in 1995

	May 1995, Percent	July/August 1995, Percent
< 00°N 65°E[a]	99 ± 2 (16)	104 ± 1 (7)
00°N 65°E - 14.45°N 65°E[a]	101 ± 2 (34)	105 ± 3 (116)
14.45°N 65°E - 20.45°N 65°E[b]	103 ± 1.5 (21)	-
18°N 65°E (D1)	102 ± 1 (100)	-
10°N 65°E (D2)	99 ± 2 (71)	103 ± 1 (13)
03°N 65°E (D3)	102 ± 2 (23)	105.5 ± 1 (12)
Open Ocean Upwelling (15.3°N 63.4°E - 16.6°N 60.9°E)	-	120 ± 7 (54)
Coastal Upwelling (18°N 58.3°E - 18.6°N 57.2°E)	-	230 ± 46 (42)

Numbers in parentheses indicate number of measurements.
[a] Including data from stations D1 and D2.
[b] Including data from station D3.

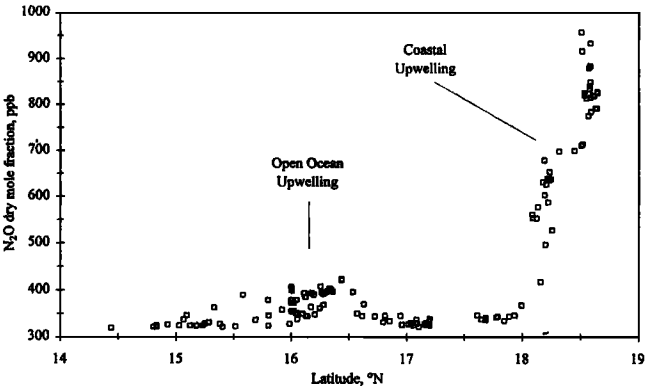

Figure 3. N_2O of equilibrated seawater in the open ocean and coastal upwelling areas during August 1995.

[1990] for the upwelling area is lower than ours (230%, Table 1), because Law and Owens's measurements were performed during the decline of the SW monsoon. Between 62.3°E and 60.3°E we crossed an open ocean upwelling system with mean saturation of 120±7 % (Table 1). *Law and Owens* [1990] did not report the observation of an open ocean upwelling system thus comparable N_2O data are not available.

N_2O Air-Sea Exchange

The air-sea exchange flux density (F, pmol m^{-2} s^{-1}) of N_2O can be parameterized as $F = k_w (C_w - C_a)$, where k_w is the gas transfer coefficient. C_w is the actual N_2O seawater concentration and C_a is the equilibrium water concentration calculated with the corresponding actual atmospheric N_2O dry mole fraction. To calculate k_w, we used the tri-linear k_w/wind speed relationship from *Liss and Merlivat* [1986] (hereinafter referred to as LM86) or, alternatively, the quadratic k_w/wind speed relationship established by *Wanninkhof* [1992] (hereinafter referred to as W92). The exchange coefficients were adjusted to N_2O by multiplying k_w with $(Sc/600)^{-n}$ (n = 2/3 for wind speeds < 3.6 m s^{-1} and n = 1/2 for wind speeds > 3.6 m s^{-1}) for LM86 and $(Sc/660)^{-0.5}$ for W92, where Sc is the Schmidt number for N_2O. Sc was calculated using empirical equations for the kinematic viscosity of seawater [*Siedler and Peters*, 1986] and the diffusion coefficient of N_2O in water [*Broecker and Peng*, 1974]. The wind speeds, measured at 38 m height, were normalized to 10 m height by using the relationship of *Garratt* [1977].

In order to obtain an estimate of the N_2O emissions we stratified our data into those from the central Arabian Sea and those from the coastal upwelling areas. Then, we calculated mean flux densities and semi-annual N_2O emissions for these two oceanographic regimes from the actual flux densities (Table 2). We assumed that our measurements are representative for the intermonsoon and monsoon period. We were not able to calculate emissions for the open ocean upwelling areas because of the high temporal and spatial variability.

By adding the semi-annual emissions listed in Table 2, we obtain mean annual N_2O emissions in the range from 0.8 (LM86) to 1.5 Tg N_2O (W92). Our estimate is considerably higher than that of *Naqvi and Noronha* [1991] who calculated an annual N_2O emission of 0.44 Tg. However, their estimate did not include data from upwelling areas. Additionally, they used climatological

Table 2. Mean N_2O Flux Densities and Semi-annual Emissions in the Arabian Sea for the Intermonsoon and SW Monsoon in 1995

		May 1995		July/August 1995	
	Area, 10^6 km^2	Flux density[e], pmol m^{-2} s^{-1}	Emissions[f], Tg N_2O $(0.5yr)^{-1}$	Flux density[e], pmol m^{-2} s^{-1}	Emissions[f], Tg N_2O $(0.5yr)^{-1}$
Coastal Upwelling[a]	1.47[c]	-	-	730.8 / 1388	0.74 / 1.41
Open Ocean[b]	4.76	3.8 / 6.2	0.01[g] / 0.02[g]	10.6 / 17.3	0.04 / 0.06
Sum	6.23[d]	-	0.01 / 0.02	-	0.78 / 1.47
Open Ocean Upwelling	?	-	-	67.9[h] / 116.9[h]	?

? indicates that the area covered by open ocean upwelling systems is not known and thus the calculation of emissions is questionable.
[a] Estimate based on our data from 18°N 58.3°E - 18.6°N 57.2°E.
[b] Estimate based on our data from 0 - 21.5°N 65°E.
[c] Area assumed to equal 0.5 x area of the Northwest Arabian Upwelling province as defined by *Longhurst et al.* [1995].
[d] Area as used by *Naqvi and Noronha* [1991].
[e] First value calculated according to *Liss and Merlivat* [1986]; second value calculated according to *Wanninkhof* [1992].
[f] Emissions = Area x flux density.
[g] Calculated using the total area of the Arabian Sea.
[h] The flux densities for open ocean upwelling areas were not included in the overall estimate for the Arabian Sea.

wind speeds which could differ considerably from actual wind speeds. *Law and Owens* [1990] calculated N_2O emissions in the range of 0.22-0.39 Tg yr^{-1} by using a mean annual wind speed (5 m s^{-1}) instead of using the actual wind speeds. Obviously, the annual N_2O emissions from the Arabian Sea (Table 2) are dominated by the enormous concentrations found in the coastal upwelling area in conjunction with the high wind speeds during the SW monsoon (up to 19 m s^{-1}). Nevertheless, our estimate is conservative because: (1) We have no data from the coastal upwelling during the intermonsoon which are probably higher than those from the central Arabian Sea. (2) We have no data from the Somali and the western Indian shelf upwelling. We caution, however, that our estimate is based on data from two seasons of the same year and thus does not take into account the large inter-annual variability of the Arabian Sea.

Summary

We observed a modest, but significant increase in the N_2O saturations measured in surface waters of the central Arabian Sea from May 1995 (99-103 %) to July 1995 (103-106 %). These differences may be related to the transition from the intermonsoon to the SW monsoon. Highest N_2O saturations were observed in the coastal upwelling areas (up to 308 %). Significantly enhanced N_2O saturations were observed in an area of open ocean upwelling. We calculated annual N_2O emissions of 0.8 - 1.5 Tg for the Arabian Sea. This is considerably higher than previous estimates indicating that N_2O fluxes from the Arabian Sea alone may account for 12-52 % of the global N_2O emissions [*Butler et al.*, 1989; *Bange et al.*, 1996a]. Obviously, previous estimates underestimated the role of upwelling regions, such as the eastern tropical Pacific and the Arabian Sea, in budgets of global oceanic N_2O emissions. Future work should focus on repeated N_2O measurements in coastal and open ocean upwelling areas to account for the seasonal and inter-annual variability.

Acknowledgments. We thank G. Schebeske and Th. Kenntner for technical assistance and acknowledge the help of other colleagues, and the officers and crews of the R/V *Meteor*. Thanks are due to the chief scientists on the *Meteor* cruise legs M32/3 and M32/5, F. Pollehne and B. Zeitzschel, respectively. Special thanks are due to H. Thomas who provided the nitrogen during the first leg. The investigations were financially supported by the German *Bundesministerium für Bildung und Forschung* (BMBF) through grant no. 03FO137A and the Max Planck Society.

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(Received June 21, 1996; revised October 1, 1996;
accepted October 4, 1996)