

**Proposal for Scientific Committee on Ocean Research (SCOR) Working Group  
Dissolved N<sub>2</sub>O and CH<sub>4</sub> measurements: Working towards a global network of ocean  
time series measurements of N<sub>2</sub>O and CH<sub>4</sub>**

**Overview**

This proposal aims to improve and consolidate measurements of the greenhouse gases nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) dissolved in seawater. This work will be achieved over a 4 year time period by conducting the following activity: Firstly, an intercalibration exercise will be conducted amongst WG members targeting discrete N<sub>2</sub>O and CH<sub>4</sub> measurements. Recommendations and protocols for calibration, quantification, and data reporting will be published following this exercise. This part of the project will also provide a review of existing and near-future methods for quantifying N<sub>2</sub>O and CH<sub>4</sub> in seawater including spectroscopy measurements. The second part of the project will be to conduct an overall assessment on the status of dissolved N<sub>2</sub>O and CH<sub>4</sub> measurements in the global oceans. Key regions and recommendations on the necessary temporal and spatial scale for sampling will be identified. Conducting this N<sub>2</sub>O and CH<sub>4</sub> work within the SCOR framework will bring available information and international expertise together and develop community-based and accepted procedures. In this regard, the successful track record of SCOR in conducting international intercalibration exercises (e.g. WG2 ‘Carbon Dioxide in the Ocean’, and WG16 ‘General Problems of Intercalibration and Standardization’) will be very beneficial.

**Scientific Background**

*Why measure N<sub>2</sub>O and CH<sub>4</sub> in the marine environment?*

In the Earth’s atmosphere, N<sub>2</sub>O and CH<sub>4</sub> account for 24% of the total radiative forcing associated with greenhouse gases. Whilst CO<sub>2</sub> is the most abundant greenhouse gas, N<sub>2</sub>O and CH<sub>4</sub> are more virulent, respectively exerting ~300 and 25 times more radiative forcing than CO<sub>2</sub> over a period of 100 years (IPCC, 2007). The atmospheric burden of N<sub>2</sub>O and CH<sub>4</sub> is increasing at an annual rate of 0.4% and 0.25%, respectively, and there is an ever increasing need to better constrain and understand the sources and sinks of both gases at the Earth’s surface (Keeling 2008). The global oceans represent a source of both N<sub>2</sub>O and CH<sub>4</sub> to the overlying atmosphere. The IPCC (2007) estimates oceanic CH<sub>4</sub> emissions range from 4-15 Tg CH<sub>4</sub> yr<sup>-1</sup> and the rate of oceanic N<sub>2</sub>O emissions to range from 1.8-5.8 Tg N yr<sup>-1</sup>, although it should be noted that this is considered to be an underestimation by at least a factor of 2 (Bange 2006; Naqvi et al. 2000). The biogeochemical cycling of both gases in the environment is sensitive to temperature and redox conditions, and thus potential feedbacks to anthropogenic perturbations such as global warming, eutrophication, and spreading anoxia represent challenges for future marine scientific research.

*Conducting measurements of N<sub>2</sub>O and CH<sub>4</sub> in seawater*

N<sub>2</sub>O and CH<sub>4</sub> are routinely measured in diverse parts of the world’s oceans either as discrete or continual measurements. Discrete measurements rely on the collection, preservation, and subsequent analysis of seawater samples using widely available gas chromatography (GC) techniques (e.g. Elkins 1980). Continual measurements of surface water saturations rely on a seawater equilibrator unit connected to an underway systems

(e.g. Weiss 1981). More recently, within the last 5 years, there has been increasing use of Cavity Ring-down Spectroscopy and Off-Axis Integrated Cavity Output Spectroscopy analyzers (CRDS and OA-ICOS) for the analysis of trace gases. The use of optical absorption technology to measure trace gases including N<sub>2</sub>O and CH<sub>4</sub> has advanced rapidly and offer precise measurements with unprecedented time resolution (Gülzow et al. 2011, 2013). To date, CRDS and OA-ICOS have been used in continual sampling mode, however it will not be long before they are also used to analyze discrete samples.

It should be clarified that the focus of the intercalibration exercise is discrete measurements of N<sub>2</sub>O and CH<sub>4</sub> dissolved in seawater. Discussion and comparison of other analytical systems e.g. equilibrator units, spectroscopy technology, will follow on from the intercalibration of discrete measurements. We envisage that the WG meetings will be used to discuss use of the CRDS and OA-ICOS analyzers for both continual measurements and discrete analysis. Sales and engineer representatives from the manufacturing companies (LGR and/or Picarro) can attend a WG meeting and demonstrate the application of their analyzers (see Terms of Reference #1)

#### *Why conduct an intercalibration exercise for N<sub>2</sub>O and CH<sub>4</sub> measurements?*

A number of laboratories throughout the world have developed analytical systems for measuring dissolved N<sub>2</sub>O and CH<sub>4</sub> in seawater and undoubtedly new groups will make these measurements in the future. To maximize the scientific value of these studies, it is important that the measurements made by all groups are intercomparable and of the highest possible accuracy and precision. We adopt the definition of intercalibration as “The process, procedures, and activities used to ensure that the several laboratories engaged in a monitoring program can produce compatible data. When compatible data outputs are achieved and this situation is maintained, the laboratories can be said to be intercalibrated (Taylor, 1987).”

Similar exercises have been conducted for other oceanographic analyses including DIC (Dickson 2010), dissolved organic carbon (Sharp et al. 2002), sulfur hexafluoride and chlorofluorocarbons (Bullister and Tanhua 2010), halocarbons (Jones et al. 2011), and trace elements (Cutter et al. 2010). Therefore we will work with members of the scientific community actively involved in inter-laboratory collaborative exercises e.g. John Bullister at NOAA PMEL and Andrew Dickson at SIO to learn from their experience. Improvements to the CO<sub>2</sub> analytical system (Dickson et al. 2003) and implementing best practices (Dickson et al. 2007) represent several decades of coordinated effort, however the successes are apparent with the accurate reporting of CO<sub>2</sub> increase in seawater (Dore et al. 2009; Keeling et al. 2004; Winn et al. 1998) and the concomitant decrease in seawater pH (Dore et al. 2009). It is imperative to set the N<sub>2</sub>O and CH<sub>4</sub> on the correct path if we are to accurately determine the role of the oceans in climate change as detailed in the ‘Scientific Background’.

#### *Network of time series measurements of N<sub>2</sub>O and CH<sub>4</sub>.*

Time series measurements of dissolved trace gases are a critical element of marine sciences. They are crucial to decipher the feedbacks between formation and emissions of climate relevant trace gas and short- and long-term environmental repercussions such as climate change, eutrophication, ocean deoxygenation and acidification. Currently,

dissolved trace gases such as N<sub>2</sub>O and CH<sub>4</sub> are regularly measured at only a few time series sites such as Stn. ALOHA (Hawaii), CaTS (off Goa, India), Line P (North Pacific), Boknis Eck (SW Baltic Sea) and off Chile. With a common measurement protocol, we will establish the basis for a world-wide network of compatible measurements of oceanic N<sub>2</sub>O and CH<sub>4</sub>.

Beginning in Year 2 of the project, the SCOR working group will compile existing measurements of N<sub>2</sub>O and CH<sub>4</sub> in the marine environment including both time series and repeat hydrographic surveys. It will provide a framework for linking and bringing together existing measurements (e.g. in a joint internet platform such as MEMENTO\* which provides access to the data from all sites), and recommend locations for new N<sub>2</sub>O/CH<sub>4</sub> time series measurements which may either be undersampled or be more susceptible to change due to natural or anthropogenic perturbations.

\*MEMENTO (the MarinE MethanE and NiTrous Oxide database) has been recently established as a subproject of SOPRAN which is the German contribution to SOLAS. Dr. Annette Kock, nominated as Associated Member of this WG will coordinate the activities MEMENTO. Moreover, MEMENTO will be powered and maintained by the Kiel Data Management Team, thus MEMENTO has a long-term commitment by GEOMAR including the establishment of a joint internet platform beyond the duration of SOPRAN and the SCOR WG. All data archived in MEMENTO will be linked to and archived at CDIAC, PANGAEA etc. as well.

### **Working Group Composition**

The Full Members of the Working Group represents a balance between scientists actively engaged in measuring N<sub>2</sub>O and CH<sub>4</sub> as part of time-series programs and having a global distribution of scientists with both senior and early career personnel. Associate members are represented by analytical experts in either trace gas chemistry and/or previously involved in intercalibration exercises. We have also attached an Appendix to this proposal which provides a brief outline of the members research interests as they relate to N<sub>2</sub>O and CH<sub>4</sub> in the marine environment. (m) and (f) flag male or female members, respectively.

#### Full members

- Hermann Bange (m), Co-chair (GEOMAR; Kiel, Germany) *Time series: Boknis Eck*
- Mercedes de la Paz Arándiga (f) (Instituto de Investigaciones Marinas-CSIC, Vigo, Spain)
- Laura Farias (f) (COPAS Center; Concepción, Chile) *Time series: ESP-OMZ*
- Cliff Law (m) (NIWA; Wellington, New Zealand)
- Wajih Naqvi (m) (National Institute of Oceanography, Goa, India) *Time series: Candolim*
- Gregor Rehder (m) (IOW, Warnemünde, Germany)
- Philippe Tortell (m) (UBC; Vancouver, Canada) *Time series: Line P Program*
- Rob Upstill-Goddard (m) (University of Newcastle; Newcastle, UK)
- Sam Wilson (m), Co-chair (C-MORE; Hawaii, USA) *Time series: Stn ALOHA*
- Guiling Zhang (f) (Ocean University of China, Qingdao, China)

Associate members

- John Bullister (m) (NOAA-PMEL, Washington, USA)
- Jan Kaiser (m) (UEA, Norwich, UK)
- Annette Kock (f) MEMENTO (GEOMAR, Kiel, Germany)
- Andy Rees (m) (Plymouth Marine Lab; Plymouth, UK)

### Terms of Reference

We outline four Terms of Reference for this WG. These activities are integrated into the international meetings, which are outlined in the Timetable below. The publications resulting from the activity of this WG are indicated in Terms of Reference #3 and #4.

1. Conduct an intercalibration exercise between the time series programs
2. Establish the appropriate standards to be used by the scientific community
3. Recommend the analytical reporting procedures to be used for N<sub>2</sub>O and CH<sub>4</sub>
4. Establish framework for an N<sub>2</sub>O/CH<sub>4</sub> ocean time series network and write a global oceanic N<sub>2</sub>O/CH<sub>4</sub> summary paper for publication in an open access journal.

#### *1. Conduct an intercalibration exercise between the time series programs.*

The first intercalibration exercise will occur in Year 1 of the project in time to present the findings at the first WG meeting, prior to the Ocean Sciences conference in Honolulu, Hawaii. Its purpose is to fully evaluate the analytical procedures for quantifying N<sub>2</sub>O and CH<sub>4</sub> dissolved in seawater. A second intercalibration exercise has also been included in the timetable scheduled to occur in Year 2 of the project to resolve long-term issues associated with the analysis *e.g.* preservation and storage of samples. Each intercalibration exercise will consider specific items:

- Instrument set-up: Calibration procedures, sample blanks, the stripping efficiency, and instrument drift over a 1 year period.
- Transportation and preservation of samples. This will also help determine the possibility of reference material.
- Exchange seawater samples in order to determine any offset between the N<sub>2</sub>O and CH<sub>4</sub> datasets.

Ultimately, the intercalibration exercise will help improve the analytical systems used by the different laboratories. It will also help recommend an 'ideal' analytical system for future laboratories establishing reduced gas analysis. The WG will also host a practical demonstration of an analytical system capable of delivering high-precision measurements of N<sub>2</sub>O and CH<sub>4</sub>.

#### *2. Initiate common protocols, including primary N<sub>2</sub>O and CH<sub>4</sub> standards, working standards, and measurement of N<sub>2</sub>O and CH<sub>4</sub> in the overlying atmosphere.*

- Laboratory gas standards. To assist the compatibility of the measurements, at least one of the standard gas mixtures used by the separate laboratories should be derived from NOAA ESRL GMD which is the central calibration laboratory for the World Meteorological Organization (WMO), Global Atmosphere Watch (GAW). The concentration values of the laboratory reference standards will be close to that of modern air *i.e.* 0.325 ppm for N<sub>2</sub>O and 1.6 ppm for CH<sub>4</sub>. These gas standards have an accuracy of ± 1 ppb (IMBER/SOLAS Implementation Plan 2006). The approximate total cost for standard gas mixtures of N<sub>2</sub>O and CH<sub>4</sub> (150 cubic ft. cylinder) is \$2600.

The cost of the cylinders will be handled by each laboratory and if financial support is required, funding will be requested from the respective national agencies.

- **Liquid Reference Materials.** In addition to gas standards, we will investigate the feasibility of incorporating control measurements into the analytical procedures. Other analyses refer to these as Certified Reference Materials which are used to relate the concentration of dissolved  $N_2O$  or  $CH_4$  to a reference database for calibration. We will assess the suitability of having non-certified liquid reference materials for  $N_2O$  or  $CH_4$  during Year 2 of the project. For example, a seawater sample equilibrated with a known atmospheric concentration at a fixed temperature.

**Ensure all Working Group members have access to primary standards by May 2014 and establish the feasibility of a working standard reference material by May 2015 (see timeline below).**

### *3. Establish $N_2O$ and $CH_4$ reporting procedures*

The information to be included in the reporting procedures will be agreed upon by the WG. This documentation should be provided with the  $N_2O$  and  $CH_4$  datasets stored at publicly available national and international data centers. Publication of the intercalibration exercise (Terms of Reference #1) will provide an opportunity to highlight these reporting procedures to the wider oceanographic scientific community. This publication will be drafted before the second planned WG meeting which will be held in Kiel, Germany, in September 2015 at the SOLAS Open Science Conference. We will collaborate with relevant major international programmes such as SOLAS, IMBER, and CLIVAR to make sure that the WG recommendations for reporting procedures are recognized for future  $N_2O/CH_4$  measurements.

**The outcome and conclusions of the intercalibration exercise will be published in a refereed scientific journal, alongside the reporting procedures outlined in Terms of Reference #1.**

### *4. Establish a framework for an $N_2O/CH_4$ ocean time series network*

The SCOR WG will compile available  $N_2O$  and  $CH_4$  data from the global ocean (both open and coastal), sourcing both peer reviewed publications, unpublished reports and data archives such as MEMENTO. In instances of data being stored with other repositories, we will provide a link to these separate archives. These data will be reviewed and checked for data consistency. Maps of the global  $N_2O/CH_4$  distribution in the ocean will be produced (if possible with a monthly resolution). Based on these data, locations for new time series measurements (sites and lines for VOS, volunteer observing ships) will be identified. Additionally, recommendations will be published on how to link the existing time series data and how to make them available to the public in order to facilitate the use of data by modellers, stakeholders, and policy makers.

**The recommendations for a global network of  $N_2O/CH_4$  oceanic measurements will be published in a refereed scientific journal. To aid this coordinating work, WG members will submit  $N_2O$  and  $CH_4$  datasets using the agreed  $N_2O$  and  $CH_4$  reporting procedures to a publicly available data center (MEMENTO; Bange et al., 2009) by December 2014.**

## Timeline

Calendar Year	Key dates	WG activity
2013	May: Submission of proposal  Nov: Decision by SCOR on support	We would like the first intercalibration exercise to be completed prior to the Feb 2014 WG meeting.
2014	Feb: WG meeting in Hawaii, (followed by ASLO 2013)	In June-Dec 2014, a 2 <sup>nd</sup> intercalibration exercise is planned to fulfill this part of the project
2015	Sept: WG meeting in Germany, (followed by SOLAS conf)	
2016	Feb: Publish recommendations for analysis and reporting	Presentation of intercalibration results at SOLAS.
2017	February: 3 year review and Working Group meeting followed by Ocean Sciences  Publication of recommendation for N <sub>2</sub> O/CH <sub>4</sub> Time Series Station Network	In Year 3-4, the WG assesses our ability to track changes in N <sub>2</sub> O and CH <sub>4</sub> concentrations in the marine environment.

## Capacity Building

To help achieve the objectives of this proposal and build the capacity to improve and sustain accurate N<sub>2</sub>O and CH<sub>4</sub> measurements we will encourage all the Working Group core members to involve an early career scientist in the intercalibration exercise. This working group proposal engages oceanographers across the world and we will insure full participation in the international meetings to be held in 2014 and 2015 by core members of the Working Group and make the resulting publications are freely available. The WG plans to get in contact with the Partnership for Observation of the Global Oceans, POGO, to see if the WG procedures could be added to POGO's portfolio of training & education activities. This will facilitate the establishment and maintenance of additional high quality N<sub>2</sub>O/CH<sub>4</sub> time series measurements world-wide. We do not believe the financial costs of participating in the intercalibration exercise to be prohibitive as all participating laboratories currently conduct the measurements. The main costs will be shipping, travel, and the certified gas standards.

## References

- Bange, H.W. (2006) New Directions: The importance of the oceanic nitrous oxide emissions. *Atmos Environ* 40:198-199.
- Bange, H.W., Bell, T.G., Cornejo, M., Freing, A., Uher, G., Upstill-Goddard, R.C., and Zhang, G. (2009) MEMENTO: a proposal to develop a database of marine nitrous oxide and methane measurements. *Environ Chem* 6:195–197.
- Bullister, J.L. and Tanhua, T. (2010) Sampling and measurement of chlorofluorocarbons and sulfur hexafluoride in seawater. IOCCP Report No. 14 ICPO Publication Series No. 134, Version 1.
- Cutter, G., Andersson, P., Codispoti, L., Croot, P., Francois, R., Lohan, M., Obata, H. And van der Loedd, M.R. (2010) Sampling and sample-handling protocols for GEOTRACES cruises. Version 1.0
- Dickson, A.G., Afghan, J.D. and Anderson, G.C. (2003) Reference materials for oceanic CO<sub>2</sub> analysis: A method for the certification of total alkalinity. *Mar Chem* 80:185-197.
- Dickson, A.G., Sabine, C.L. and Christian, J.R. (eds.) (2007) Guide to best practices for ocean CO<sub>2</sub> measurements. PICES Special Publication 3.
- Dickson, A.G. (2010) Standards for ocean measurements. *Oceanography* 23:34-47.
- Dore, J.E., Lukas, R., Sadler, D.W., Church, M.J. and Karl, D.M. (2009) Physical and biogeochemical modulation of ocean acidification in the central North Pacific. *Proc Natl Acad Sci USA* 106:12235-12240.
- Elkins, J.W. (1980) Determination of dissolved nitrous oxide in aquatic systems by gas chromatography using electron-capture detection and multiple phase equilibration. *Anal Chem* 52:263-267.
- Gülzow, W., Rehder, G., Schneider, B., Schneider v. Deimling, J. and Sadkowiak B. (2011) A new method for continuous measurement of methane and carbon dioxide in surface waters using off-axis integrated cavity output spectroscopy (ICOS): An example from the Baltic Sea. *Limnol Oceanogr* 9:176-184.
- Gülzow, W., Rehder, G., Schneider von Deimling, J., Seifert, T., Tóth, Z. (2013) One year of continuous measurements constraining methane emissions from the Baltic Sea to the atmosphere using a ship of opportunity. *Biogeosciences Discuss* 9:9897-9944.2012.
- IMBER/SOLAS Report (2006) Joint SOLAS-IMBER Ocean Carbon Research. Implementation Plan
- IPCC (2007) Climate Change 2007: The physical science basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor, and H.L. Miller (eds) Cambridge, U.K. and New York, U.S.A., Cambridge University Press
- Jones, C.E, Andrews, S.J., Carpenter, L.J., Hogan, C., Hopkins, F.E., Laube, J.C. Robinson, A.D., Spain, T.G., Archer, S.D. et al. (2011) Results from the first national UK inter-laboratory calibration for very short-lived halocarbons. *Atmos Meas Tech* 4:865-874.
- Keeling, C.D., Brix, H. and Gruber, N. (2004) Seasonal and long-term dynamics of the upper ocean carbon cycle at Station ALOHA near Hawaii. *Global Biogeochem Cycles* 18:10.1029/2004GB002227.
- Keeling, R.F. (2008) Recording Earth's vital signs. *Science* 319:1771-1772.
- Naqvi, S.W.A., Jayakumar, D.A., Narvekar, P.V., Naik, H., Sarma, V.V.S.S., D'Souza, W., Joseph, S. and George, M.D. (2000) Increased marine production of N<sub>2</sub>O due to intensifying anoxia on the Indian continental shelf. *Nature* 408:346-349.
- Sharp, J.H., Carlson, D.A., Peltzer, E.T., Castle-Ward, D.M., Savidge, K.B. and Rinker, K.R. (2002) Final dissolved organic carbon broad community intercalibration and preliminary use of DOC reference materials. *Mar Chem* 77:239-253.
- Taylor, J.K. (1987) Quality Assurance of Chemical Measurements. Lewis Publishers, Michigan, 328 pp.

- Weiss, R.F. (1981) Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography. *J Chromatogr* 19:611-616.
- Winn, C.D., Li, Y.-H., Mackenzie, F.T. and Karl, D.M. (1998) Rising surface ocean dissolved inorganic carbon at the Hawaii Ocean Time-series site. *Mar Chem* 60:33-47.

## **Appendix A. Research interests of WG members**

This appendix contains an outline of the Working Group member's research interests as they relate to N<sub>2</sub>O and CH<sub>4</sub> oceanic measurements.

**Mercedes de la Paz Arándiga:** My research deals with the dynamics of climatically active trace-gas cycling of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> and air–sea exchange in coastal and oceanic waters. As part of my postdoc research at the Oceanography department in Vigo, I initiated a new research line leading the project OSIMON for the development of the chromatographic technique for the simultaneous analysis of N<sub>2</sub>O and CH<sub>4</sub>. As a member of the Department of Oceanography at the IIM-CSIC I participated in several projects (e.g. MOC, CATARINA and GIFT) determining N<sub>2</sub>O and CH<sub>4</sub> in different areas of the North Atlantic Ocean. Currently, I am involved in the European project for Integrated non-CO<sub>2</sub> Greenhouse Observing Systems (InGOS), which aims to harmonize, exchange and disseminate data on the EU greenhouse gas budget. As a result of the work carried out in these projects, we have generated the following N<sub>2</sub>O and CH<sub>4</sub> databases, the availability of which is specifically detailed below:

1) MOC Project: analysis of N<sub>2</sub>O and CH<sub>4</sub> full water samples in the Atlantic section 8°N in May of 2010, which is a repetition of the WOCE–A06 section done in 1993.

2) GIFT series comprise of data from 3 stations throughout the east-west axis of the Gibraltar Strait where discrete samples were collected at 5 depths. This strategy is aimed at collecting samples within the different water bodies present in the Strait. N<sub>2</sub>O and CH<sub>4</sub> were already collected in Sept 2011, Nov 2011 and Feb 2012, and the time series is expected to continue in progress.

3) CATARINA project: The OVIDE repeated hydrography section, which connects the Portuguese coast with Greenland, was occupied during July 2012 to assess the vertical distribution of N<sub>2</sub>O and CH<sub>4</sub>. The OVIDE was conceived as a decadal experiment that commenced back in 1997 and has been sampled every two years ever since, but until 2012 no trace gases measurements were done. The next cruise is scheduled for summer 2014, and trace gas measurements are integrated in the cruise plan.

**Hermann Bange:** My research interest includes N<sub>2</sub>O and CH<sub>4</sub> measurements (both continuous surface and depth profiles) in order to estimate their oceanic emissions to decipher their oceanic distributions. Since 1991 I have been involved in several studies about N<sub>2</sub>O and CH<sub>4</sub> in the major basins of the Atlantic, Indian and Pacific Oceans as well as in the Baltic and North Seas and the Mediterranean Sea. I am coordinating the activities the Boknis Eck Time Series Station (SW Baltic Sea). Monthly measurements of N<sub>2</sub>O and CH<sub>4</sub> at the Boknis Eck site started in July 2005 and June 2006, respectively.

**John Bullister:** My scientific research interests regarding N<sub>2</sub>O and CH<sub>4</sub> include the large scale distribution of these compounds in the global ocean and potential changes in the distributions and air–sea fluxes of these compounds in the future. Our group is currently developing techniques for routinely including measurements of dissolved N<sub>2</sub>O in the water column as part of the CLIVAR/GO-SHIP Repeat Hydrography program. The goal of this program is to repeat (at ~ 10 year intervals) a set of key hydrographic sections in all of the major ocean basins. Hydrographic stations are occupied at ~ 60 nautical mile spacing along each of these sections, and collect full water column profiles of a variety of physical and chemical parameters. By including dissolved N<sub>2</sub>O measurements on these sections, we hope to be able to detect long-term changes in the global distribution of dissolved N<sub>2</sub>O in the ocean interior, and possible relationships to other ocean processes (expanding low-oxygen zones, changes in the nitrogen cycle) as well as changes in air–sea fluxes of this compound. Data from CLIVAR sections will be archived at: <http://cchdo.ucsd.edu/>. We also interested in dissolved methane in Arctic regions, and using

radiocarbon as a tracer to help determine the impact of methane released from warming permafrost on observed methane super-saturations in this region.

**Laura Farias:** Time series: ESP-OMZ

**Jan Kaiser:** Over the past 2 years, we have used Los Gatos Integrated Cavity Output Spectrometers to measure N<sub>2</sub>O, CH<sub>4</sub>, CO and CO<sub>2</sub> concentrations in seawater. The analysers have been deployed on four cruises (AMT20, October 2010, Southampton to Punta Arenas; D366, Summer 2011, Ocean acidification cruise around the UK [incl. North Sea, Skagerrak, North Atlantic, Irish Sea, Celtic Sea, English Channel]; ARK XXVII/1, June 2012 Bremerhaven to Spitsbergen [incl. Fram Strait]; AMT22, October 2012, Southampton to Punta Arenas) and run mostly successfully. Consequently, we have several large datasets, which are currently being analysed, calibrated and processed. Two PhD students and one research technician have been involved directly with the work at UEA. In the future, we are planning to participate in AMT23, October 2013, again from Southampton to Punta Arenas as part of the NERC-funded project RAGNARoCC. Additional funding for N<sub>2</sub>O/CH<sub>4</sub> related work on voluntary observing ships has been allocated to Watson & Schuster via the European FP7 infrastructure project INGOS. In addition to greenhouse gas abundance measurements in the ocean, I am interested in particular in using their isotopic composition as an additional constraint on sources and sinks. We have built an extraction system for N<sub>2</sub>O isotopologue measurements, which, in principle, could also be used for dissolved N<sub>2</sub>O concentration measurements (albeit at reduced precision).

**Annette Kock:** I have been involved in several N<sub>2</sub>O/CH<sub>4</sub> measurements campaigns in the tropical Atlantic Ocean, off Peru, in the Arabian Sea and in the Labrador Sea as well as at the Boknis Eck Time Series site. Moreover, I am especially interested in the effect of surfactants on trace gas exchange. Since the beginning of 2013 I am coordinating the activities of MEMENTO (the Marine Methane and Nitrous Oxide database).

**Cliff Law:** My interest is primarily in understanding the mechanisms of production and cycling of both gases via Lagrangian studies of surface phytoplankton blooms in NZ waters, laboratory culture experiments and isotope measurements. Current field measurements focus on methane production and emission from NZ methane hydrate seeps and in NZ coastal regions. The Biophysical Moorings Time Series programme has just ended and so we don't currently operate an open ocean CH<sub>4</sub> & N<sub>2</sub>O time-series in NZ, but opportunities exist on the Munida line (South Island, New Zealand, includes neritic, sub-tropical & sub-Antarctic water, bimonthly sampling for CO<sub>2</sub> & carbonate system), & also on a ship of opportunity transect between NZ and Japan (every 3-4 months). We have collected a large dataset (~3000 measurements) of surface water CH<sub>4</sub> measurements from around the New Zealand Economic Exclusion Zone over the last decade; this should be published in the next year and so the dataset will be available.

**Wajih Naqvi:** Time series: Candolim Time Series Station off Goa (Arabian Sea); Greenhouse gases in the ocean: Production, consumption and emission to the atmosphere of CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub> and halocarbons.

**Andy Rees:** Historical data-sets collected during JGOFS & SOLAS cruises to the Bellingshausen Sea (1992) and Mauritanian Upwelling (2009) have been submitted to Memento and British Oceanographic Data Centre (BODC), these data are freely available. More recently my group have collected data (N<sub>2</sub>O & CH<sub>4</sub>) over 12 months at the Plymouth Marine Laboratory time station site L4 (2011 & 2013 onwards), during UK ocean acidification cruises; around UK (2011), Arctic (2012) and Antarctic (2013). This data is or will soon be deposited at the BODC

and can be deposited with Memento in the near future. I have funding for N<sub>2</sub>O (only) analysis during the UK Shelf Seas Biogeochemistry Programme (3 cruises in the Celtic Sea during 2014) and in collaboration with Jan Kaiser funding for N<sub>2</sub>O and CH<sub>4</sub> analysis during the UK Greenhouse Gases Programme (3 cruises in the North Atlantic 2013 – 2015). To date all PML data has been collected by GC (ECD and FID), though we have funding to purchase 2 cavity ringdown analysers under the Greenhouse Gas funding which hopefully will be deployed from 2014 onwards.

**Gregor Rehder:** I have been mostly focusing on methane measurements covering a vast variety of areas in the past. However, in the framework of this proposal, the most important part is the effort in the Baltic Sea since I started to establish the volatile group at the Baltic Sea Research Institute. Since late 2009, we emended a continual measurement system for methane to the pCO<sub>2</sub> system on board the VOS Finnmaid running between Helsinki and Travemünde (Gülzow et al., 2011 and 2013). The system will be extended to the measurement of N<sub>2</sub>O by the end of the year, and is a designated component of the ocean component of the German Contribution to ICOS, with a long term commitment by the institute for at least a decade. It has a special situation in ICOS, as it is bridging the land efforts and the ocean component, and therefore it is the only ocean component measuring the non-CO<sub>2</sub> greenhouse gases (i.e. our favorites). We have also established “continuous” sampling at the central stations of the Arkona Basin, Bornholm Basin and Gotland Basin since 2 years. Cont. measurement here means organizing the sampling during all monitoring stations, i.e. 5 times per year. It is however not sure that we will / can continue this series.

**Philippe Tortell:** We have been collecting samples 3 x per year (~ Feb., June, Aug.) since 2007 of CH<sub>4</sub> and N<sub>2</sub>O along Line P in the Subarctic NE Pacific. A number of profiles were analyzed using a static head-space equilibration technique with a GC-MS. More recently, we've put a large amount of effort moving towards a fully automated purge and trap system. In terms of scientific questions, there are a number of interesting avenues related to the effects of declining ocean O<sub>2</sub> levels on N<sub>2</sub>O and CH<sub>4</sub> production, as well as continental vs. open ocean sources of these gases. I also think it would be extremely valuable to put together time-series observations comparing CH<sub>4</sub> and N<sub>2</sub>O in the Chilean, Hawaiian programs with the Line P data. This would give us some insight into patterns which may exist across different sub-regions of the Pacific Ocean.

**Rob Upstill-Goddard:** My research has involved evaluating the marine biogeochemical cycling of N<sub>2</sub>O and CH<sub>4</sub> since 1992. My research group has been involved in cruises in the Arabian Sea/NWIO, the Atlantic, Arctic and Southern Oceans and in the North Sea, as well as carrying out surveys of several UK estuaries and mangrove surrounding waters in India. We have estimated air-sea fluxes in all open ocean and coastal work and in addition have examined sediment cycling/fluxes in coastal work. We also carried out an evaluation of potential geological sources of atmospheric methane on the UK continental shelf and have an interest in N<sub>2</sub>O and CH<sub>4</sub> cycling at estuarine turbidity maxima. We are also involved in quantifying the controls on air-sea trace gas exchange and to that end we are examining CH<sub>4</sub> and N<sub>2</sub>O transfer velocities under varying environmental conditions using a laboratory gas exchange tank of our own design. A new project is involved in quantifying the role of coastal sediment denitrification in N<sub>2</sub>O cycling using laboratory mesocosm experiments. To date we have tended not to be involved in time-series measurements at a single station although there is potential to do that by incorporating CH<sub>4</sub> and N<sub>2</sub>O measurements into those currently made routinely at Newcastle as part of the "Dove Time Series", which involves long-term sampling of several variables at sites located approximately 10 and 20 km offshore of Newcastle in the North Sea, which are indicators of long-term ecosystem variability <http://www.mba.ac.uk/mecn/timeseries.htm>

**Sam Wilson:** My research involves measuring trace gases in the surface waters of oligotrophic North Pacific Ocean, mainly at the Hawaiian Ocean Time (HOT) series program station. The trace gases include N<sub>2</sub>O, CH<sub>4</sub>, H<sub>2</sub>, CO, and DMS. N<sub>2</sub>O measurements were conducted for 4 years in the mid-1990's at Stn ALOHA by John Dore and others and more recently by myself from 2008 onwards. In addition to the trace gas measurements we try to understand the microbial biogeochemical cycling that lead to their formation such as N<sub>2</sub> fixation, nitrification, and sinking particles.

**Guling Zhang:** My present research is mainly focused on the biogeochemistry of trace gases (CH<sub>4</sub> and N<sub>2</sub>O) in the rivers, estuaries, coastal and shelf waters of China Seas. Dissolved CH<sub>4</sub> and N<sub>2</sub>O have been observed monthly at the most downstream main channel station Xuliujing of Yangtze River since 2007 and at station Kenli of Yellow River since 2008 to monitor the long term variations of dissolved CH<sub>4</sub> and N<sub>2</sub>O in large Chinese rivers. Distributions and sea-to-air fluxes of CH<sub>4</sub> and N<sub>2</sub>O in the Yellow Sea, the Yangtze River Estuary and the East China Sea were determined during the period of 2001-2011. Annual CH<sub>4</sub> and N<sub>2</sub>O input to the East China Sea via Yangtze River, CH<sub>4</sub> and N<sub>2</sub>O exchange between sediment-water interface and between shelf and Kuroshio waters were also estimated and preliminary CH<sub>4</sub> and N<sub>2</sub>O budgets were obtained for the East China Sea.

Dr Ed Urban  
Executive Officer  
Scientific Committee on Oceanic Research  
College of Earth, Ocean, and Environment  
Robinson Hall  
University of Delaware  
Newark, DE 19716 USA

6 May, 2013

**Subject:** SOLAS support for SCOR Working Group on Dissolved N<sub>2</sub>O and CH<sub>4</sub> measurements:  
Working towards a global network of ocean time series measurements of N<sub>2</sub>O and CH<sub>4</sub>

Dear Ed,

With this letter SOLAS expresses strong support for the proposal to establish a SCOR Working Group on Dissolved N<sub>2</sub>O and CH<sub>4</sub> measurements, submitted by Hermann Bange, Sam Wilson, and others. The proposal is a response to the need for intercalibration and standardization of protocols for the measurement of oceanic dissolved N<sub>2</sub>O and CH<sub>4</sub>. This effort will enhance the scientific value of the existing database for these greenhouse gases, and improve the quality of the data going forward. Intercalibration and standardization will improve the utility of the database both for the study of processes controlling the distribution and cycling of these gases and for the detection of future ocean change. This is a frontier issue scientifically and one of the scientific priorities for SOLAS.

The SOLAS IPO, as you know, has limited financial resources with which it must support activities across the full scope of the SOLAS Science Plan. As a result, there are insufficient resources available for SOLAS to fund the proposed activity. SOLAS will support the group to the best of its ability, ensure access to the communications and organizational capabilities of the IPO, and help link the Working Group's activities to other ongoing SOLAS planning activities and scientific meetings. We expect that regular communiqués on the group's activities can be published via the SOLAS Newsletter and e-Bulletin.

The international team assembled for this Working Group is well qualified to carry out its mission and we hope that SCOR will be able to support the proposal. I look forward to this becoming one more area in which SOLAS and SCOR can continue our productive cooperation.

With very best regards,



Eric S. Saltzman  
Chair, SOLAS Scientific Steering Committee