Distribution of nitrous oxide and methane in the Arabian Sea

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Measurements of the two important biogenic gases N_2O and CH_4 have been made both in the water column and in air of the Arabian sea during April–May 1994 and February–March 1995, as part of the JGOFS (India) programme. The average abundances of N_2O and CH_4 in the air are 313 ± 7 ppbv and 1.69 ± 0.05 ppmv respectively. During both the periods, the vertical profiles of N_2O in the water column show a double peak structure with the dominant peak in the 500–1000 m depth region with concentrations of 70–80 nmol. The entire water column is supersaturated with respect to N_2O and in the major peak region it is supersaturated by as much as 600–800%, suggesting this region of the Arabian sea to be an important reservoir of N_2O. During February–March 1995, sea–air flux of N_2O is calculated to be about 0.26 pg cm^{-2} s^{-1}, while the flux calculated for April–May 1994 is not significantly different from zero. Methane concentrations were measured only down to 400 m depth. Its distribution shows a peak concentration of 6–8 nmol in the 100–200 m depth region. Supersaturation (up to 200–400% at the peak) is found for CH_4 in most of the profiles. Average sea–air flux of methane during April–May 1994 and February–March 1995 is 0.0001 and 0.033 pg cm^{-2} s^{-1}, respectively.

Nitrous oxide (N_2O) and methane (CH_4) are important minor constituents of the earth's atmosphere. Recently, N_2O is being studied with growing interest due to its greenhouse warming potential[1] and as a source of NO radicals in the stratosphere which participates in the catalytic ozone depleting reactions[2]. N_2O emanates from the earth's biosphere due to various natural and anthropogenic activities, the latter include biomass burning, fertilizer use and land use. It is estimated that the oceans also contribute significantly (20–30%) to the global budget[1] of N_2O. Recent studies in the Arabian Sea show a significant ocean to atmosphere flux of N_2O in spite of its relatively small area (0.43%) of the world oceans[3,4].

Methane plays an important role in controlling the abundance of atmospheric water vapour and hydroxyl radical[5], and it also takes part in tropospheric ozone chemistry and greenhouse warming. Major sources of methane to the atmosphere are wetlands, paddy fields and enteric fermentation[1]. In general, oceans are a relatively minor source of methane. Sub-surface ocean water has been found to be supersaturated at different locations[6–8]. Under the Joint Global Ocean Flux Study (India) programme, these trace gases have been measured both in air and in the water column during April–May 1994 (cruise No. SK-91) and February–March 1995 (cruise No. SK-99) in the north-east Arabian Sea (11°N–22.5°N, 64°E–74°E). In this article we describe the results and provide estimates of the sea–air fluxes of N_2O and CH_4.

Experimental procedure

Measurements of N_2O and CH_4 were made using two gas chromatographs (GCs) installed on board the ORV *Sagar Kanya*. N_2O was measured using a Varian VISTA series gas chromatograph equipped with an electron capture detector (GC-ECD). The ECD is widely used to measure nitrous oxide and various kinds of halocarbons[9–11] due to its high sensitivity and sufficient linear response[12]. A 5 m × 0.32 cm stainless steel column packed with Porapak-Q (80/100 mesh), maintained at 40°C, was used for N_2O analysis. A Shimadzu GC equipped with a flame ionization detector was used for measuring CH_4. A stainless steel column of dimension 5 m × 0.32 cm, packed with molecular sieve-13X maintained at 60°C was used. Atmospheric pressure inside the laboratory was recorded using an MKS baratron sensor for pressure correction.

Air samples were collected in 50 ml B–D plastic syringes from the bow of the ship while cruising (i.e. between stations). Samples were injected into the GC column after passing through a moisture trap and using a 4 ml loop connected to a 6 port valve. Both these were flushed with the same sample before final injection. Each sample was run 2–3 times to obtain representative concentrations. Sea-water samples were collected from various depths using 1.7 l Niskin bottles during SK-91 cruise and 30 l Go-Flo bottles fitted to a CTD Rosette during the SK-99 cruise. During April–May 1994, water samples were collected down to a depth of 3000 m at several stations, but during February–March 1995 the depth of sampling was restricted to a maximum of 1000 m. Samples were drawn from these bottles into 50 ml glass bottles and stored in a refrigerator until analysis. Most of the sample analyses were completed within 24 hours of collection using standard techniques. 25 ml of water sample and 25 ml pure He were equili-

brated in a B–D syringe for about 5 minutes at room temperature. 4 ml of this equilibrated He was injected on to the GC column after passing through a moisture trap filled with $Mg(ClO_4)_2$. A similar procedure was followed for CH_4 analyses except that in this case 30 ml of sea water was equilibrated with 20 ml of pure He. Duplicate samples were analysed periodically to check for reproducibility of results and to evaluate the precision of measurements. The replicate measurements were found to be within 10%. A 50 l cylinder filled with air (from PRL, Ahmedabad) was used as the laboratory standard which was analysed frequently to check for stability of the instruments. This standard was calibrated for N_2O and CH_4 using standard mixtures of known concentrations. The concentrations of N_2O and CH_4 in the standard air were estimated to be 313 ppbv and 1.94 ppmv respectively.

Concentrations and fluxes

Concentrations of N_2O and CH_4 in air are calculated by comparing the GC response with the response obtained from the laboratory standard. The mole concentrations of dissolved gases in sea water are calculated based on the principle of multiple phase equilibrium as given by McAullife[13]. For example, the concentration of N_2O in sea water in nmol can be expressed as

$$N_2O\ (\text{nmol}) = 0.0409 \times \frac{1}{H_x} \times P_L \times \frac{298}{T_L} \times N_2O\ (\text{ppbv}), \quad (1)$$

where H_x is Henry's law constant, which is a function of temperature and salinity, P_L and T_L are the laboratory pressure (atm) and temperature (K) respectively, N_2O (ppbv) is the mixing ratio of nitrous oxide in the zeroth order equilibrated air with sea water, and the constant (0.0409) is the conversion factor from mixing ratio (ppbv) to concentration (nmol) at STP. This concentration is defined as observed concentration (C_{obs}). A similar equation is used for calculating the methane concentration.

Saturation concentrations (C_{sat}) of the respective gases in water were calculated by multiplying their partial pressure in the ambient marine air with their solubility in sea water at the appropriate temperature and salinity. The solubility of N_2O and CH_4 in sea water was calculated by using the relations of Weiss and Price[14] and Atkinson and Richards[15], respectively. The flux (F) in nmol cm^{-2} s^{-1} between air and water was calculated by using the wind speed dependent transfer velocities[16] and can be expressed as

$$F = k \times \Delta C, \quad (2)$$

where ΔC is the difference in concentrations ($= C_{obs} - C_{sat}$) and k is the gas transfer velocity in cm h^{-1}. The value of k depends on wind velocity and is evaluated using one of the following equations

$$k = 0.17U_{10}(660/S_c)^{2/3} \quad U_{10} \le 3.6$$

$$k = (2.85U_{10} - 9.65)(660/S_c)^{1/2} \quad 3.6 < U_{10} \le 13 \quad (3)$$

$$k = (5.9U_{10} - 49.3)(660/S_c)^{1/2} \quad U_{10} > 13\,.$$

U_{10} is the wind speed (m s^{-1}) at 10 m height from the sea surface, S_c is the Schmidt number of the respective solute gas, calculated using the expressions given by Wanninkhof[17]. Note that the constant 660 which is the Schmidt number of CO_2 at 20°C in sea water has been used instead of 600, which is for the freshwater, as proposed in a more recent analysis[17]. A negative flux value suggests ocean as a sink for the solute gas whereas a positive value implies ocean to be a source to the atmosphere.

Results

Latitudinal distributions in the concentrations of N_2O measured in air during SK-91 and SK-99 along 64°E are shown in Figure 1. The data show a significant scatter, from about 300 to 335 ppbv without any systematic trend. The average concentration was found to be 313 ± 7 (1σ ppbv). The spread ($\pm 1\sigma$) is similar to analytical precision (2%), however, the error in absolute concentrations could be larger (±5%) due to calibration uncertainties. Figure 2 shows typical distributions of N_2O in sea water down to 3000 m depth during the SK-91 cruise. The concentration of N_2O increases very sharply from about 6 nmol in the surface water to about 50 nmol at around 150–200 m depth. At depths between 200 and 300 m, there is a decrease in the concentration particularly in the northern latitudes. N_2O concentration increases again to values as high as 60–80 nmol at around 700 m depth; below which it decreases with depth to a value of 20 nmol at around 3000 m. Figure 2 also shows the expected concentrations of N_2O for 100% saturation (dotted line). It is evident from Figure 2 that N_2O is at or above saturation throughout the water column. At the major peak (500–1000 m), supersaturation is in the range of 600% to 800%. Even at 3000 m depth the value ranges between 130% and 160%. Similar general features in the vertical distribution of N_2O have also been observed in the profiles measured during subsequent cruise (SK-99).

Figure 3 shows a contour plot of N_2O concentrations for the latitude region of 11 to 22°N measured during SK-91. The distribution shows three high N_2O concentration regions centered at 13°N, 17°N and 22°N with

values as high as 77 nmol, with the maximum values occurring at deeper depths in higher latitudes; at 13°N it is located around 500 m depth while at 22°N it is at ~ 900 m depth. Along 64°E longitude the shallower peak is more intense towards northern latitudes. Although somewhat similar features have been reported during measurements made in December 1988 in the Arabian sea along 67°E longitudinal transect[4], such detailed structures have not been observed. A comparison of N_2O concentrations in sea water obtained during the two

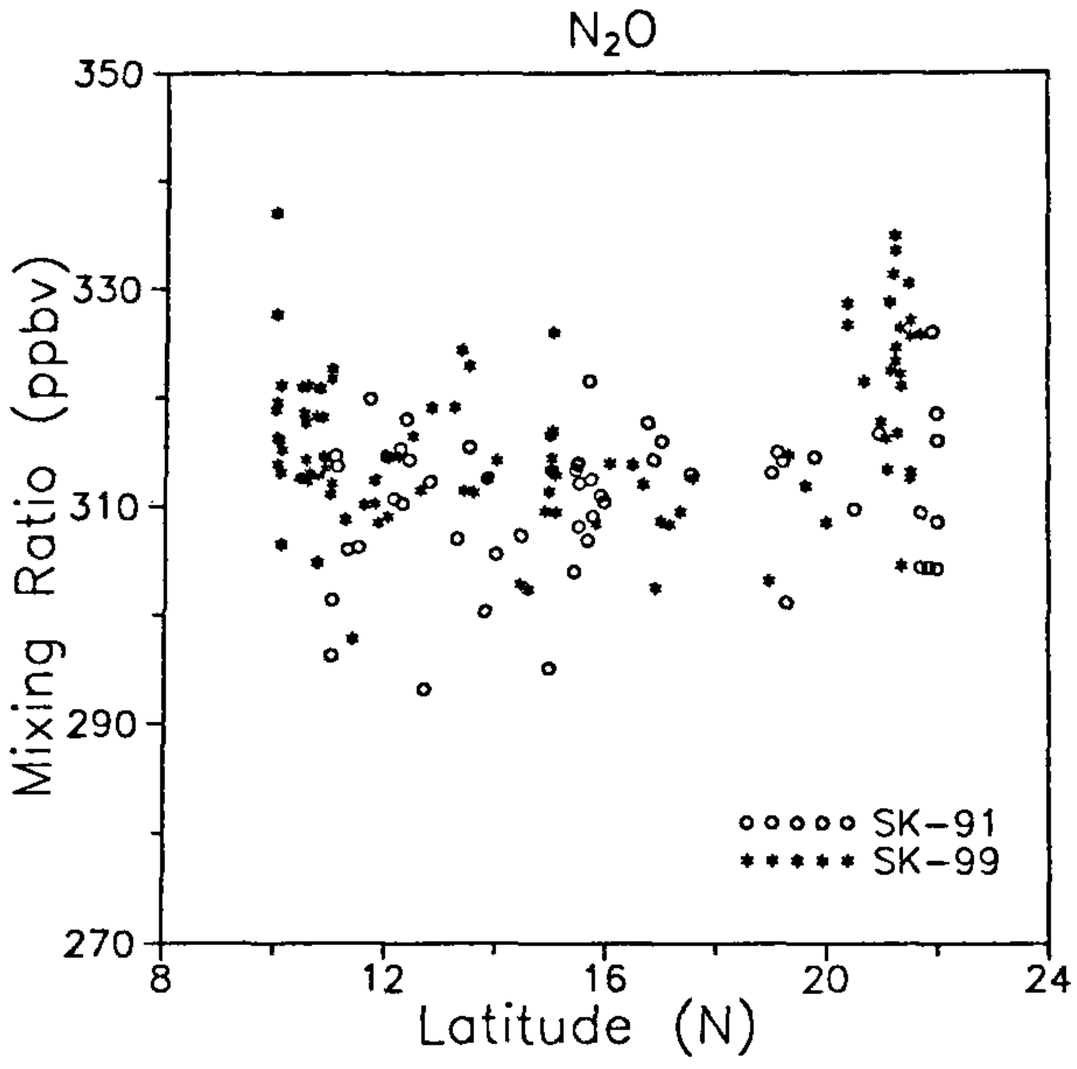

Figure 1. Distribution of nitrous oxide in the Arabian Sea air measured along the cruise track during April–May 1994 (SK-91) and February–March 1995 (SK-99).

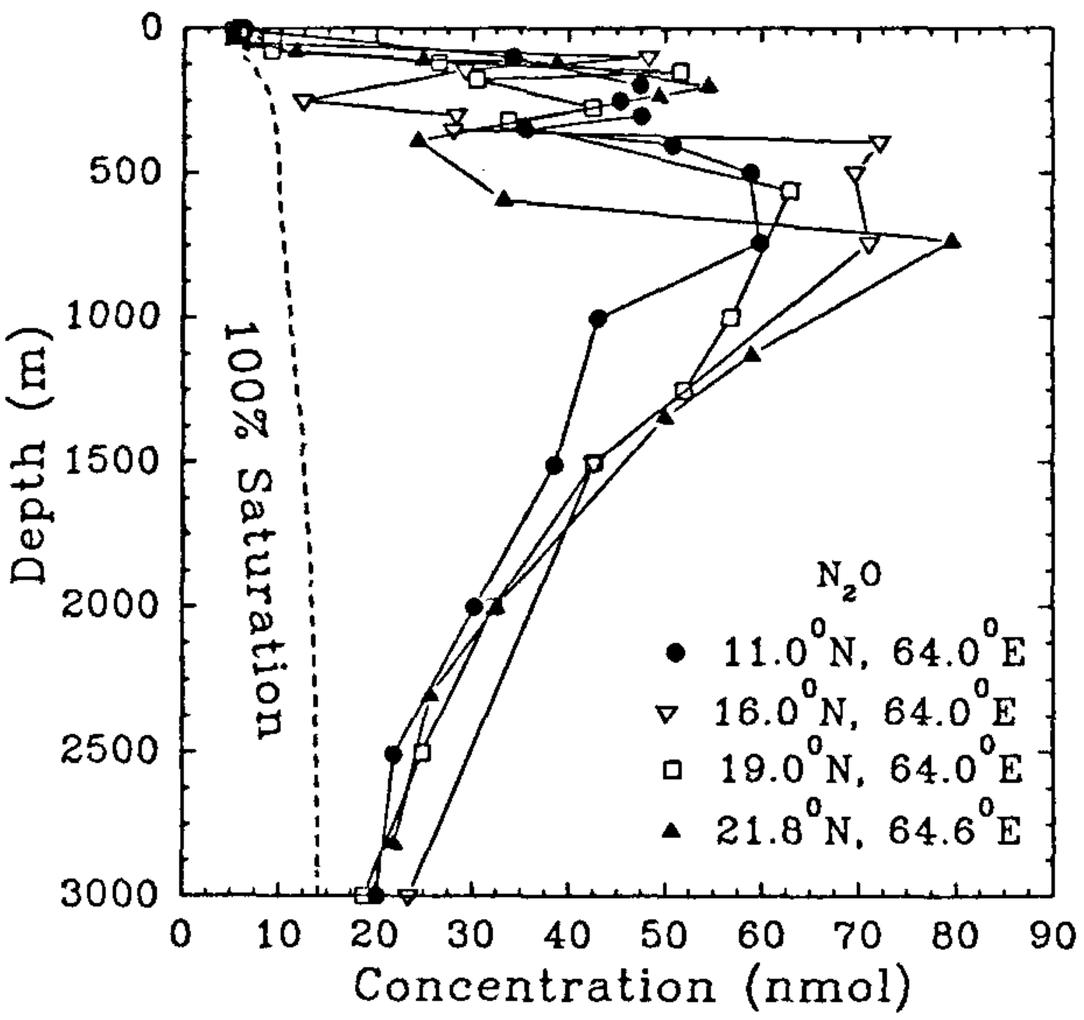

Figure 2. Examples of the vertical distribution of N_2O in the water column along 64°E longitude.

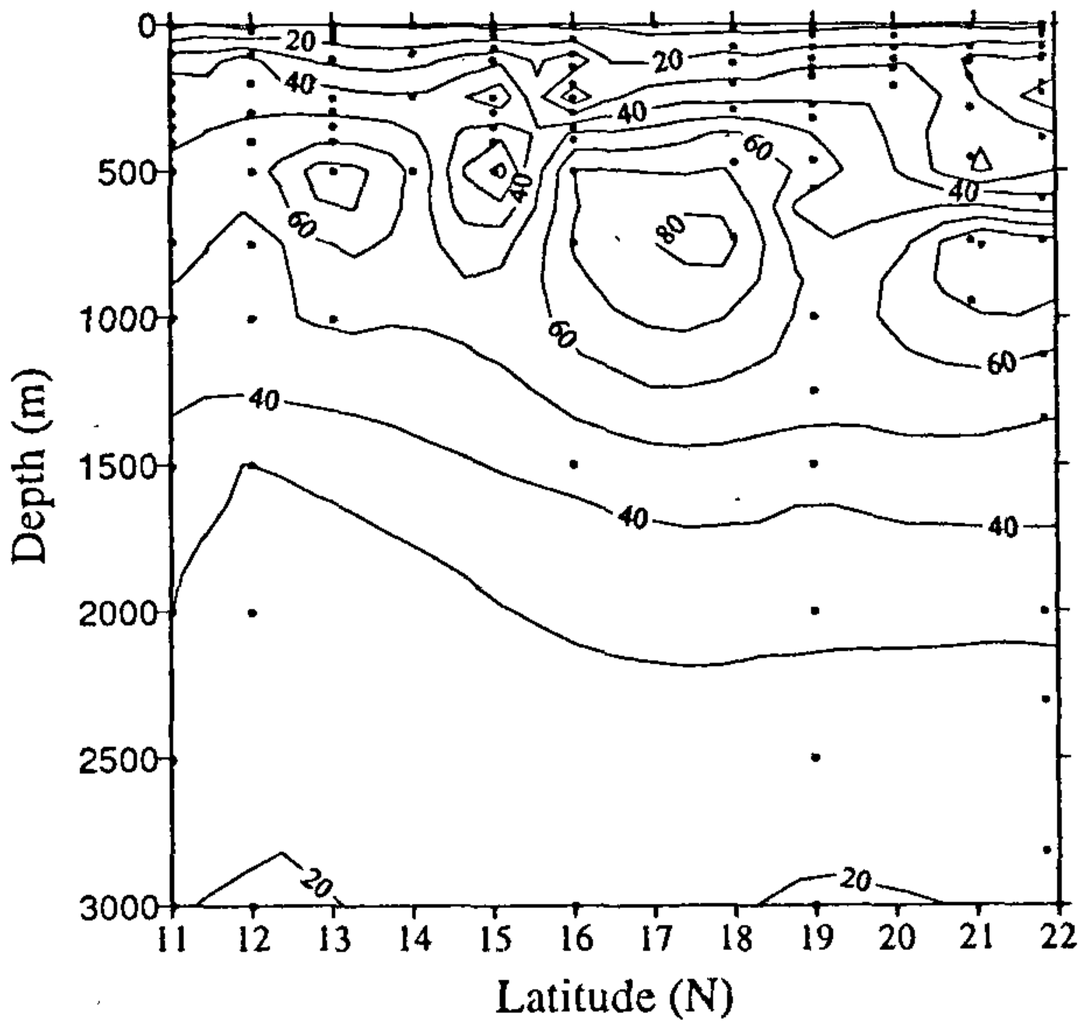

Figure 3. Distribution of nitrous oxide (nmol) showing the latitudinal variability down to 3000 m depth observed during SK-91 cruise.

cruises is shown in Figures 4 *a* and 4 *b*. A broad maximum around 17–18°N latitude and 800 m depth was seen during both the cruises. However, the finer scale features in the shallow depths (0–600 m) are different. The two low N_2O regions which were located around 500 m depth during SK-91 were observed at a shallower depth (300–400 m) during SK-99. During both these cruises higher concentrations of N_2O were observed, centered around 17°N, between these two minima.

Figure 5 shows methane concentrations in air during SK-91 and SK-99 cruises. The results show marginally higher CH_4 concentrations (1.70) during SK-91 than those (1.66) during SK-99, with an average value of 1.69 ± 0.05 ppmv for the combined data of both the cruises. The spread is within the range of analytical errors. Measurements of methane in the water column were made for the north of 16°N of the cruise track during SK-91 and along the complete track during SK-99. Typical concentration profiles observed during SK-99 are shown in Figure 6. The concentration of methane in the surface water was observed to be about 3 nmol, increasing to value of 4–9 nmol at around 100–200 m. Below this depth, its concentration decreased gradually to 2–4 nmol. Methane is supersaturated at almost all depths from the surface down to 400 m depth. Supersaturation at the maximum concentration varied from 200 to 400%.

There is a large variability in methane distribution from open ocean to the coast. In the shallow coastal waters, the maximum CH_4 concentration was higher. The vertical profiles of CH_4 as depicted in Figure 6 for 16°N and 18°N represent features of the open ocean, the one at 22°N shows characteristics of a coastal region. Prior to these studies, the only other reported measurements of CH_4 in the Arabian Sea were due to Owens *et al.*[7]. These results also showed a supersaturation of CH_4, however, the nature of the CH_4 profiles, particularly the depth of CH_4 maximum differs in these two studies. Figures 7 *a* and 7 *b* show the spatial and depth variations of methane concentration along the 64°E meridian. The major peak in methane was observed at 19°N around 150 m depth during SK-91 whereas the peak was found to be at shallower depth (~ 125 m) during the later cruise (SK-99). It can also be seen that the depth of

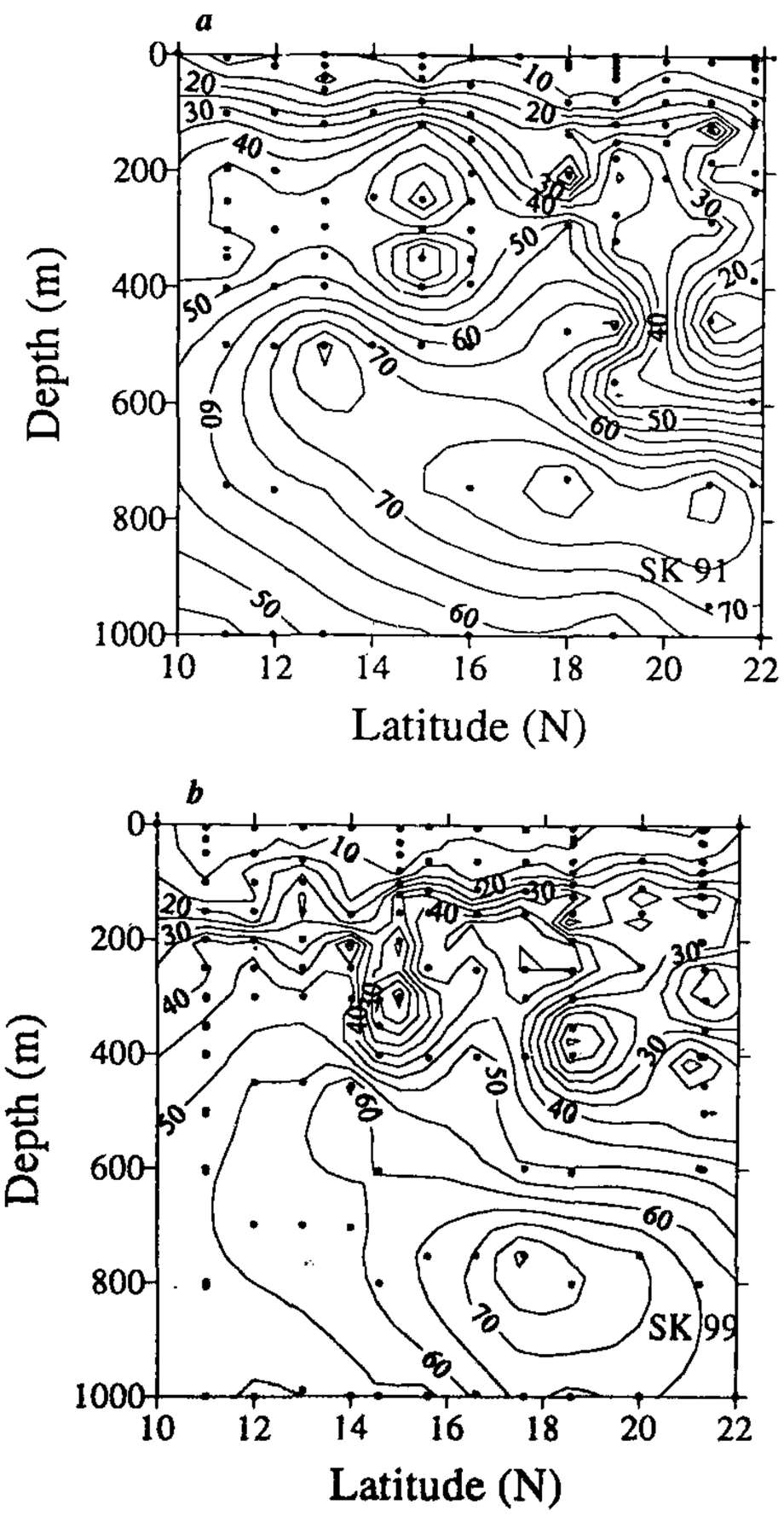

Figure 4. Distribution of nitrous oxide (nmol) showing latitudinal distribution down to 1000 m depth for SK-91 (*a*) and for SK-99 (*b*). All contours are shown at an interval of 5 nmol.

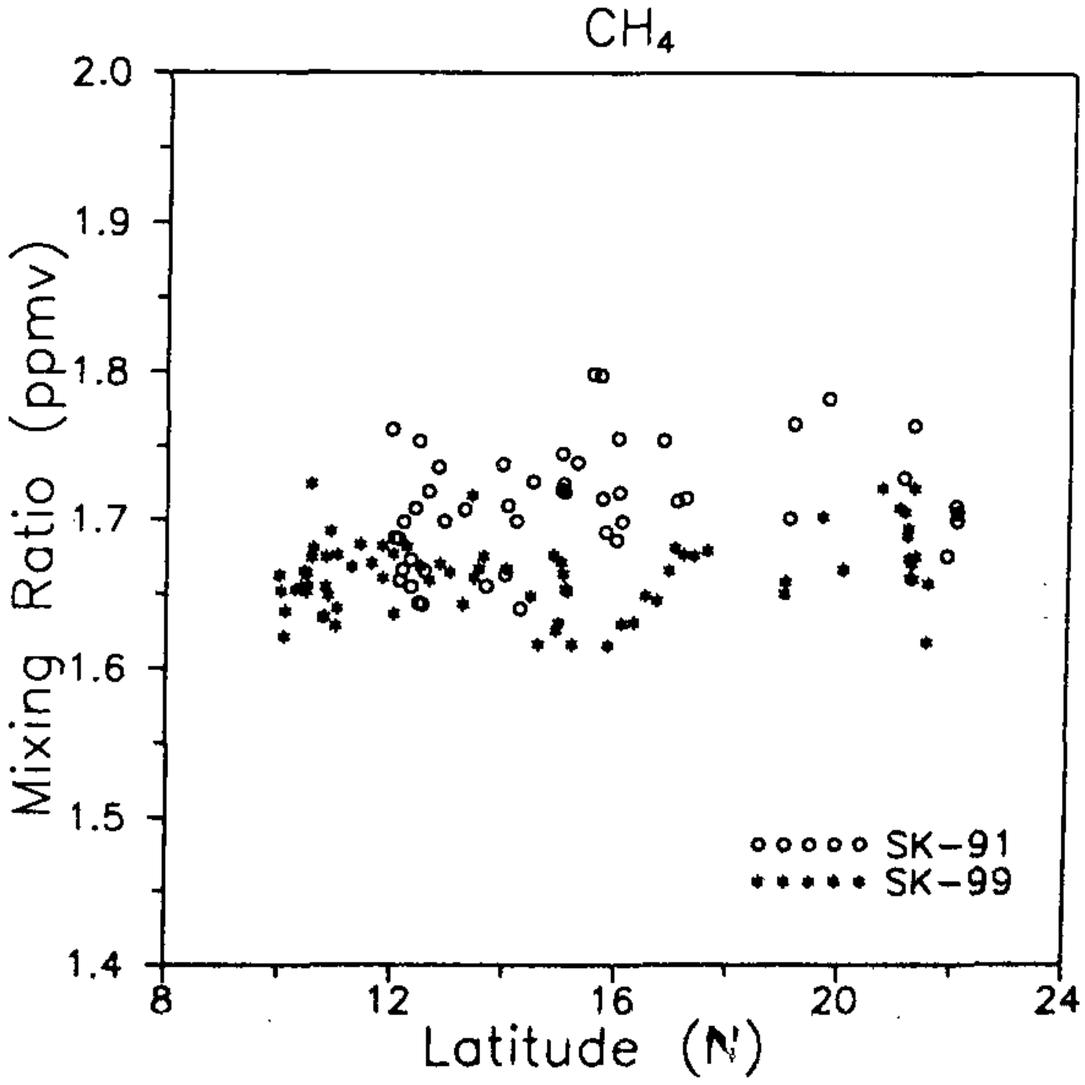

Figure 5. Mixing ratios of methane as observed in marine air during SK-91 and SK-99 cruises.

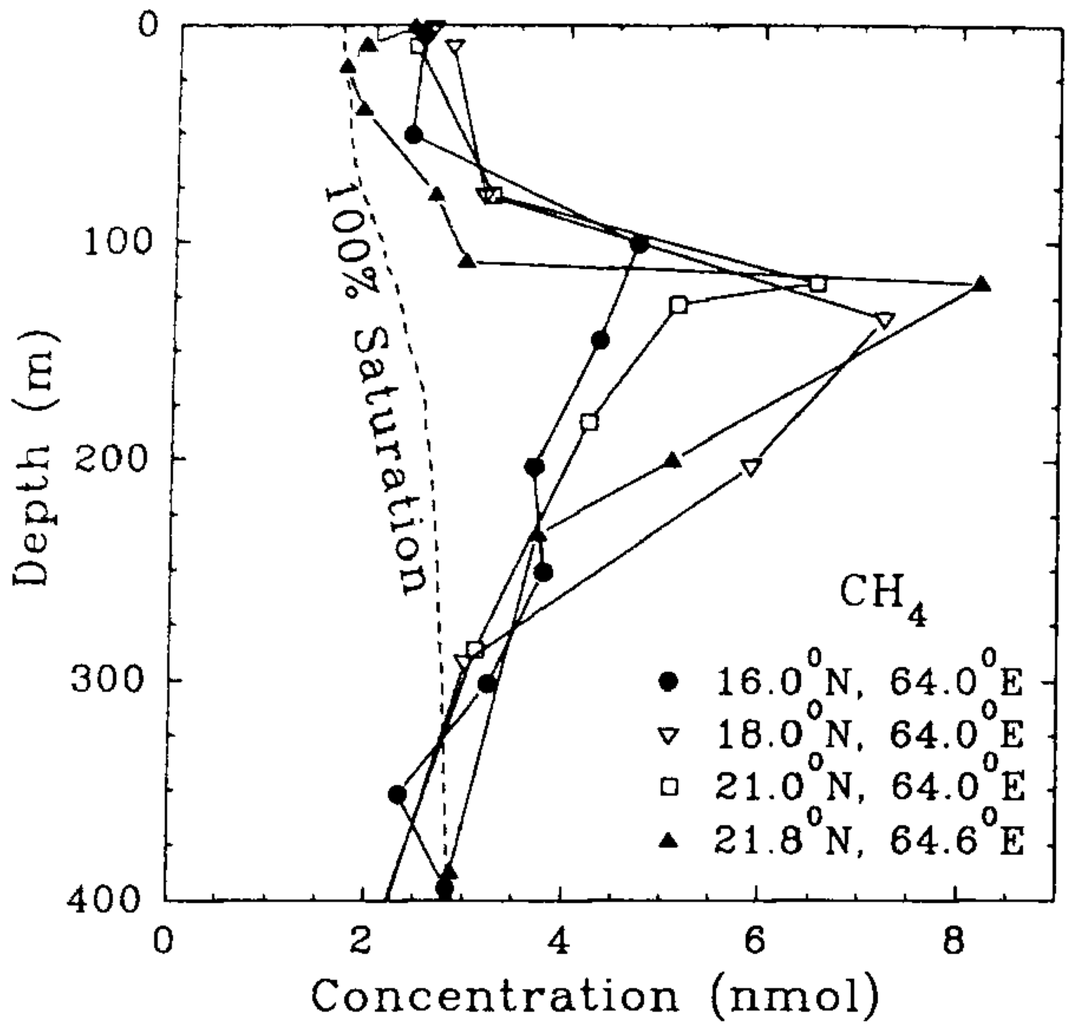

Figure 6. Examples of the vertical distribution of CH_4 (nmol) in the water column during SK-91 cruise.

methane maximum decreases with increase in latitude (Figure 7 *b*). Thus at 11°N the methane maximum occurs at a depth of about 200 m, while at 19°N it is observed at around 125 m depth (Figure 7 *b*).

The sea–air fluxes of CH_4 and N_2O have been computed using equations (2) and (3) described earlier. Fluxes from or into sea water depend upon the degree of saturation in surface water and the wind speed. There is no significant supersaturation of N_2O in the surface water during SK-91 (April–May 1994). The N_2O content in surface water during this period is within ± 10% of the concentration expected from the partial pressure in air, however, an average flux of about 0.003 pg cm^{-2} s^{-1} can be calculated. The range of ΔC in surface waters during this cruise is within errors (± 1σ) of measured N_2O concentrations. However, during SK-99 (February–March 1995), there is a distinct supersaturation of N_2O in surface water, leading to an average ocean–air N_2O flux of about 0.26 pg cm^{-2} s^{-1}. Our values are within the range of earlier reported values of 0.44 ± 0.22 pg cm^{-2} s^{-1} (September–October, 1986)[3] in north-west Arabian Sea and 0.23 ± 0.1 pg cm^{-2} s^{-1} in the north-east Arabian Sea[4].

The average methane flux from the surface water into the atmosphere was estimated to be about 0.0001 ± 0.006 (1σ) pg cm^{-2} s^{-1} during SK-91, while during SK-99 the average flux was found to be about 0.033 ± 0.046 pg cm^{-2} s^{-1}. Owens *et al.*[7] measured methane fluxes in the range of 0.08 to 0.26 pg cm^{-2} s^{-1} (0.46 to 1.4 nmol cm^{-2} day). Low values of both N_2O and CH_4 fluxes measured during April–May 1994 period are due to lesser degree

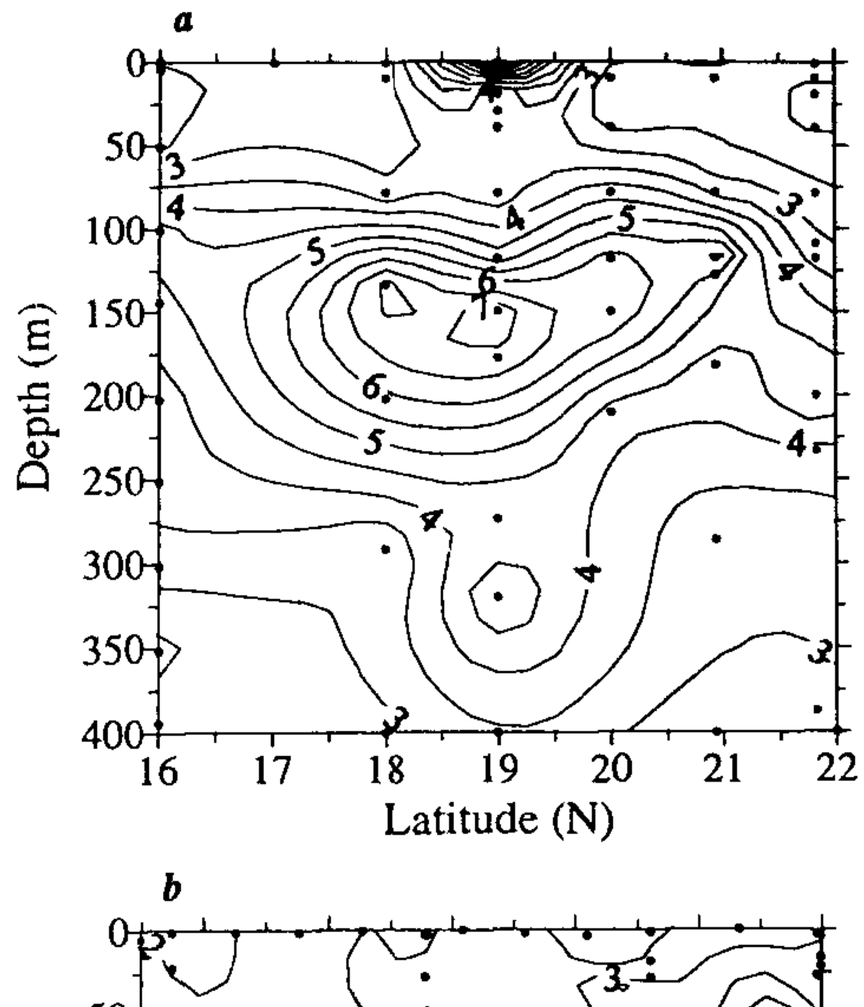

Figure 7. Latitudinal depth contour plots of methane (nmol) observed during SK-91 (*a*) and during SK-99 (*b*). Alternate contours are labelled.

of supersaturation and lower wind speed prevailing in the Arabian Sea.

Discussion

The distributions of N_2O with depth in water show two peaks. The shallow peak in the 150–200 m depth region is more pronounced in the northern region, beneath which is a concentration maximum in the 500–1000 m depth. Below this maximum the concentration gradually decreases with depth, down to 3000 m. The low concentrations between the two peaks coincide with the secondary nitrite maximum resulting from denitrification. In this region N_2O itself is reduced by the bacteria. Both nitrification and denitrification are considered to be the processes responsible for the production of N_2O

in sea water[4,9,10,18,19]. Besides the supersaturation of N_2O in the entire water column, large latitudinal and longitudinal variations were observed. During the SK-91 cruise (April–May 1994) there is no appreciable N_2O sea–air flux, whereas during SK-99 (February–March 1995) an average flux of about 0.26 pg cms is estimated. During SK-91, the sea surface conditions were more quiet and there was no clear supersaturation in surface water which lead to insignificant flux of this gas across the boundary. During SK-99 period, wind speeds were relatively higher and the waters were relatively more supersaturated. The mixed layer depth (MLD) was much deeper during SK-99, in the range of 70 to 120 m while during SK-91 it ranged between 20 and 35 m (ref. 20). A higher MLD is likely to give rise to higher concentration due to mixing with deeper N_2O and CH_4 rich water. The MLD was observed to be deepest at 16°N during SK-91 and at 17°N during SK-99 where high N_2O concentrations were observed to be protruding upwards. Compared to the results of present measurements Law and Owens[3], and Naqvi and Noronha[4] have observed significantly different fluxes of N_2O to the atmosphere in September–October 1986, and December 1988 respectively which, in general, suggest strong seasonal dependence of its fluxes.

Measurements of CH_4 are made for the first time in the north-eastern part of the Arabian Sea. These data show maximum concentrations in the region of 100 to 200 m depth. Owens *et al.*[7] in their studies in western Arabian Sea observed the peak to be located at around 60–100 m depth. This difference is attributed to the deeper Chlorophyll *a* layer in the eastern region (~ 60 m)[21] than in the western region (30–40 m)[7] of the Arabian Sea. During both cruises the methane fluxes to the atmosphere have been observed, with higher fluxes in the SK-99 period. Owens *et al.* observed methane fluxes ranging from 0.08 to 0.26 pg cm^{-2} s^{-1} in the western Arabian Sea, considerably higher than those observed in other oceanic regions[8] and this study.

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