

## MEMENTO: a proposal to develop a database of marine nitrous oxide and methane measurements

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**Environmental context.** Nitrous oxide and methane are atmospheric trace gases and, because they are strong greenhouse gases, they contribute significantly to the ongoing global warming of the Earth's atmosphere. Despite the well established fact that the world's oceans release nitrous oxide and methane to the atmosphere, the oceanic emission estimates of both gases are only poorly quantified. The MEMENTO (Marine Methane and Nitrous Oxide) database initiative is proposed as an effective way by which existing nitrous oxide and methane measurements can be used to reduce the uncertainty of the oceanic emissions estimates by establishing a global database.

**Additional keywords:** database, methane, nitrous oxide, oceanic emissions.

Nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) are infrared-active, atmospheric trace gases with long atmospheric lifetimes of ~114 (N<sub>2</sub>O) and ~12 years (CH<sub>4</sub>). Their contributions to atmospheric radiative forcing are currently ranked second (CH<sub>4</sub>) and fourth (N<sub>2</sub>O) by the Intergovernmental Panel on Climate Change (IPCC).<sup>[1]</sup> However, because of a steady decline in CFC-12 emissions over the past two decades N<sub>2</sub>O should soon replace CFCs as the third most important tropospheric greenhouse gas given its current atmospheric growth.<sup>[1]</sup> Therefore, assessments of radiative forcing from long-lived greenhouse gases now, more than ever, depend on an accurate synthesis of the global distribution and magnitudes of N<sub>2</sub>O and CH<sub>4</sub> sources and sinks.

Marine waters, especially coastal regions including shelf areas, coastal upwellings, estuaries and mangrove forests, are significant contributors to the global flux of atmospheric N<sub>2</sub>O and CH<sub>4</sub>,<sup>[2–5]</sup> and thus should be adequately accounted for in any such synthesis.

The flux of a trace gas such as N<sub>2</sub>O or CH<sub>4</sub> across the ocean–atmosphere interface ( $F_{\text{ase}}$ , in mol m<sup>-2</sup> s<sup>-1</sup>) is usually calculated as:

$$F_{\text{ase}} = k_w \Delta C \quad (1)$$

where  $k_w$  (in m s<sup>-1</sup>) is the air–sea gas transfer velocity and  $\Delta C$  (in mol L<sup>-1</sup>) is the gas concentration difference across the air–sea interface. More formally  $\Delta C$  can be defined as:

$$\Delta C = C_w - \beta x' P \quad (2)$$

where  $C_w$  is the in-situ concentration (in mol L<sup>-1</sup>) of dissolved gas,  $\beta$  is the Bunsen solubility (in mol L<sup>-1</sup> atm<sup>-1</sup>),  $x'$  is the atmospheric dry mole fraction and  $P$  is the atmospheric pressure. The difficulties inherent in deriving accurate estimates of  $k_w$  are well documented and arise from the control of gas exchange by a range of geophysical forcings whose effects are, in the main, not well quantified.<sup>[6]</sup> Nevertheless, most contemporary



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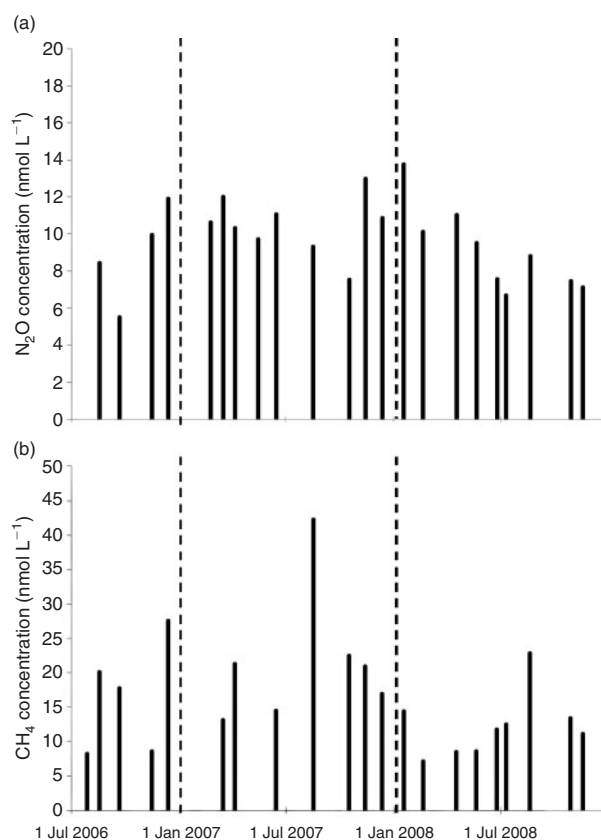
estimates of sea-to-air gas fluxes derive  $k_w$  from ambient wind speeds based on one or more  $k_w$  versus wind speed relations extracted from the results of dual tracer releases,<sup>[7,8]</sup> despite the inherent uncertainties.<sup>[6,9]</sup> Specifying an appropriate value of  $\Delta C$  may, however, be equally problematic. While  $k_w$  may often be assumed to be rather constant over large areas with uniform wind-wave fields,  $\Delta C$  is often subject to substantial small-scale spatial variability, especially in coastal regions where fluxes are highest.<sup>[6]</sup>

Atmospheric dry mole fractions of  $N_2O$  and  $CH_4$  have been routinely available since the late 1970s and they benefit from a highly coordinated global monitoring network.<sup>[10]</sup> In stark contrast, although measurements of marine  $N_2O$  and  $CH_4$  date back over almost four decades, they lack the temporal continuity and area coverage of their atmospheric counterparts. This is because almost all of them relate to single cruises or, at best, coordinated cruise programs of rather limited scope. In large part this reflects the high costs and organisational difficulties of mounting large coordinated oceanographic campaigns, especially at the international level. Not surprisingly, oceanic data coverage remains fragmentary.

Issues impacting the quality of marine emissions estimates for  $N_2O$  and  $CH_4$  may be summarised as follows:

1. *Limited database.* Large parts of the ocean have little to no spatial data coverage.
2. *Seasonal and interannual variabilities.* The concentrations of dissolved  $N_2O$  and  $CH_4$  and their seasonal variability reflect the imprint of seasonally varying biology (i.e. nitrification/denitrification and methanogenesis) on an underlying hydrographic regime (e.g. coastal upwelling, mixing, etc.) which also varies seasonally. Both gases thus show considerable temporal variability in the surface ocean. An example for the seasonal and interannual variability of  $N_2O$  and  $CH_4$  is shown in Fig. 1. In addition, research cruises are predominantly scheduled during the (calm and comfortable) summer, which lends considerable seasonal bias to the resulting datasets.
3. *Strong spatial heterogeneity in coastal areas.* Large horizontal and vertical gradients arise through various mechanisms including tidal exchange with adjacent water bodies, stratification in deep waters because of insolation or when tidal or wind shear is relatively weak, and interaction of river inputs with tidal currents and wind stress.<sup>[6]</sup> For  $CH_4$  in particular diffusional or bubble inputs from intertidal sediments may be important. Under some circumstances bubble plumes may directly export  $CH_4$  from sediments to the atmosphere. However, such events are difficult to track and are, therefore, not well represented in  $CH_4$  emission estimates.<sup>[11]</sup>
4. *Strong spatial gradients between coastal and open ocean areas.*  $N_2O$  and  $CH_4$  are predominantly produced in and released from coastal areas. Therefore, significant concentration differences exist between coastal areas (such as upwelling areas), estuaries and the adjacent open ocean. An example is given from the Arabian Sea, where the seasonally occurring coastal upwelling events along the coast of the Arabian Peninsula lead to significant concentration gradients (Table 1).

A cost effective way by which the existing  $N_2O$  and  $CH_4$  measurements can be used to improve the value of marine emissions estimates, despite the data limitations, is by establishing a global database. To this end we have launched MEMENTO (MarinE MethanE and NiTrous Oxide; MEMENTO is the Latin



**Fig. 1.** Monthly  $N_2O$  (a) and  $CH_4$  (b) surface concentrations measured at the Boknis Eck coastal time series station in the Eckernförder Bay (SW Baltic Sea) (H. W. Bange, K. Bergmann, H. P. Hansen, A. Kock, C. Ostrau, B. Schweiger, unpubl. data).

**Table 1.**  $N_2O$  and  $CH_4$  surface concentrations (in  $nmol L^{-1}$ ) during a cruise in the Arabian Sea in June/July 1997. For details see Bange et al.<sup>[13,14]</sup>

Avg. and s.d. stand for average and standard deviation respectively; 'max' stands for maximum concentration observed

Emission	Central Arabian Sea avg. $\pm$ s.d.	Coastal upwelling off Oman avg. $\pm$ s.d. (max)
$N_2O$	$5.9 \pm 0.3$	$12.0 \pm 3.6$ (21.7)
$CH_4$	$1.77 \pm 0.03$	$2.15 \pm 0.19$ (2.88)

word for 'remember!') as a joint initiative between SOLAS (Surface Ocean Lower Atmosphere Study; see [www.solas-int.org](http://www.solas-int.org), accessed 25 May 2009) and COST Action 735 (European Cooperation in the Field of Scientific and Technical Research; see [www.cost-735.org](http://www.cost-735.org), accessed 25 May 2009). The official MEMENTO logo is shown in Fig. 2.

MEMENTO's aims are to:

1. Collect available  $N_2O$  and  $CH_4$  data from the global ocean (both open and coastal), sourcing both peer reviewed publications and unpublished reports (i.e. 'grey' literature, e.g. cruise or project reports, diploma or master theses, etc. which are not available for the public).
2. Archive the data in a database with open access for the scientific community.
3. Process the data according to the procedure outlined in Bange and Freing.<sup>[12]</sup>



**Fig. 2.** Logo of MEMENTO illustrating the idea of collecting widespread and unsorted data in order to form a database: N, 2, O, C, H and 4 are falling out from the sea of data to form CH<sub>4</sub> and N<sub>2</sub>O as stored in the database.

4. Compute global fields of dissolved N<sub>2</sub>O and CH<sub>4</sub> concentrations as well as air–sea fluxes in both open and coastal ocean.
5. Publish the database and the derived flux data with a wide authorship inclusive of the data originators.
6. Keep the database ‘live’ in the future by widely publicising its availability and encouraging data submission following their prior release to the public domain.

MEMENTO will be linked to and cooperate with well established CO<sub>2</sub> databases. We envisage that once all existing datasets have been incorporated into MEMENTO it will rapidly become a valuable tool for identifying regions of the world ocean that should be targeted in future work to improve the quality of emission estimates.

We have already incorporated our own datasets into MEMENTO and are in the process of circulating some initial data requests, but we would encourage all colleagues in the international N<sub>2</sub>O and CH<sub>4</sub> community to proactively participate. In the first phase of MEMENTO all archive data will be assimilated. In the second phase new datasets will be added routinely as they are published. Further details of the MEMENTO initiative and how to contribute your data as well as full details of data requirements including ancillary and metadata can be obtained by contacting the corresponding author or see [http://www.bodc.ac.uk/solas\\_integration/implementation\\_products/group3/](http://www.bodc.ac.uk/solas_integration/implementation_products/group3/) (accessed 25 May 2009).

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### References

- [1] IPCC, *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change 2007* (Cambridge University Press: Cambridge, UK).
- [2] H. W. Bange, New Directions: The importance of the oceanic nitrous oxide emissions. *Atmos. Environ.* **2006**, *40*, 198. doi:10.1016/J.ATMOSENV.2005.09.030
- [3] H. W. Bange, U. H. Bartell, S. Rapsomanikis, M. O. Andreae, Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane. *Global Biogeochem. Cy.* **1994**, *8*, 465. doi:10.1029/94GB02181
- [4] J. Barnes, R. Ramesh, R. Purvaja, A. Nirmal Rajkumar, B. Senthil Kumar, K. Krithika, K. Ravichandran, G. Uher, R. Upstill-Goddard, Tidal dynamics and rainfall control N<sub>2</sub>O and CH<sub>4</sub> emissions from a pristine mangrove creek. *Geophys. Res. Lett.* **2006**, *33*, L15405. doi:10.1029/2006GL026829
- [5] R. C. Upstill-Goddard, J. Barnes, T. Frost, S. Punshon, N. J. P. Owens, Methane in the southern North Sea: Low-salinity inputs, estuarine removal, and atmospheric flux. *Global Biogeochem. Cy.* **2000**, *14*, 1205. doi:10.1029/1999GB001236
- [6] R. C. Upstill-Goddard, Air–sea exchange in the coastal zone. *Estuar. Coast. Shelf Sci.* **2006**, *70*, 388. doi:10.1016/J.ECSS.2006.05.043
- [7] P. S. Liss, L. Merlivat, Air–sea exchange rates: introduction and synthesis, in *The Role of Air–Sea Exchange in Geochemical Cycling* (Ed. P. Buat-Ménard) **1986**, Series C: Mathem. & Phys. Sciences, pp. 113–127 (D. Reidel Publishing Company: Dordrecht).
- [8] R. Wanninkhof, Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* **1992**, *97*, 7373. doi:10.1029/92JC00188
- [9] R. Wanninkhof, The impact of different gas exchange formulations and wind speed products on global air–sea CO<sub>2</sub> fluxes, in *Transport at the Air–Sea Interface* (Eds C. S. Garbe, R. A. Handler, B. Jähne) **2007**, pp. 1–23 (Springer: Berlin).
- [10] R. G. Prinn, R. F. Weiss, P. J. Fraser, P. G. Simmonds, D. M. Cunnold, F. N. Alyea, S. O’Doherty, P. Salameh, et al., A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. *J. Geophys. Res.* **2000**, *105*, 17 751. doi:10.1029/2000JD900141
- [11] G. Etiope, New Directions: GEM – Geologic emissions of methane, the missing source in the atmospheric methane budget. *Atmos. Environ.* **2004**, *38*, 3099. doi:10.1016/J.ATMOSENV.2004.04.002
- [12] A. Freing, H. W. Bange, Towards a global database of oceanic nitrous oxide measurements. *IMBER Update* **2007**, *8*, 3. Available at [http://www.imber.info/products/IMBER\\_Update\\_Oct07.pdf](http://www.imber.info/products/IMBER_Update_Oct07.pdf) [Verified 3 June 2009]
- [13] H. W. Bange, R. Ramesh, S. Rapsomanikis, M. O. Andreae, Methane in the surface waters of the Arabian Sea. *Geophys. Res. Lett.* **1998**, *25*, 3547–3550. doi:10.1029/98GL02710
- [14] H. W. Bange, T. Rixen, A. M. Johansen, R. L. Siefert, R. Ramesh, V. Ittekkot, M. R. Hoffmann, M. O. Andreae, A revised nitrogen budget for the Arabian Sea. *Global Biogeochem. Cycles* **2000**, *14*, 1283. doi:10.1029/1999GB001228

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