Proposal for Scientific Committee on Ocean Research (SCOR) Working Group Dissolved N_2O and CH_4 measurements: Working towards a global network of ocean time series measurements of N_2O and CH_4

Overview

This proposal aims to improve and consolidate measurements of the greenhouse gases nitrous oxide (N_2O) and methane (CH_4) 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_2O and CH_4 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_2O and CH_4 in seawater including spectroscopy measurements. The second part of the project will be to conduct an overall assessment on the status of dissolved N_2O and CH_4 measurements in the global oceans. Key regions and recommendations on the necessary temporal and spatial scale for sampling will be identified. Conducting this N_2O and CH_4 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_2O and CH_4 in the marine environment?

In the Earth's atmosphere, N_2O and CH_4 account for 24% of the total radiative forcing associated with greenhouse gases. Whilst CO_2 is the most abundant greenhouse gas, N_2O and CH_4 are more virulent, respectively exerting ~300 and 25 times more radiative forcing than CO_2 over a period of 100 years (IPCC, 2007). The atmospheric burden of N_2O and CH_4 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_2O and CH_4 to the overlying atmosphere. The IPCC (2007) estimates oceanic CH_4 emissions range from 4-15 Tg CH_4 yr^{-1} and the rate of oceanic N_2O emissions to range from 1.8-5.8 Tg N yr^{-1}, 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_2O and CH_4 in seawater

N_2O and CH_4 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_2O and CH_4 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_2O and CH_4 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_2O and CH_4 measurements?
A number of laboratories throughout the world have developed analytical systems for measuring dissolved N_2O and CH_4 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_2 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_2 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_2O and CH_4 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_2O and CH_4.
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_2O and CH_4 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_2O and CH_4.
Beginning in Year 2 of the project, the SCOR working group will compile existing measurements of N_2O and CH_4 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_2O/CH_4 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 comittment 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_2O and CH_4 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_2O and CH_4 in the marine environment.

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

Associate members
- John Bullister (NOAA-PMEL, Washington, USA)
- Jan Kaiser (UEA, Norwich, UK)

- Annette Kock MEMENTO (GEOMAR, Kiel, Germany)
- Andy Rees (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_2O and CH_4
4. Establish framework for an N_2O/CH_4 ocean time series network and write a global oceanic N_2O/CH_4 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_2O and CH_4 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_2O and CH_4 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_2O and CH_4.

2. Initiate common protocols, including primary N_2O and CH_4 standards, working standards, and measurement of N_2O and CH_4 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_2O and 1.6 ppm for CH_4. These gas standards have an accuracy of ± 1 ppb (IMBER/SOLAS Implementation Plan 2006). The approximate total cost for standard gas mixtures of N_2O and CH_4 (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 intenational programmes such 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 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. In June-Dec 2014, a 2nd intercalibration exercise is planned to fulfill this part of the project Presentation of intercalibration results at SOLAS. In Year 3-4, the WG assesses our ability to track changes in N_2O and CH_4 concentrations in the marine environment.
2014	Feb: WG meeting in Hawaii, (followed by ASLO 2013)	
2015	Sept: WG meeting in Germany, (followed by SOLAS conf)	
2016	Feb: Publish recommendations for analysis and reporting	
2017	February: 3 year review and Working Group meeting followed by Ocean Sciences Publication of recommendation for N_2O/CH_4 Time Series Station Network	

Capacity Building

To help achieve the objectives of this proposal and build the capacity to improve and sustain accurate N_2O and CH_4 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_2O/CH_4 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_2 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_2 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_2O 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.