Seasonal and spatial variability in \( \text{N}_2\text{O} \) distribution in the Arabian Sea

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Abstract

Extensive measurements of nitrous oxide (\( \text{N}_2\text{O} \)) were made in the central and eastern Arabian Sea during the northeast monsoon (February–March), intermonsoon (April–May) and southwest monsoon (July–August) seasons. The latitudinal and longitudinal variations, along with seasonal changes with respect to winter convection and coastal upwelling, are clearly discernible. Vertical profiles collected down to 1000 m show that the Arabian Sea water column is supersaturated with \( \text{N}_2\text{O} \) at all depths. However, \( \text{N}_2\text{O} \) consumption at intermediate depths, coincident with the oxygen minimum and associated with sediment–water interfaces, and in the denitrifying zone, coincident with NO\textsubscript{2} secondary maxima, are also apparent. The \( \text{N}_2\text{O} \) concentration varies from \( \sim \)10 nM near the surface to about 80 nM in the secondary peak region (\( \sim \)800 m). Interrelationships with chemical parameters suggest nitrification to be the main process for the production of \( \text{N}_2\text{O} \) in the oceanic water. Plots of apparent oxygen utilization vs production of \( \text{N}_2\text{O} \) indicate a consistent linear relationship for AOU between 0 and 200 \( \mu \text{M} \).

1. Introduction

Nitrous oxide (\( \text{N}_2\text{O} \)) in the atmosphere warrants special attention because of its deleterious effects on the ozone layer (Graedel and Crutzen, 1993) and because it has a large radiative forcing \( \sim \)200 times that of \( \text{CO}_2 \) on a per molecule basis (IPCC, 1995). Atmospheric \( \text{N}_2\text{O} \) has both natural and anthropogenic sources, but their...
relative contributions are unclear. Oceans are believed to contribute up to 20% of the total annual input of $\sim 15$ Tg/yr (IPCC, 1995). The Arabian Sea is recognized as a region of high $\text{N}_2\text{O}$ emission (Law and Owens, 1991; Naqvi and Noronha, 1991; Lal et al., 1996) due to high $\text{N}_2\text{O}$ production rates in the water column and seasonal upwelling of subsurface waters. The $\text{N}_2\text{O}$ is produced in seawater as a byproduct of both nitrification and denitrification processes (Yoshinari, 1976; Elkins et al., 1978; Cohen and Gordon, 1979; Yoshida et al., 1989; Naqvi et al., 1990, 1991; Mantoura et al., 1993). Nitrification, which is believed to be the major contributor to the production of $\text{N}_2\text{O}$ in seawater, has a yield equivalent to only 0.1% of the moles of $\text{O}_2$ consumed during the conversion from $\text{NH}_4^+$ to $\text{NO}_3^-$ (Najjar, 1992). However, in suboxic waters $\text{N}_2\text{O}$ is consumed by the process of denitrification (Cohen and Gordon, 1978; Naqvi et al., 1990; Mantoura et al., 1993). In addition, sediments have been found to play an important role in controlling the $\text{N}_2\text{O}$ abundances in estuarine waters (Law et al., 1993). A similar mechanism could influence the distribution of $\text{N}_2\text{O}$ along the continental margins of the Arabian Sea (Naqvi and Noronha, 1991). In this paper, we discuss the distributions and seasonal variability, particularly in relation to denitrification in the subsurface layers, of $\text{N}_2\text{O}$ in the Arabian Sea based on extensive measurements carried out under the Joint Global Ocean Flux Study (India).

2. Materials and methods

Measurements of $\text{N}_2\text{O}$ were made in three different seasons on board ORV Sagar Kanya during cruises SK 91 (April–May 1994; Intermonsoon), SK 99 (February–March 1995; Northeast monsoon), and SK 104 (July–August 1995; Southwest monsoon) in the Arabian Sea. Station locations and the cruise tracks are shown in Fig. 1. Temperature and salinity were measured with a Sea-Bird CTD system, and seawater samples were collected with a rosette fitted with 12 Niskin bottles of 1.8, 12, or 30 l capacity. About 125 ml of water was drawn to stoppered glass bottles for the measurement of $\text{N}_2\text{O}$ and $\text{CH}_4$ and stored in a refrigerator until analysis. Most of the analyses were completed within 24 h of collection of the samples. Dissolved $\text{N}_2\text{O}$ was estimated with an electron capture gas chromatograph (EC-GC) by adopting the method of multiple phase equilibrium (McAuliffe, 1971). The experimental details are described elsewhere (Lal et al., 1996). Oxygen ($\text{O}_2$) was estimated by Winkler titration during the intermonsoon, and by spectrophotometric measurement of iodine (Pai et al., 1993) during the northeast and southwest monsoons, which improved the precision of analysis quite significantly (at the low level of 4 $\mu$M, it is $\approx 0.1$ $\mu$M). Nitrate ($\text{NO}_3^-$) and nitrite ($\text{NO}_2^-$) were analyzed colorimetrically by a Skalar Autoanalyzer 5100/1 as discussed in de Souza et al. (1996). The precision (1$\sigma$) for $\text{NO}_2^-$ and $\text{NO}_3^-$ is estimated to be about 0.02 and 0.2 $\mu$M, respectively.

Apparent oxygen utilization (AOU), the difference between the saturation and measured concentrations of oxygen, was calculated by estimating saturation values from the equation of Benson and Krause (1984). Nitrate deficits ($\Delta \text{N}$) were estimated from the empirical equations of Naqvi and Sen Gupta (1985), which are specific for the Arabian Sea. Saturation concentrations of $\text{N}_2\text{O}$ ($C_{\text{sat}}$) were calculated from the
semi-empirical formula of Weiss and Price (1980). Average N$_2$O abundances in the marine air were calculated from the measurements carried out at regular intervals during all three cruises. Absolute N$_2$O concentrations were obtained against a working standard (ambient air collected inside the PRL premises), calibrated volumetrically by a static dilution method (to be referred to as PRL-GC-STD 94). Analytical uncertainty (1$\sigma$) for N$_2$O measurements at any depth was about $\pm 3\%$, which is estimated from the analyses of duplicate water samples stored for different periods of time in a refrigerator. The precision of our N$_2$O measurements was always better than $1\%$ (at the 1$\sigma$ level). The difference ($\Delta$N$_2$O) between the saturation concentration of N$_2$O and its measured concentration ($C_{obs}$) in the seawater is used to infer its production or consumption in the oceanic water. Positive $\Delta$N$_2$O indicates production and negative $\Delta$N$_2$O its consumption in the water column.

3. Results and discussion

3.1. North–South variation

Fig. 2 shows the N$_2$O distribution in the Arabian Sea, along 64°E, for the three seasons. No measurements could be made north of 18°N during the southwest
Fig. 2. Distributions along longitude 64°E of nitrous oxide (nM) measured during the intermonsoon (a), northeast monsoon (b) and southwest monsoon (c) cruises. The distributions during the intermonsoon and northeast monsoon are reproduced from La et al. (1996). A maximum depth of 1000 m is shown to maintain uniformity and because of the scarcity of deep water measurements during the southwest monsoon cruise.

monsoon. The N₂O depth distribution has two maxima: one centered at ~300 m (varies from 200 to 400 m) and the other in the range 500–1000 m. The peak concentration in the deeper layer is more intense, with a maximum of ≥ 75 nM. This secondary maximum shoals from 800 m at the northern stations to 500 m at the southern stations. The minimum in N₂O concentration between the two peaks is
attributed to its greater consumption relative to production by denitrification, and it occurs at depths ranging from 300 to 700 m. The lowest concentration (≈ 10 nM) observed in Fig. 2 is greater than that reported by Naqvi and Noronha (1991).

Nevertheless, seasonal trends in N$_2$O distribution are conspicuous in Fig. 2. N$_2$O concentrations of < 30 nM in the oxygen minimum layer were confined to the region ≥ 20°N during the intermonsoon, whereas such low levels extended up to 14°N during the northeast monsoon. This is in fairly good agreement with the distribution of oxygen in different seasons (Fig. 3). An intense oxygen deficit (dissolved oxygen abundances lower than 5 µM) is observed in the depth range 200–1000 m in the latitude range 14–22°N during the northeast monsoon (Fig. 3b), whereas in the same depth range similar O$_2$ levels are observed only in a limited area (18–22°N) during the intermonsoon (Fig. 3a). In general, O$_2$ concentrations are much higher (15 µM or more) in the study region during the southwest monsoon (Fig. 3c).

Similarly, nitrate deficits (ΔN) were more intense in the northeast monsoon, although deficiencies were also noted in other seasons. A maximum ΔN of 10 µM is observed in the northern intermediate waters during the northeast monsoon (de Sousa et al., 1996), and associated with this a relatively thick layer of low levels of N$_2$O was observed at around 400 m depth (Fig. 2b). Interestingly, oxygen levels (see Fig. 3) are higher in the intermediate waters (~ 300 m) during the southwest monsoon. However, a nitrate deficiency persists at these depths and is associated with low levels of N$_2$O. N$_2$O is paradoxically consumed at 16°N at around 300 m depth, where O$_2$ levels are quite high (≈ 45 µM); however, this minimum is coincident with a secondary NO$_2^-$ peak (concentration ~ 2.5 µM). No significant spatial variation in N$_2$O distributions in the sub-surface layers (depth range ~ 70–170 m) is apparent during the inter- and southwest monsoons (Fig. 2a and c), and the gradient with latitude in N$_2$O distribution during the northeast monsoon (Fig. 2b) is associated with enhanced mixing in the northern Arabian Sea due to winter convection (Prasannakumar and Prasad, 1996), and its lateral transport to the southern part along the 24 sigma-T (characteristic of the Arabian Sea High Salinity Water mass, ASHSW) surface as the N$_2$O production is inhibited in the euphotic layer (Horrigan et al., 1981) and vertical mixing is reduced due to the beginning of thermal stratification towards the end of March. The formation of ASHSW at the surface in the north during early winter (November–December) and its movement towards the south during late winter is discussed by Prasannakumar and Prasad (1998) using hydrographic parameters.

Variations in N$_2$O distributions in the surface layer are caused mainly by the sea surface conditions, e.g. higher N$_2$O abundances to the north of 14°N are due to upwelling associated with a divergent wind regime governed by the Findlater Jet and deepening of the 10 nM contour (Fig. 2c) to the south of 14°N associated with sinking; for instance, the mixed layer was found to be as deep as 100 m (Murlidharan and Prasannakumar, 1996).

3.2. East–West variation

The distributions of N$_2$O at around 11°N (Fig. 4) show no significant longitudinal or seasonal variations except during the southeast monsoon, when a strong upwelling
was noticed to the east of 72°E. The N₂O distribution correlates fairly well with that of temperature, dissolved oxygen, and nitrate (de Sousa et al., 1996; Murliidharan and Prasannakumar, 1996), revealing the influence of upwelling on the distribution of N₂O in the surface layers. Fig. 4 suggests that subsurface waters with N₂O concentrations of ~14–16 nM are brought to the surface, where the excess N₂O can easily escape. Thus, during the southwest monsoon, enhanced emanation of N₂O could occur along the southwest coast of India due to the occurrence of intense upwelling.
Fig. 4. Observed distributions of N$_2$O (nM) during three JGOFS cruises ((a) intermonsoon, (b) northeast monsoon and (c) southwest monsoon) along nearly constant latitude of 11°N (see text for details).

The distribution of N$_2$O above about 150 m along 21°N shows a gradient from west to east during the northeast monsoon, while a localized depression at around 66.5°E is observed during the intermonsoon (Fig. 5). The distribution of dissolved O$_2$ (not shown here) also reveals a similar feature suggesting a relevance of the in situ biogeochemistry to the N$_2$O distribution. In the intermonsoon, the gradient below about 150 m seems to have been driven by variations in the magnitude of denitrification. During the northeast monsoon, the low N$_2$O abundance at ~67.5°E and ~250 m and the high N$_2$O zone at ~71.5°E and ~200 m appear to be due,
respectively, to consumption and production (or no consumption) at the sediment–water interface. \( \text{N}_2\text{O} \) would be consumed during bacterial respiration in sediments under extremely reducing conditions (e.g. at 67.5°E) where dissolved \( \text{O}_2 \) was below 5 \( \mu \text{M} \) (at this particular location \( \text{O}_2 \) was undetectable). Relatively higher availability of \( \text{O}_2 \) (~30 \( \mu \text{M} \)) at 71.5°N probably results in the sustenance of higher \( \text{N}_2\text{O} \) concentration. Higher near-surface \( \text{N}_2\text{O} \) concentrations (~10 nM) along this transect during the northeast monsoon than during the intermonsoon are caused by the winter convection process, effective in particular in the northern part of the Arabian Sea. Vertical sections of simultaneous measurements of physical and chemical parameters indicated deep mixing governed by the winter-time overturning in the northern Arabian Sea (see for example Prasannakumar and Prasad, 1996; de Sousa et al., 1996).

3.3. Inter-relationship and control of \( \text{N}_2\text{O} \)

The scatter plots of \( \Delta \text{N} \) (nitrate deficit) and \( \text{N}_2\text{O} \) (Fig. 6) do not show any well-defined inter-relationship, although a weak positive relationship is seen in the intermonsoon and southwest monsoon periods. We have divided the data into two
Fig. 6. Intercorrelations of nitrate deficit (μM) and N₂O concentration (nM) for the intermonsoon (a), northeast monsoon (b), and southwest monsoon (c) periods. Results are segregated into two spatial regimes: filled circles for latitudes > 15°N, and plus signs for latitudes < 15°N.

sets by taking 15°N as the boundary. To the south less reducing, denitrifying conditions occur relative to the north. However, the separation of the data did not improve the ΔN vs N₂O relationship. The high concentrations of N₂O in these figures occurred at the boundaries of the denitrifying zone. The areas of low N₂O and high ΔN were found in the core of the denitrifying layer at the northern latitudes, particularly during the northeast monsoon, as shown by the encircled area (Fig. 6b).

Vertical profiles of O₂, NO₃⁻, NO₂⁻ and N₂O at four selected stations with different physico-chemical conditions are shown in Fig. 7. The stations shown in Fig. 7 represent regions of (a) no denitrification, (b) moderate denitrification, (c) intense denitrification, and (d) nearshore. Profiles are shown down to 600 m depth or to near
Fig. 7. Vertical profiles of $N_2O$ (nM), oxygen ($\mu$M), $NO_2^-$ ($\mu$M) and $NO_3^-$ ($\mu$M) measured during SK 99 at stations located around 11°N, 64°E (a); 15°N, 64°E (b); 21°N, 64°E (c); 21°N, 67°E (d).

bottom in the case of the station at 21.3°N, 67.4°E. The shallower peak of $N_2O$ is usually observed to coincide with the lower boundary of the oxycline, particularly intense in the north, due to its production as an intermediate species during nitrification (Cohen and Gordon, 1979; Law and Owens, 1990; Mantoura et al., 1993). The $NO_3^-$ concentration also shows a small peak at these depths, which is also more prominent in the northern Arabian Sea. The $N_2O$ minimum at around 300 m depth is intensified at 15°N compared to that at 11°N, in proportion to the oxygen minimum,
and a secondary NO$_2^-$ peak is present. The extent of reduction in N$_2$O is inversely related to the magnitude of dissolved O$_2$. This indicates that N$_2$O itself is consumed in suboxic waters by anaerobic bacteria. Mantoura et al. (1993) suggested that this depletion is forced by coupled nitrification and denitrification processes in the presence of enhanced supply of organic matter. Such depletions of N$_2$O have been observed in other oceanic regions as well and are generally attributed to denitrification (Cohen and Gordon, 1978; Yoshida et al., 1989). However, the limiting dissolved oxygen abundances for these two processes to occur are yet to be resolved. The threshold oxygen abundances (or critical oxygen concentrations) are suggested to be about 6.0 and 3.9 $\mu$M for the onset of denitrification by estuarine and open ocean bacteria (Devol, 1978). However, total bacterial abundances (Ramaiah et al., 1996) do not seem to have any direct correlation with the production or consumption of N$_2$O. A study of bacterial community structure would be required to find any relationship with production and consumption of N$_2$O.

In the oxygen deficit and NO$_3^-$ rich environment, the nitrate reducing and denitrifying bacteria should proliferate (Devol, 1978). Therefore, it is most likely that in the oxygen minimum zone (OMZ) of the Arabian Sea, denitrification (dissimilatory nitrate reduction) would dominate:

$$\text{NO}_3^- \xrightarrow{K_1} \text{NO}_2^- \xrightarrow{K_2} \text{N}_2\text{O}, \text{NO} \xrightarrow{K_3} \text{N}_2. \quad (1)$$

The occurrence of NO$_2^-$ with low N$_2$O could be explained by the faster reaction rates for $K_1$ and $K_3$ and relatively slower rates for $K_2$. This means NO$_3^-$ and N$_2$O would decrease, whereas NO$_2^-$ could increase. These reaction rates will depend on the nature and abundance of bacterial populations in the samples under study. On the other hand, during nitrification a similar situation can also arise:

$$\text{NH}_4^+ \xrightarrow{K_4} (Y) \xrightarrow{K_5} \text{N}_2\text{O}, \text{NO} \xrightarrow{K_6} \text{N}_2, \quad (2)$$

where (Y) is an intermediate compound. In this process, due to overall poising of the redox potential, oxidation of NH$_4^+$ is inhibited whereas N$_2$O itself is consumed to produce N$_2$ by the anaerobic bacterial. However, from these observations it can only be concluded that the simultaneous N$_2$O and high NO$_2^-$ are a result of competitive intermediate processes involved during both denitrification and nitrification. In addition, the primary N$_2$O maximum in the Arabian Sea is always found to be located well below the primary NO$_2^-$ maximum – mostly at the base of the euphotic zone, which, however, does not support the hypothesis that N$_2$O production can also be associated with microflora, e.g. phytoplankton communities (see for example Devol, 1978). It is, therefore, appropriate to suggest that N$_2$O consumption and production in oceanic water are controlled mainly by bacterially mediated processes.

The secondary maximum in N$_2$O at the lower boundary of the oxygen minimum zone is well documented and attributed mostly to the production of N$_2$O during nitrification through Eq. (2) (Yoshinary, 1976; Cohen and Gordon, 1979; Naqvi and Sen Gupta, 1985; Yoshida et al., 1987; Law and Owens, 1990). In the depth region below about 500 m, concentrations of dissolved oxygen do not support denitrification.
(oxygen levels are well above the critical value), but the causative factors are not known.

The relationship between AOU and $\Delta N_2O$ shows a positive correlation, particularly in the range $0 \leq AOU \leq 200 \mu M$ during all seasons (Fig. 8), and the same has been reported by a number of workers in different oceanic regions (Elkins et al., 1978; Cohen et al., 1979; Hahn, 1981). However, for $AOU > 0$ and $AOU < 200$, such linear relations are not apparent (see Table 1). Statistical analysis of these data sets indicates

Fig. 8. Relations between apparent oxygen utilization (AOU) and $\Delta N_2O$ production in the Arabian Sea during various seasons: (a) for SK 91 (intermonsoon), (b) for SK 99 (northeast monsoon), and (c) for SK 104 (monsoon).
that a single linear relationship does not explain N\textsubscript{2}O production completely, since two processes (viz., nitrification and denitrification) control N\textsubscript{2}O abundances, especially in the oxygen minimum zone. The break in the relationship at the AOU value of nearly 200 \textmu M indicates that nitrification is the only process responsible for \(0 < \text{AOU} < 200 \text{ \mu M}\), but both nitrification and denitrification influence the N\textsubscript{2}O increase at AOU > 200. However, nitrification is largely responsible for N\textsubscript{2}O production, because its production can increase under suboxic conditions, although it is an aerobic process. But in the oxygen minimum zone, an anaerobic process, i.e., denitrification, is largely responsible and dominates the nitrification (Yoshida et al., 1989). In fact, it was estimated (Yoshida et al., 1989) that nitrification accounts for only one-tenth to one-fifth of the N\textsubscript{2}O produced in the oxygen minimum zone (OMZ). It is also known that the production ratio of N\textsubscript{2}O and NO\textsubscript{3}~ changes greatly with dissolved oxygen level (Devol, 1978). The nitrate concentration increases with decreasing dissolved oxygen, as a result of organic matter decomposition, and a low dissolved oxygen concentration favours the occurrence of anaerobic microsites in which nitrate can be reduced to produce N\textsubscript{2}O. Consequently, excess N\textsubscript{2}O concentration would be proportional to the apparent oxygen utilization.

In the well-oxygenated subsurface water (AOU \(\leq 0 \text{ \mu M}\)), N\textsubscript{2}O is not expected to be produced significantly, as the N\textsubscript{2}O production processes in this region are inhibited by the presence of sunlight (nitrification) and availability of oxygen (denitrification) (Horrigan et al., 1981). However, the small positive gradients, although not statistically very significant, arise from the transport of deep N\textsubscript{2}O rich water to the sub-surface layer. Due to summertime stratification, mixing is reduced in the surface layers. As a result a near-zero gradient (more appropriately near equilibrium N\textsubscript{2}O concentration) was observed during the intermonsoon period (April–May). However, during the southwest monsoon period (July–August), the Arabian Sea experiences strong upwelling along the Indian west coast (Fig. 4) and also larger turbulent mixing due to intense wind fields (Murlidharan and Prasannakumar, 1996), which transport N\textsubscript{2}O from its concentration maximum. The northeast monsoon (January–February) exhibits an average gradient in N\textsubscript{2}O concentration with increasing AOU.
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