Version 03 April 09

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

Hermann W Bange[1*], Tom G Bell[2], Marcela Cornejo[3], Alina Freing[1], Günther Uher[4], Rob C Upstill-Goddard[4], and Guiling Zhang[5]

[1] IFM-GEOMAR, Kiel, Germany
[2] University of East Anglia, Norwich, UK
[3] University of Concepcion, Chile
[4] University of Newcastle upon Tyne, UK
[5] Ocean University of China, Qingdao, China

*corresponding author
ph +49-431-600 4204
fax +49-431-600 4202
e-mail hbange@ifm-geomar.de

ms submitted to Environmental Chemistry; Environ. Chem. ms# 09033

key words: nitrous oxide, methane, oceanic emissions, database

Nitrous oxide (N_2O) and methane (CH_4) are infrared-active, atmospheric trace gases with long atmospheric lifetimes of ~114 (N_2O) and ~12 years (CH_4). Their contributions to atmospheric radiative forcing are currently ranked second (CH_4) and fourth (N_2O) by the Intergovernmental Panel on Climate Change (IPCC).[1] However, due to a steady decline in CFC-12 emissions over the past two decades N_2O should soon replace CFC's as the third most important tropospheric greenhouse gas given its current atmospheric growth.[1] 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_2O and CH_4 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_2O and CH_4,[2-5] and thus should be adequately accounted for in any such synthesis.

The flux of a trace gases such as N_2O or CH_4 across the ocean-atmosphere interface *(F_{ase})* is usually calculated as

$F_{ase} = k_w \Delta C$

where k_w is the air-sea gas transfer velocity and ΔC is the gas concentration difference across the air-sea interface. More formally ΔC can be defined as:

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

where C_w is the in-situ concentration of dissolved gas, β is the Bunsen solubility, 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.[6] Nevertheless most contemporary estimates of sea-to-air gas fluxes derive k_w from ambient wind speeds based on one or more k_w vs. wind speed relations extracted from the results of dual tracer releases,[7,8] despite the inherent uncertainties.[6,9] Specifying an appropriate value of ΔC may however be equally problematic. While k_w may often be assumed to be rather constant over large areas with uniform wind/wave fields, ΔC is often subject to substantial small-scale spatial variability, especially in coastal regions where fluxes are highest.[6]

Atmospheric dry mole fractions of N_2O and CH_4 have been routinely available since the late 1970's and they benefit from a highly coordinated global monitoring network.[10] In stark contrast, although measurements of marine N_2O and CH_4 date back over almost four decades, they lack the temporal continuity and areal coverage of their atmospheric counterparts. This is because almost all of them relate to single cruises or at best coordinated cruise programmes 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. Additionally, 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 due to insolation or when tidal or wind shear is relatively weak, and interaction of river inputs with tidal currents and wind stress.[6] 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 emissions estimates.[11]

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 via establishing a global database. To this end we have launched MEMENTO (MarinE MethanE and NiTrous Oxide; MEMENTO is the Latin word for 'remember!') as a joint initiative between SOLAS (Surface Ocean Lower Atmosphere Study; see www.solas-int.org) and COST Action 735 (European Cooperation in the Field of Scientific and Technical Research; see www.cost-735.org). 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;
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,[12]
4. compute global fields of dissolved N_2O/CH_4 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" into the future by widely publicising its availability and encouraging data submission following their prior release to the public domain.

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 the emissions 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_2O and CH_4 community to pro-actively participate. In a first phase of MEMENTO all archive data will be assimilated by the End of August 2009. In a second phase new datasets will be added routinely as they are published until March 2010. 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.

Acknowledgements

MEMENTO is an outcome of discussions held at the COST Action 735 Working Group 3 Technical Workshop on coastal CO_2/N_2O/CH_4 data held at IFM-GEOMAR, Kiel, Germany, 22/23 January 2009. The workshop was funded by COST Action 735 and IFM-GEOMAR. We especially thank Emily Brévière (COST Action 735 and SOLAS International Project Office) for the administrative handling of the workshop. T. Bell is supported by a UK SOLAS Knowledge Transfer grant (NE/E001696/1).

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.

[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. Cycles*, **1994**, *8*, 465.

[4] J. Barnes, et al., Tidal dynamics and rainfall control N_2O and CH_4 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. Cycles*, **2000** *14*, 1205.

[6] R.C. Upstill-Goddard, Air-sea exchange in the coastal zone, *Estuar. Coastal Shelf Sci.* **2006** *70*, 388.

[7] P.S. Liss, L. Merlivat, in The role of air-sea exchange in geochemical cycling (Ed P. Buat-Ménard) **1986** 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.
[9] R. Wanninkhof, in Transport at the air-sea interface (Eds C.S. Garbe, R.A. Handler, B. Jähne) **2007** pp. 1-23 (Spinger: Berlin).
[10] R.G. Prinn, et al., A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *J. Geophys. Res.*, **2000** *105*, 17,751.
[11] G. Etiope, New Directions: GEM - Geologic emissions of methane, the missing source in the atmospheric methane budget, *Atmos. Environ.* **2004** *38*, 3099.
[12] A. Freing, H.W. Bange, Towards a global database of oceanic nitrous oxide measurements, *IMBER Update,* **2007** *issue 8*, 3.