Air-sea exchange of nitrous oxide and methane in the Arabian Sea:
A simple model of the seasonal variability

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With a simple box model the seasonal variability of N₂O and CH₄ were simulated in surface layers in the central and western Arabian Sea. The model was able to reproduce the N₂O measurements except for times when cold water filaments occur (i.e., during the SW monsoon). Based on the comparison of model results and measurements, it is concluded that the saturation of N₂O in the surface layer of the Arabian Sea is mainly controlled by (i) the wind-driven air-sea exchange during the SW monsoon, (ii) entrainment of N₂O from the subsurface layer, and (iii) sea surface temperature variability. However, the contribution of the factors listed above to the seasonality of the N₂O saturations is different in the selected areas. The overall good agreement of model results and the majority of N₂O measurements suggest that N₂O formation in the surface layer of the Arabian Sea is negligible. The comparison of model’s results and CH₄ measurements revealed a more complex situation, partly due to considerable inconsistencies in the available CH₄ data. Thus, the situation for CH₄ remains unresolved and inconclusive.

[Key words: Nitrous oxide, methane, Arabian Sea, air-sea exchange, box model]

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Both nitrous oxide (N₂O) and methane (CH₄) are atmospheric trace gases, which directly and indirectly, influence the present-day climate of the Earth. N₂O and CH₄ are naturally produced during microbial processes such as nitrification/denitrification (N₂O) and methanogenesis (CH₄) in considerable amounts in terrestrial and oceanic environments. Measurements of atmospheric and dissolved N₂O and CH₄ in oceanic areas are still sparse and the derived emission estimates are associated with large uncertainties mainly due to the fact that an adequate seasonal data coverage is mostly lacking. However, due to the activities during the Arabian Sea Process Study [as part of the international Joint Global Ocean Flux Study (JGOFS) program] and other investigations, an increasing number of N₂O and CH₄ data sets for the Arabian Sea are now available. In order to reveal the major mechanism for the observed seasonality of N₂O and CH₄ in the Arabian Sea surface layer, a model approach was chosen in which the seasonal variability of the dissolved gases is estimated from basic meteorological and hydrographical parameters. A successful modelling would allow developing tools for future monitoring of N₂O and CH₄ surface distributions and their emissions to the atmosphere in the Arabian Sea area.

A simple box model was developed to simulate the temporal variability (δC_w/δt) of N₂O and CH₄ concentrations in the mixed layer (Fig. 1):

\[ \delta C_w/\delta t = (\delta C_w/\delta t)_{ase} + (\delta C_w/\delta t)_{mix} \] … (1)

where \((\delta C_w/\delta t)_{ase}\) stands for the air-sea gas exchange across the ocean-atmosphere interface, \((\delta C_w/\delta t)_{mix}\) stands for the vertical mixing of N₂O or CH₄ into or out of the mixed layer. The present model consists of one box, the mixed surface layer, where temperature and gas concentration are homogeneously distributed. Time series of monthly seawater temperature, mixed layer depth, and wind speed were used to simulate the seasonal variability of N₂O and CH₄ at three stations in the central and western Arabian Sea (Figs. 2 and 3, Table 1).
Fig. 1—Outline of the box model; $C_w$ stands for concentration of N$_2$O or CH$_4$ in the mixed layer, $C_{ssl}$ stands for concentration of N$_2$O or CH$_4$ in the subsurface layer, $x'$ stands for the mole fraction of N$_2$O or CH$_4$ in the atmosphere, and MLD stands for mixed layer depth.

**Table 1—Model parameters**

<table>
<thead>
<tr>
<th>Target areas</th>
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<tbody>
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<td>SAST</td>
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<td>CAST</td>
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<td>WAST</td>
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<table>
<thead>
<tr>
<th>Input parameters</th>
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<tr>
<td>Water temperature</td>
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<tr>
<td>Mixed layer depth</td>
</tr>
<tr>
<td>Wind speed</td>
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<tr>
<td>N$_2$O atmospheric mole fraction</td>
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<td>CH$_4$ atmospheric mole fraction</td>
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$^a$ World Ocean Atlas$^{12}$.

$^b$ Data Set Atlas for Oceanographic Modelling Samuels & Cox$^{13}$

$^c$ ECMWF Re-Analysis Project$^{14}$

$^d$ During the SW monsoon the atmospheric mole fraction is lower due to fact that air masses from the southern hemisphere enter the Arabian Sea region as a consequence of the northward shift of the Intertropical Convergence Zone (ITCZ).

Fig. 2—Map of the Arabian Sea showing the areas WAST (Western Arabian Sea Station), CAST (Central Arabian Sea Station) and SAST (Southern Arabian Sea Station) selected for this study.

In this model, the temporal variability of gas exchange depends on the air–sea exchange flux density ($F$) and the mixed layer depth (MLD)$^{15}$:

$$(\frac{\partial C_w}{\partial t})_{ase} = F / \text{MLD} \quad \ldots \quad (2)$$

$F$ was parameterised as:

$$F = k_w(u) (C_w - C_a) \quad \ldots \quad (3)$$

where $k_w$ is the gas transfer coefficient as a function of wind speed ($u$), $C_w$ is the N$_2$O seawater concentration, and $C_a$ is the equilibrium gas concentration in seawater. $C_a$ was calculated as:

$$C_a = \beta(SST, S) x', \quad \ldots \quad (4)$$

where $x'$ is the atmospheric dry mole fraction and $\beta$ is the Bunsen solubility, which is a function of the water temperature ($SST$) and salinity ($S$)$^{16,17}$. To calculate $k_w$, the tri-linear $k_w$–$u$ relationship of Liss & Merlivat$^{18}$ (LM86), the quadratic $k_w$–$u$ relationship for climatological wind data of Wanninkhof$^{19}$ (W92), and the combined linear and cubic $k_w$–$u$ relationship from Wanninkhof & McGillis$^{20}$ (WM99) were used. $k_w$ was adjusted by multiplying 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$^{18}$, $(Sc/660)^{-0.5}$ for W92$^{19}$ and WM99$^{20}$, where $Sc$ is the Schmidt number for N$_2$O. $Sc$ at a salinity of 35°/oo was calculated using empirical equations for the kinematic viscosity of seawater$^{21}$ and the diffusion coefficients of N$_2$O and CH$_4$ in water$^{22,23}$. 

Subsurface layer

[Diagram of subsurface layer]
The gas concentration mixed into the surface layer by entrainment ($\Delta C_{\text{mix}}$) at a given time step was computed with the approach of Peng et al.\textsuperscript{24}:

$$\Delta C_{\text{mix}} = (C_{\text{sSL}} - C_w(t)) \frac{\Delta \text{MLD}}{(\text{MLD}(t) + \Delta \text{MLD})} \quad \ldots (5)$$

where $C_{\text{sSL}}$ stands for the gas concentration in the subsurface layer (i.e., below the lower boundary of the mixed layer) and $\Delta \text{MLD}$ represents the change of the MLD at the given time step. The general shapes of $\text{N}_2\text{O}$ and $\text{CH}_4$ depth profiles in the Arabian Sea suggest that surface production is not dominating their vertical distributions.\textsuperscript{25,27} Thus, it seems reasonable to assume downward mixing to be negligible (in this case $\Delta C_w = 0$). The reported values of 8 nmol L$^{-1}$ and 3 nmol L$^{-1}$ were adopted for the $C_{\text{sSL}}$ of $\text{N}_2\text{O}$ and $\text{CH}_4$, respectively.\textsuperscript{25,26} There are indications that significant spatial and seasonal variations of $C_{\text{sSL}}$ for both $\text{N}_2\text{O}$ and $\text{CH}_4$ exist.\textsuperscript{27,28} However, seasonal and spatial variations of $C_{\text{sSL}}$ were not introduced since appropriate time series measurements are not available. The concentration of the dissolved gases $C_w$ at time $t$ was calculated as follows:

$$C_w(t + \Delta t) = C_d(t + \Delta t) + \Delta C_w \quad \ldots (6)$$

$$\Delta C_w = \left(\frac{F}{\text{MLD}}\right) \Delta t + \Delta C_{\text{mix}} \quad \ldots (7)$$

where $C_d(t)$ is the equilibrium concentration computed with the atmospheric mixing ratio depending on the seawater temperature and salinity at the time $t$. The time step $\Delta t$ was set to 12 hours, a value that is lower than the system’s typical relaxation time, which is of the order of days or weeks depending on the wind speed and the mixed layer depth. At time $t = 0$, $C_w$ was calculated using a prescribed saturation ($\text{Sat}$ in %, i.e., 100% = equilibrium):

$$C_w(0) = C_d(0) \frac{\text{Sat}}{100} \quad \ldots (8)$$

The results of the model computations are presented as saturation $\text{Sat}(t)$ of at time $t$ in the mixed surface layer:

$$\text{Sat}(t) = 100 \frac{C_w(t)}{C_d(t)} \% \quad \ldots (9)$$

The model results become stable within the first model year, thus results from the second model year are shown (days 366–745).

Model input parameters are listed in Table 1. Model results were compared to saturation data from the data sets for $\text{N}_2\text{O}$\textsuperscript{29–32} as well as for $\text{CH}_4$\textsuperscript{26,32,33}.

**Results and Discussion**

**Nitrous oxide ($\text{N}_2\text{O}$)**

Figure 4 shows the results of the $\text{N}_2\text{O}$ model runs for the SAST (Southern Arabian Sea Station at 10°N 65°E), CAST (Central Arabian Sea Station at 14.5°N 65°E) and WAST (Western Arabian Sea Station at 16.3°N 60.5°E) areas. Generally, the model results show enhanced $\text{N}_2\text{O}$ saturations during the first intermonsoon period from March to late May with maximum values at the end of April (around model day 486). This is caused by the seasonal increase of the SST, which causes higher $\text{N}_2\text{O}$ saturation because of lower solubility and the fact that the variation in SST is faster than the equilibration time of the air-sea
Fig. 4—Results of the N$_2$O model; (a) WAST, (b) CAST and (c) SAST. Measurements are given as mean values with standard deviation (when available). Three different air-sea exchange models were applied (see text for details). The air-sea exchange models of Liss & Merlivat$^{18}$ and Wanninkhof$^{19}$ envelop the range of model results.

During the southwest (SW) monsoon (late May–September, model days 510–638), N$_2$O saturations are driven by both the high monsoonal wind speeds and the seasonal deepening of the MLD. However the effects are counteracting. High wind speeds lead to high emissions and subsequent depletion of N$_2$O in the mixed layer, whereas deepening of the mixed layer leads to an entrainment of N$_2$O from the subsurface layer. Since the mixed layer deepening is most pronounced at SAST (Fig. 2), the effect of entrainment is most pronounced at SAST, but almost not visible at station WAST. The winter deepening of the MLD during the end of the second intermonsoon and the northeast (NE) monsoon from mid of October to January (model days 653–745) leads to a third period of enhanced saturations because of the entrainment of N$_2$O from the subsurface layer.

In order to check the model sensitivity for the choice of C$_{ssl}$, we performed model runs for station SAST with extreme values for C$_{ssl}$ (0 and 16 nmol L$^{-1}$) (Fig. 5). The incorporation of moderate entrainment (C$_{ssl}$ = 8 nmol L$^{-1}$, Fig. 4c) brings the model results at station SAST (and at station CAST, sensitivity runs not shown) into a good agreement with the measurements, indicating that the basic assumption of C$_{ssl}$ = 8 nmol L$^{-1}$ is reasonable.

For comparison, N$_2$O saturations based on measurements are shown in Fig. 4. There is a good agreement between the measurements and model results for SAST and partly for stations CAST and WAST as well. At station WAST, maximum N$_2$O saturations of up to 135% have been reported for the SW monsoon period, however, these values are not matched by the model results. This discrepancy is due to the fact that the WAST area is influenced by cold water filaments which originate from upwelling centres at the coast of the Arabian peninsula$^{34}$. Arabian Sea filaments typically show enhanced N$_2$O concentrations$^{30,35}$. Filaments might cause the mismatch of model results and measurements at CAST during the late SW monsoon as well. However,
this result is not surprising, since advective processes are not parameterised in the model. Lal & Patra\textsuperscript{36} reported surface N\textsubscript{2}O saturations for the NE and SW monsoons and for the intermonsoon (April–May) at stations in the proximity of SAST and CAST. Their values lie in the range from 110\% to 152\% with highest values during the NE monsoon in February/March (136\% at stations close to SAST and 152\% at stations close to CAST). It appears that the present model when extended to their stations would not represent the monsoon data by Lal & Patra\textsuperscript{36}. The reason for the apparent discrepancy might be due to strong advective processes during the SW monsoon together with an unusual deepening of the mixed layer during the NE monsoon.

\textit{Methane (CH\textsubscript{4})}

Figure 6 shows the modelled CH\textsubscript{4} saturations for the stations SAST, CAST and WAST. The general shape of the model results is similar to the N\textsubscript{2}O model results (see previous section). In contrast to the N\textsubscript{2}O model, a comparison of CH\textsubscript{4} model results and measurements reveal significant discrepancies. At SAST the model generally underestimates the observed CH\textsubscript{4} saturations, whereas at CAST and WAST some of the measurements are in very good agreement with the model results. Therefore, a general conclusion is difficult to draw. On the one hand, one might argue that a missing CH\textsubscript{4} formation in the surface layer might be the reason for a general underestimation of the model. On the other hand, the very good agreement of some measurements and model results at CAST and WAST does not imply a missing CH\textsubscript{4} source. Additionally, some of the discrepancies arise because there is considerable inconsistency in the CH\textsubscript{4} measurements. For example, at CAST a difference in the CH\textsubscript{4} observations of up to 40\% CH\textsubscript{4} saturation was noted, based on two independent observations on the same day and the same year. Similar inconsistencies also occur in the data set of the WAST area.

\textbf{Conclusion}

With a simple box model the seasonal variability of the saturations of N\textsubscript{2}O and CH\textsubscript{4} in surface layers of three areas in the central and western Arabian Sea have been simulated. The model was able to reproduce the N\textsubscript{2}O measurements except for times when cold water filaments occur (i.e., at WAST and CAST during the SW monsoon). Based on the comparison of model results and measurements, it is concluded that the saturation of N\textsubscript{2}O in the surface layer of the Arabian Sea is mainly controlled by (i) the wind-driven air-sea exchange during the SW monsoon, (ii) entrainment of N\textsubscript{2}O from the subsurface layer, and (iii) SST variability. However, the contribution by the factors listed above to the seasonality of the N\textsubscript{2}O saturations is different. For example, N\textsubscript{2}O saturations at CAST during the non-monsoon season are mainly determined by the seasonal variability of the SST, whereas at the southernmost area (SAST), the entrainment of N\textsubscript{2}O results in maximum N\textsubscript{2}O saturations during the SW monsoon season. It has been suggested that N\textsubscript{2}O might be produced in the ocean surface layer of the
subtropical Pacific Ocean and the Caribbean Sea. However, the overall good agreement of model results and measurements suggests that N₂O formation in the surface layer of the Arabian Sea is negligible. This is in agreement with the results by Naqvi & Noronha.

The situation for CH₄ appears to be more complex. The comparison of model results and CH₄ measurements at SAST revealed a considerable underestimation by the model, possibly indicating an in-situ source of CH₄ in the surface layer as suggested by various authors. However, the results for stations CAST and WAST are not in line with this result, partly due to the considerable inconsistency of the available CH₄ measurements. Thus, the situation for CH₄ remains unresolved and no final conclusion can be drawn for CH₄.

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