Oceanic Methane and Nitrous Oxide: The Present Situation and Future Scenarios

Workshop organizers: Sam Wilson (University of Hawaii), Bonnie Chang (University of Washington), Curtis Deutsch (University of Washington), John Kessler (University of Rochester), Tina Treude (University California Los Angeles), Dave Valentine (University California Santa Barbara), Bess Ward (Princeton University)

Aim: The overall aim of this workshop is to identify as a community the oceanic regions which are most susceptible to long-term changes in water-column methane and nitrous oxide concentrations. This assessment comes at a critical time as the ocean inventory of methane and nitrous oxide is anticipated to be affected by the ever-increasing effects of climate change which will thereby cause the emission of these greenhouse gases to the overlying atmosphere to vary. We will assess our ability as a global community to measure and predict these future changes by evaluating our biogeochemical understanding of the relevant processes, our analytical capabilities (*e.g*. laboratory and sensor-based measurements) and our observational capacities (*e.g*. ship and remote measurements) which all feed into our modeled predictions. The outcome of this workshop will be a report which lists the research priorities for both measuring and modeling future oceanic concentrations of methane and nitrous oxide.

Key Questions

- Where are the critical locations in the global oceans to measure dissolved methane and nitrous oxide in order to document long-term changes to the oceans as a source of these greenhouse gases?
- Do we have the analytical, modeling, and observation requirements to predict and measure changes in oceanic methane and nitrous oxide inventories over the appropriate time and space scales?
- To what extent do controlled laboratory measurements of microbial production and consumption of methane and nitrous oxide inform environmental measurements?

How does this workshop support and advance OCB research? With its emphasis on methane and nitrous oxide dynamics, the goals of this workshop are highly relevant to the Ocean Carbon and Climate Change Program. Out of the six current research priorities listed on the OCB website, at least four of them are directly related to the goals of this workshop, including carbon fluxes and processes, climate changes in ocean chemistry, and responses of microorganisms to a changing environment. By convening the scientific expertise on oceanic methane and nitrous oxide, the outcomes of the workshop will help the community identify the best approaches to understanding, measuring, and modeling the trace gas dynamics in future oceans.

Scientific Background

Background to the workshop: For the past four years (2013-2017), a group of 15-20 scientists have organized global intercalibration and intercomparison exercises to improve our analyses of oceanic methane and nitrous oxide. This exercise is currently being concluded and the results will be presented at the 2018 Ocean Sciences meeting in Portland, Oregon. The activity occurred as a Scientific Committee on Oceanic Research (SCOR) Working Group (#143). The specific work involved multiple exchanges of seawater samples for analysis by each laboratory and also the production of high-pressure primary gas standards by John Bullister and David Wisegarver at NOAA Pacific Marine and

Environmental Laboratory (PMEL). The standards were distributed to eleven laboratories globally (www.scor-int.org/SCOR_Publications/SCOR_143_Technical_Report). As a result of this activity, we have now addressed the analytical differences associated with the measurements and the inherent variability that arises from multiple independent laboratories conducting the analyses. Furthermore, we have established strong communications between many of the laboratories that regularly conduct at-sea measurements of dissolved methane and nitrous oxide. The proposed workshop represents the next step for a better comprehension of the production and consumption of methane and nitrous oxide in the global ocean. Therefore, in a sense, the workshop seeks to apply the improved analytical awareness to our observational capacity.

Background to nitrous oxide: Nitrous oxide is primarily considered to be inadvertently released during ammonia oxidation (nitrification) or nitrate reduction (denitrification) by both bacteria and archaea. However, the nitrogen cycle in relation to nitrous oxide production and consumption processes is now known to be much more complicated. For example, it is now known that nitrification and denitrification cannot be considered completely independent pathways despite their differences in oxygen tolerance (Figure 1). This workshop will specifically focus on the relationship between oxygen as a dominant driver of water-column nitrous oxide concentrations, whilst also considering the importance of microbial community composition, nutrient availability, and the wider nitrogen cycle. Therefore we will discuss the relationship between the production of nitrous oxide and oxygen concentrations for both laboratory-maintained cultures and field-derived measurements. The wider environmental context for such considerations is ocean deoxygenation which has serious implications for ocean and human health. Since nitrous oxide production increases as oxygen concentrations decreases (until a certain threshold value at which point net nitrous oxide consumption occurs) there are large ramifications to the water-column inventory of nitrous oxide with any changes to dissolved oxygen content (Figure 1). However there is much uncertainty about the production (and consumption) of nitrous oxide during nitrification, denitrification, and related processes. For example, it is unclear whether nitrous oxide production from bacterial nitrification increases exponentially or linearly with decreasing oxygen and it is also not clear whether there is a threshold value of oxygen that is representative of the point at which net nitrous oxide production switches to nitrous oxide consumption.

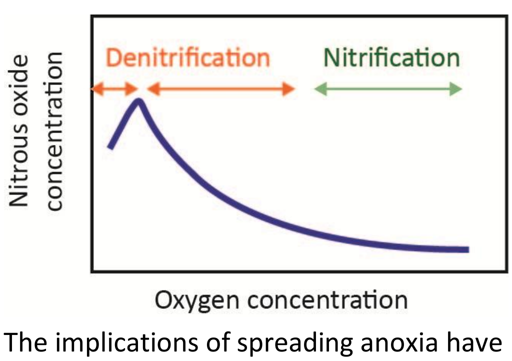

Figure 1. Nitrous oxide and oxygen. As oxygen concentrations decrease, there is a corresponding increase in nitrous oxide concentrations. The rate of increase is more rapid when denitrification becomes the dominant pathway. Below certain oxygen concentration, net nitrous oxide consumption occurs as the final step of denitrification (nitrous oxide to nitrogen) becomes more prevalent.

The implications of spreading anoxia have been recognized since the early measurements of nitrous oxide and were discussed by Codispoti et al. (2001). There has been a recent acceleration in scientific interest in this topic with articles directly looking at implications of deoxygenation on nitrous oxide including Bianchi et al. (2012), Landolfi et al. (2017), Martinez-Rey et al. (2015). However, it is unclear in the open ocean water-column whether emissions of nitrous oxide will increase or decrease as sub-anoxic conditions become more prevalent (Figure 2). The workshop will evaluate our mechanistic understanding of the relationship between ambient oxygen concentrations and the production of nitrous oxide. We will seek to relate this knowledge to our understanding and predictions of oxygen deoxygenation and nitrogen cycling.

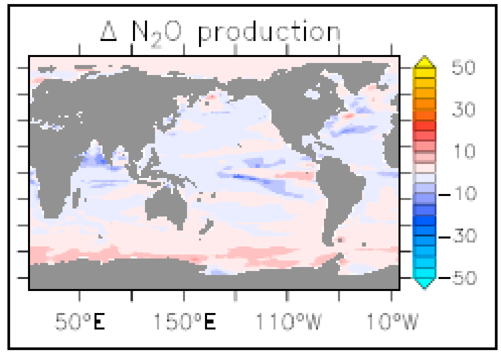

Figure 2. Predicted changes to the oceanic inventory of nitrous oxide under one set of model experiments (Landolfi et al., 2017). Overall, the authors predict a decline in oceanic nitrous oxide emissions by 2100 due to the decrease in organic matter export and human-driven changes in ocean circulation and atmospheric nitrous oxide concentrations.

Scientific background to methane: Similar to the mechanisms that influence nitrous oxide production and consumption, our understanding of the metabolic processes that produce and consume methane has evolved in the past decade. For example, it is now known that under certain conditions, methane can be produced aerobically by a wide variety of microorganisms which contributes to the small standing stock of methane in open ocean oxygenated waters (Karl et al., 2008). Below the sunlit surface waters and away from any benthic sources, methane is oxidized to threshold levels of approximately 0.5 nM (Valentine 2009). In contrast to the slow turnover of methane in the pelagic environment, along mid-ocean ridges and continental margins methane has a much different dynamic. This is due to the large amounts of methane which is stored in the form of gas hydrates, gaseous reservoirs, or dissolved in pore waters. Some portion of this benthic methane escapes the sediments and reaches the overlying ocean water column. The fate of this methane is a specific focus of the proposed workshop. Consideration will be given to the water-column sources *e.g*. ebulliton, advection, diffusion from the sediment, and *in situ* production, and the sinks *e.g*. methane oxidation and loss to the atmosphere. In particular, we are interested in the role of the water-column as a buffer to prevent methane from reaching the sea surface and being released to the atmosphere. In the oxygenated water-column, aerobic oxidation of methane is performed by methanotrophic bacteria. However, despite their important role for minimizing the release of methane to the atmosphere, the environmental factors that influence the efficiency of methane oxidation and how it varies between different locations and ocean current systems are not well-constrained (Steinle et al. 2015). Moreover, the conversion of methane to carbon dioxide by aerobic bacteria in the water column adds to the ocean acidification problem (Biastoch et al., 2011).

An increasing concern about the subsurface reservoirs of methane is their sensitivity to increases in temperature. This is particularly noteworthy in the northern latitudes where methane fluxes from the shelf seas have a high level of uncertainty. Furthermore, most observations derive from short-term expeditions and it is difficult to account for either short or long-term temporal variability. More recently, monitoring data derived from a cabled observatory was used to study the emission of methane gas bubbles off British Columbia (Römer et al., 2016). As part of Question #1, this workshop will discuss potential mechanisms for long-term monitoring of methane emissions from benthic habitats and its subsequent turnover within the water-column (Figure 3).

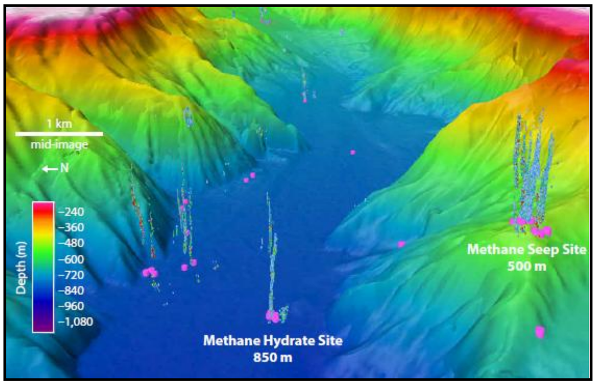

Figure 3. Location of methane bubbles emitted from hydrates and seeps in Astoria canyon off the coast of Oregon (Embley et al., 2017). Assessing our capacity for monitoring such emissions of methane from the seafloor and understanding the capacity of the water-column to act as a buffering mechanism to prevent the methane from reaching the sea-surface is a goal of this workshop.

Workshop outcomes: The primary objective of the workshop will be a White Paper that summarizes our current comprehension of oceanic nitrous oxide and methane and outlines the necessary observations, measurements, and modeling that are required to improve our understanding. This White Paper will be of use to the various Ocean Observing forums including the Integrated Ocean Observing System and the International Ocean Carbon Coordination Project. Since the White Paper will also include the perspective of microbiologists, the document will also form a connection between ocean chemistry and microbiology. A recent 'Microbes and Climate Change' workshop was hosted by AGU and ASM in 2016, however the workshop report did not outline potential scenarios for either methane or nitrous oxide and we wish to rectify this. It is expected that the White Paper will be turned into an open access peer-reviewed publication which will serve as the ultimate reference for the workshop scientific outcomes.

Workshop logistics

- **Nitrous oxide and/or methane.** The workshop organizers have discussed the advantages and disadvantages of having the workshop include both nitrous oxide and methane. The alternative scenario would be to focus solely on one of these trace gases since there are few identified biogeochemical links between methane and nitrous oxide. However, we feel that including both methane and nitrous oxide broadens the scientific expertise of the workshop participants such that new perspectives and opinions can be shared.
- **Workshop format and output.** The workshop would be held over a 3 day period with a potential date in the Fall 2018. It is anticipated that Day One would focus on nitrous oxide, Day Two on methane; and Day Three would be discussing observational and analytical capacity for both gases. Like most workshop agendas, this is an ambitious schedule, but successful outcomes are achievable with careful planning and exchange of material and discussion items prior to the workshop. Therefore, 2-3 months prior to the workshop we will host a Web-based conference call for all workshop attendees where we will present key documents and the framework for the workshop. This would facilitate the exchange of ideas and help finalize the workshop agenda. We also propose to ask all workshop participants to provide responses to 10 questions/statements concerning oceanic methane and nitrous oxide dynamics. The workshop participants will then be asked to

update their responses at the end of the meeting. The intention of this exercise is to improve the scientific input as a collective group of individuals. The workshop itself will include presentations and assessments of the most up-to-date knowledge concerning current and future scenarios of oceanic methane and nitrous oxide. To achieve this, the agenda will consist of invited talks by leading experts, panel discussions, and a poster session to increase the breadth and depth of presented material and to encourage input from and interaction among all workshop participants.

- **Budget.** We have based our draft budget on 50 participants and it being hosted at a convenient location on the U.S. West Coast, since 4 out of the 7 coorganizers are located in either California or Washington.

Item	Calculation	Cost
Food	$75 per person for 3 days for 50 people	$11,250
Travel & accomm for coorganizers	$2000 per person (for 7 people)	$14,000
Travel & accomm for invited speakers	$2000 per person (for 8 people)	$16,000
Travel & accomm for early career scientists	$1000 per person (for 10 people)	$10,000
Room rental	$500 per day	$1,500
Ground transportation	$200 per person for 13 people	$2,600
Incidentals	$500	$500
	Requested amount	$55,850

- **Letters of Support.** Attached are two letters of support for the workshop, from the international Surface Ocean - Lower Atmosphere Study (SOLAS) project and from the Scientific Commission on Oceanic Research (SCOR).

References

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28 November 2017

Dr. Sam Wilson
Department of Oceanography
University of Hawai'i at Mānoa
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Honolulu, HI 96822

Dear Sam:

I am writing to support your application to the Ocean Carbon and Biogeochemistry (OCB) program for a workshop on nitrous oxide and methane in the ocean. As you and your colleagues explain in the proposal, this workshop would build on the foundation of intercalibrations and method development conducted by the Working Group 143 on Dissolved N_2O and CH_4 measurements: Working towards a global network of ocean time series measurements of N_2O and CH_4, of the Scientific Committee on Oceanic Research (SCOR). It is timely to take this next step, given the new level of skill in measurements of methane and nitrous oxide, and the need for better understanding of the oceanic cycles of these compounds.

If your proposal to OCB is approved, you can apply to SCOR for support of scientists from developing countries to attend the workshop and can request to use any leftover funds from the WG 143 budget for the workshop.

I hope that your proposal is successful!

Best regards,

Edward R. Urban Jr.
SCOR Executive Director

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Xiamen, 22.11.2017

Subject: SOLAS Support for the workshop on "Oceanic Methane and Nitrous Oxide: The Present Situation and Future Scenarios" for 2018 OCB Activity Solicitation

Dear OCB Scientific Steering Committee,

With this letter SOLAS expresses strong support for the proposal to organize a workshop on "Oceanic Methane and Nitrous Oxide: The Present Situation and Future Scenarios" in response to the call for 2018 OCB scoping workshops.

The proposed workshop organized by Sam Wilson, Bonnie Chang, Curtis Deutsch, John Kessler, Tina Treude, Dave Valentine, and Bess Ward is aiming at identifying as a community the oceanic regions which are most susceptible to long-term changes in water-column nitrous oxide and methane. This assessment is most welcome since the ocean inventory of methane and nitrous oxide is anticipated to be affected by the ever-increasing effects of climate change which will cause the emission of these greenhouse gases to the overlying atmosphere to vary. This workshop directly addresses the research topics of Core Theme 1 on "Greenhouse gases and the oceans" from the SOLAS 2015-2015 Science Plan and Organisation: *Linking Ocean-Atmosphere Interactions with Climate and People.*
(http://www.solas-int.org/files/solas-int/content/downloads/Resources/SOLAS-SPO.pdf)

With its emphasis on methane cycling and nitrous oxide dynamics, the goals of this workshop are highly relevant to OCB's research priorities, including carbon fluxes and processes, climate changes in ocean chemistry, and responses of microorganisms to a changing environment. The outcomes of the workshop will be a report which will list the research priorities for both measuring and modeling future oceanic concentrations of nitrous oxide and methane. This will be instrumental to help the community identify the best approaches to understanding, measuring, and modeling the trace gas dynamics in future oceans.

The team assembled for organizing this workshop is extremely well qualified to make a success out of this initiative and we hope that OCB will be able to support this activity. We look forward to this becoming one area in which SOLAS and OCB can foster a productive cooperation.

With very best regards,

Dr. Véronique Garçon
Chair, SOLAS Scientific
Steering Committee

Dr. Li Li
Project Officer
SOLAS International Project Office