Authors Response to Reviewers

4 September 2020

Dear Dr. Wilson,

We are pleased to inform you that the open discussion of your following BG manuscript was closed: Title: Ideas and perspectives: A strategic assessment of methane and nitrous oxide measurements in the marine environment; MS No.: bg-2020-270; MS Type: Ideas and perspectives.

No more referee comments and short comments will be accepted. Now the public discussion shall be completed as follows. You - as the contact author - are requested to individually respond to all referee comments by posting final author comments on behalf of all co-authors no later than 25 Sept 2020 (final response phase). Please note that your revised manuscript should not be prepared at this stage.

The editorial support team

Copernicus Publications

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21 September 2020

To the editorial support team at Copernicus Publications.

Thank you for the opportunity to respond to the Reviewer's comments. We would particularly like to thank the three Reviewers for their thoughtful and constructive comments. We have included a point-by-point response on the following pages and revised the manuscript as appropriate.

Yours sincerely,

Sam Wilson, on behalf of all authors

Reviewer #1

The ocean is the net source of both CH4 and N2O, which are the second and third largest anthropogenic greenhouse gases. However, the air-sea flux of these gases remains uncertain, due mainly to the lack of sufficient reliable measurement of marine CH4 and N2O. It is thus of urgent need to further strengthen the observation of these greenhouse gases in the ocean. To this end, the authors proposed several perspectives of improving the current observation ability to better constrain and predict the marine CH4 and N2O flux. Overall, I feel these perspectives are essential and clearly stated. The manuscript has included the main findings of previous researches in this field.

Thank you for your comments

My main concern of the manuscript is that the three initiatives been proposed here are quite similar with the main ideas of the recent study by the authors themselves (i.e., Wilson et al., An intercomparison of oceanic methane and nitrous oxide measurements, 2018; Bange et al., A harmonized nitrous oxide (N2O) ocean observation network for the 21st Century, 2019).

Reviewer #1 makes the comment that the three initiatives (development of SOPs, intercomparison of seawater samples, and improved usage and output for a centralized data repository) mentioned in Section 7 'Outlook and Priorities' have already been written about in two previous manuscripts. This is a valid comment with regards to the SOPs as their need was first articulated by Wilson et al (2018) and now two years later they are again being advocated for. In our defense, the SOP documents are being produced at this very moment. The work that is currently being undertaken is listed in response to Reviewer #1's next comment.

We have now revised the third initiative that previously focused on improved use of a centralized data repository. The third initiative now highlights the need for a Global Data Product for CH_4 and N_2O. At the moment, the MEMENTO data repository collects CH_4 and N_2O concentrations which are then used by the modeling community. This activity has been very successful, but it occurs without the publication of any Data Product which would represent a quality controlled synthesis of all the concentration data that have been collected to that point. The absence of a Global Data Product impedes the progress of community-driven CH_4 and N_2O research on several levels as scientists measuring CH_4 and N_2O do not receive the appropriate acknowledgement for use of their datasets in Earth system models and there is no common Data Product for the modeling community to use. This situation for CH_4 and N_2O contrasts sharply with that of pCO_2 which releases Global Data Products on an annual basis via Surface Ocean CO_2 Atlas initiative. There are much fewer measurements of CH_4 and N_2O and it is envisaged that a Global Data Product for CH_4 and N_2O every 5 years would be sufficient.

We have revised the text and Lines 545-557 now read '*The third activity builds on the previous initiative and calls for the production of Global Data Products for dissolved CH_4 and N_2O measurements. To date, individual CH_4 and N_2O measurements are represented at the global scale by the MEMENTO database which has been very successful at compiling CH_4 and N_2O datasets and making them readily accessible to the modeling community. However, the current situation bypasses the important process of compiling a Global Data Product for dissolved CH_4 and N_2O which represents the public release of accumulated quality controlled datasets. The international marine carbon science community has widely embraced such an approach for fCO_2, by submitting data to the Surface Ocean CO_2 Atlas (SOCAT), which was initiated in response to the need for a quality controlled, publicly available, global surface CO_2 dataset (e.g. Bakker et al., 2016). Due to the fewer measurements, a similar data product for marine CH_4 and N_2O would be needed every ~5 years. We consider the production of Global Data Products for dissolved CH_4 and N_2O to be essential for supporting future global modeling efforts and to enhance and reward community engagement*'.

I would encourage more specific and further steps of practicing these initiatives, such as providing more detailed plans of developing standard operating protocols, preparing reliable reference gases and samples, planning for regular training exercises.

We are happy to inform Reviewer #1 that some these activities have been completed while some are still ongoing. A summary table of all these activities is included below for quick reference. The only activity mentioned by Reviewer #1 that is not currently being planned is cross-training exercises due to the ongoing coronavirus pandemic.

Activity	Date	Reference	Comments
Intercomparison excercises	2014-2015	Wilson et al. (2018)	Seawater collected from the Pacific Ocean and the Baltic Sea was distributed to twenty laboratories
Production of compressed gas standards	2015-2017	Bullister et al. (2016)	Two gaseous standards (low and high concentration) were shipped to twelve laboratories worldwide.
Establishing a common data portal	2009 onwards	Kock and Bange (2015)	The MEMENTO database provides an archive of CH_4 and N_2O datasets.
Community building workshop	2018	This manuscript	Sixty international scientists participated in the 2018 workshop which outlined the foundations for future activity

Standard Operating Protocols	In preparation	https://web.whoi.edu/methane-workshop/sops/	Nine SOPs are being drafted for publication of the Ocean Best Practice network
Production of consensus material for CH_4 and N_2O.	n/a	Currently being planned	This is being planned at the moment and a proposal has been submitted to NSF to fund this activity

It is also worthwhile to add some ideas for observations, e.g., episodic/ short-term event monitoring (cyclone disturbance, phytoplankton bloom. . .) and diel rhythm of emission in the coastal zone.
Reviewer #1 provides some suggestions here for discrete research projects for CH4 and N2O. However, for this overview perspective article, our preference is highlight the availability of analytical tools which can be used to answer any relevant research question and the need for increased coordination among the scientific community. There are multiple examples of this in the text:

Application of isotope analysis for methane as mentioned on Lines 241-282

Application of isotopes and isotopomers for nitrous oxide as mentioned on Lines 310-345

Eddy covariance flux towers as mentioned on Lines 499-502 '*…measurement campaigns in shallow water environments are amenable to the use of eddy covariance flux towers, and they have the potential to lever resources from existing observation networks, which in North America include the Long-Term Ecological Research network (LTER) and the National Estuarine Research Reserve (NERR) System (Novick et al., 2018). Indeed, such activities are already underway; an increasing number of flux towers are being equipped for CH4 measurements (Torn et al., 2019) and future efforts should focus on the inclusion of N2O'*

Development of mobile sampling platforms as mentioned on Lines 426-428 '*To determine the contributing factors and resolve the spatial distributions, mobile sampling platforms such as small vessels (Müller et al., 2016; Brase et al., 2017; Tait et al., 2017), and autonomous vehicles (Manning et al., 2019) are essential*'.

Meanwhile, to better understand and modeling marine CH4 and N2O, process study including molecular and isotope approaches from both lab culture and field study could also be added into the database.
We interpret this comment by Reviewer #1 to suggest that the MEMENTO data archive for CH_4 and N_2O concentrations could be extended to include other types of datasets including molecular (presumably DNA) and isotopes (presumably natural abundance water-column values).

We are strong advocates for data archival in nationally supported databases. These national data repositories lead the way in making datasets publicly available that adhere to FAIR data principles (Wilkinson et al., 2016). With regards to environmental molecular data, all genetic sequence data should be submitted to national databases (e.g., the National Center for Biotechnology Information (NCBI) GenBank database) that provide access to the most up-to-date comprehensive DNA sequence information. Similarly, water-column isotope and concentration datasets should be submitted to national oceanographic data repositories (e.g. BCO-DMO, BODC).

The MEMENTO data archive is a specialized collection of CH_4 and N_2O concentrations, and thereby facilitates the use of these trace gas data by the modeling community, as stated on Lines 172-173: "MEMENTO is now sufficiently mature to support descriptions of the broad-scale surface distributions of CH_4 and N_2O (e.g. Suntharalingam et al., 2012; Zamora and Oschlies, 2014; Buitenhuis et al., 2018; Battaglia and Joos, 2018)." The datasets should also be deposited in the appropriate national archives to ensure their long-term survival and adherence to FAIR data principles. When submitting data to MEMENTO, there is the option to cross-reference with complementary or co-collected datasets (e.g., DNA or isotope datasets) and also provide a link to publications that include this information.

Wilkinson, M.D., Dumontier, M., Aalbersberg, I.J., Appleton, G., Axton, M., Baak, A., Blomberg, N., Boiten, J.W., da Silva Santos, L.B., Bourne, P.E. and Bouwman, J., 2016. The FAIR Guiding Principles for scientific data management and stewardship. Scientific data, 3(1), pp.1-9.

In addition to CH4 and N2O observation, the standard measurement of the parameters for air-sea flux calculation, such as the gas transfer velocity or the eddy covariance, should be incorporated to derive accurate air-sea flux.

We interpret this comment by Reviewer #1 to suggest that there should be a uniform application of the gas transfer velocity. However, until there is an understanding of which parameterizations are most suitable for the different coastal environments with their inherently different characteristics of fetch, depth, and tidal currents, this is not possible.

Finally, given the profound but unclear impacts of the global change and human activities on the marine carbon and nitrogen cycles, research on CH4 and N2O cycling under various external forcing (i.e. deoxygenation, warming, acidification, eutrophication) are encouraged to be incorporated as a component of the database.

The manuscript mentioned the influences of different stressors in several places.

In the Introduction Lines 103-109 state '…*the marine environment is susceptible to an accelerating rate of anthropogenic change that will continue to modify the global cycles of carbon and nitrogen into the future. Environmental impacts on marine CH_4 and N_2O distributions include increasing seawater temperatures, decreasing concentrations of dissolved oxygen (O_2), acidification, retreat of ice and mobilization of carbon substrates from former permafrost, altering coastal run-off, and eutrophication (IPCC, 2019)*'.

In Section 3 on CH_4, Lines 220-2223 state '*Seabed CH_4 emissions are hypothesized to increase in a warming ocean through the decomposition of gas hydrates, the degradation of subsea permafrost under some high-latitude seas, and the increased biodegradation of sediment carbon (Romanovskii et al., 2005; Biastoch et al., 2011; Ruppel and Kessler, 2017; Borges et al., 2019)*'.

In Section 4 on N_2O, Lines 291-292 state '….*make upwelling regions a focal point for N_2O research, particularly since O_2 deficient ocean zones are increasing in size (Stramma et al., 2011)*'.

The O2 threshold for denitrification is still controversial, the redox potential is likely to be a better index to explore denitrification and other redox reactions relevant to N2O and CH4. In this sense, the measurements of ORP may be included in sampling campaign and database. For modelers, the ORP, which can be connected to electron flow and energy loss-gain, may be useful to advance models with new parameterizations of those chemoautotrophic microorganisms.

Reviewer #1 suggests that measuring the oxidation reduction potential (ORP) of a sample is likely to be more informative than O_2 concentrations. ORP measurements are more commonly associated with wastewater and sediments (e.g. Tumendelger et al 2019; Zhang et al., 2020) rather than the open ocean for several reasons: (1) Its not only O_2 concentrations that are useful but related parameters such as Apparent Oxygen Utilization (AOU) which inform about the deviation from theoretical equilibrium; (2) O_2 measurements are nearly always included on every hydrographic CTD cast and it is not evident that commercially available ORP sensors can withstand high pressures. Because of these factors, while we agree with Reviewer #1 that the O_2 threshold for denitrification is unresolved, we do not feel that ORP measurements represent a significantly better approach. The manuscript advocates for resolving the relationship between N_2O and O_2 with increased laboratory based studies. Lines 446-452 state '*For N_2O, laboratory studies quantifying microbial process rates, such as for nitrification and denitrification, are relatively few (e.g. Frame and Casciotti 2010; Santoro et al. 2011; Löscher et al. 2012; Ji et al. 2015; Qin et al., 2017). Consequently, models largely continue to use process rates optimized using water column concentrations of N_2O, O_2, and related nitrogen cycle quantities (e.g. Battaglia and Joos, 2018; Buitenhuis et al., 2018; Landolfi et al., 2017). Future model parameterizations for N_2O will require information on the variability of microbial process yields derived from culture studies with controlled varying conditions of O_2…'*..

Finally, Reviewer #1 also mentions modeling the flow of electrons but we feel that this is more relevant at the cellular level (e.g. Hink et al 2017) rather than the ecosystem level which is the focus of this manuscript.

Tumendelger et al (2019) Methane and nitrous oxide emission from different treatment units of municipal wastewater treatment plants in Southwest Germany. PloS one, 14(1), p.e0209763.

Zhang, X., Wang, X., Feng, W., Li, X. and Lu, H., 2020. Investigating COD and Nitrate–Nitrogen Flow and Distribution Variations in the MUCT Process Using ORP as a Control Parameter. ACS omega, 5, 4576-4587.

Hink et al (2017) Kinetics of NH3-oxidation, NO-turnover, N2O-production and electron flow during oxygen depletion in model bacterial and archaeal ammonia oxidizers, Environ. Microbiol., 19, 4882–4896.

The authors synthesized almost all recent documents, which are very useful for beginners who are interested in monitoring marine greenhouse gases. Overall, this is a well written comprehensive review.

Thank you

Some problems still, many of their statements or illustrations are not referred specifically to the corresponding figures, for example, Fig. 1a, 1b, 2a, 2b, 2c, 2d and 4. Figure 5a is not mentioned in the text.

All figures are now referenced in the text.

Reviewer #2

The authors here put together a comprehensive review of oceanic CH4 and N2O measurements and state of the knowledge. As an "ideas and prospectives" paper that is lead by the world's best in this field, this contribution is important. This is a timely review with respect to methane especially because of the recent global methane budget which just came out through the global carbon project. In terms of the journal required review criteria:

1. Does the paper address relevant scientific questions within the scope of BG? Yes, the scientific questions they bring up in the review is relevant to BG

2. Does the paper present novel concepts, ideas, tools, or data? As a review paper, they do not bring up novel concepts, but they bring together many concepts in a novel way so I think this paper checks this box.

3. Are substantial conclusions reached? They give three key initiatives they are pushing with their review. If these initiatives are followed, the scientific consequences for oceanic methane and N2O science to really move forward is clear.

4. Are the scientific methods and assumptions valid and clearly outlined? NA

5. Are the results sufficient to support the interpretations and conclusions? NA

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? NA
7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? For the most part, yes.
8. Does the title clearly reflect the contents of the paper? yes
9. Does the abstract provide a concise and complete summary? yes
10. Is the overall presentation well structured and clear? yes
11. Is the language fluent and precise? yes
12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? NA
13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? no
14. Are the number and quality of references appropriate? For the most part
15. Is the amount and quality of supplementary material appropriate? NA

Specific comments:
Line 42: reference should be 23, not 22
Thank you for catching this typographic error – it has now been changed.

Line 56: It was good to see the "numerical modeling" portion in the abstract. And modeling came up throughout the review, but it might be more informative to have a section dedicated to what is needed for these models, in a comprehensive way. Specifically, what sort of temporal and spatial resolution is needed? What sort of precision on measurements is required?
Reviewer #2 raises two important questions about the relationship between observations and models. Specifically Reviewer #2 queries (1) the level of temporal-spatial resolution and (2) the analytical uncertainty required to improve and constrain the models. Our response to these questions and instances where the text has been amended is provided below.

A useful contextual analysis of analytical uncertainty associated with CH_4 and N_2O can be provided by consideration of discerning long term trends. The ocean's response to increasing atmospheric concentrations of CH_4 and N_2O can be discerned over a timescale of 10 and 5 years respectively, with an analytical uncertainty of 1% (assuming all other parameters remain equal). Stated another way, if we wish to determine whether the oceanic inventory of dissolved CH_4 and N_2O is increasing at the same rate as the atmosphere, we need to wait 10 years for CH_4 and 5 years for N_2O, with an analytical uncertainty of 1%. This topic was also discussed in Bange et al (2019) which stated '*Detecting inter-annual N_2O signals will require a precision of better than 0.02 nmol L^{-1} (<0.2%)*'. We agree with Reviewer #2 that it is important the manuscript reflects the need for high quality CH_4 and N_2O measurements and the text has been amended to specifically include this. Lines 526-531 now read '*Currently, there is no defined level of analytical uncertainty for CH_4 and N_2O analysis that would facilitate the establishment of 'high quality' measurements. However, attaining an analytical uncertainty of ≤1% is considered achievable and for context this would permit the ocean's response to the increasing tropospheric CH_4 and N_2O mole fractions to be resolved on timescales of 10 and 5 years, respectively, assuming all other parameters remain constant*'. Achieving a <1% analytical uncertainty would facilitate more accurate inclusion of the mechanisms driving N_2O and CH_4 cycling in Earth System models, such as the relationship between N_2O yields and O_2 concentrations. However, care should be taken that the observations are providing the most useful data needed to improve the models. The manuscript already notes this by commenting that increased resolution of N_2O emissions in Earth System models would derive from greater constraint of the Michaelis-Menten kinetics associated with N_2O production as a dependent of O_2 concentration. The manuscript text states in Section 7 that this could be achieved from laboratory based measurements where Lines 450-454 read '*Future model parameterizations for*

N_2O will require information on the variability of microbial process yields derived from culture studies with controlled varying conditions of O_2, pH, temperature, and nutrients'.

The situation is different for the coastal environment which is one of the most uncertain and least predictable sources of methane and nitrous oxide. Using methane as an example, methane concentrations can vary by several orders of magnitude across spatial distances ranging from meters to kilometers. For example, Figure 5b shows methane concentrations increasing by at least 100-fold as depth decreases from 100 m to 5 m. In this setting, accumulating sufficient data points along coastal gradients to resolve the spatial distributions becomes a greater priority than achieving the highest possible analytical accuracy. We have amended the manuscript text to better reflect this and the legend for Figure 3 which illustrates the range of spatial-temporal phenomena that influences CH_4 and N_2O distributions now states on Lines 1226-1228 '*The low resolution oceanographic surveys are more likely to achieve a high level of analytical accuracy compared to high resolution coastal measurements, however this is compensated for by high temporal resolution achieved by underway sampling'.*

Reviewer #2 also queries whether the manuscript should have a section for the modeling work. However, the preference of the authors is to discuss the insights from models and observations together in the context of the different science themes. One of the workshop objectives was to promote closer collaboration between modelers and observationalists in order to create more complementary tools to answer the most pressing scientific questions.

Finally, we wish to point out that it is not just the analytical uncertainty in the CH_4 and N_2O measurements that requires improvement. As noted in the text on Lines 395-397 '*a fivefold variation in CH_4 emissions from a single system occurred when applying different parameterizations to the measured gradients in CH_4 (Ferrón et al., 2007)*'.

Line 141: check out: Gelesh, L., et al (2016). Methane concentrations increase in bottom waters during summertime anoxia in the highly eutrophic estuary, Chesapeake Bay, USA. Limnology and Oceanography 61, S253-S266.

The manuscript already cites Gelesh et al (2016) in Section 5 'CH4 and N2O in shallow marine environments'. This is our preferred location for the reference rather than long-term time-series observations.

Line 172: can you be more specific on what predictor variables are for methane and what are for N2O? Just separate the citations here for which gas they focus on and what they find are the predictors

This has now been clarified and Lines 174-178 now read '*Machine-learning mapping also recently identified the various contributions of physical and biogeochemical predictor variables for CH_4 (e.g. depth, primary production; Weber et al., 2019) and N_2O distributions (chlorophyll, sea surface temperature, apparent oxygen utilization, and mixed-layer depth; Yang et al., 2020)*.'

Line 190: "other processes". Please elaborate on what processes you mean here.

We apologize for the ambiguity associated with this sentence. The text has been revised and Lines 192-196 now state '*In the surface waters of tropical and temperate oceans, a number of factors contribute to the low supersaturation of CH_4 including direct aerobic production arising from the degradation of methylated sulfur compounds by phytoplankton (Klintzsch et al., 2019) and methyl phosphonate in phosphorus-depleted waters (Karl et al. 2008, Sosa et al., 2020), indirect production via grazing (Schmale et al., 2018) and abiotic photoproduction (Li et al., 2020).*

Line 197: check out: Lorensen, T.D., Grienert, J., and Coffin, R.B. (2016). Dissolved methane in the Beaufort Sea and the Arctic Ocean, 1992–2009; sources and atmospheric flux. Limnology and

Oceanography 61, 300-323. And, Lapham, L., et al (2017). Dissolved methane concentrations in the water column and surface sediments of Hanna Shoal and Barrow Canyon, Northern Chukchi Sea. Deep-Sea Research II doi: 10.1016/j.dsr2.2017.01.004.
The manuscript now includes the Lorenson et al. (2016) and the Lapham et al. (2017) references on Lines 204 and 205, respectively.

Line 220: check out: Lapham, L., et al (2013). Temporal variability of in situ methane concentrations in gas hydrate-bearing sediments near Bullseye Vent. Geochemistry, Geophysics, Geosystems 14, 2445-2459.
Thank you for the suggestion, this reference has now been included.

Line 242: check out: Grant, N., J., and Whiticar, M.J. (2002). Stable carbon isotopic evidence for methane oxidation in plumes above Hydrate Ridge, Cascadia Oregon Margin. Global biogeochemical cycles 16 (4), 1-13.
The Grant (2002) reference suggested by Reviewer #2 provides an in depth analysis of stable isotope methane values and concentrations to determine the quantitative fate of methane of entering water-column from the cold seeps of Hydrate Ridge. However, it doesn't include the broader analysis of higher order hydrocarbons which is the point of the text on Lines 246-249 '*For example, combining these measurements with the ratio of CH4 to higher order hydrocarbons (e.g. ethene (C2H4) and ethane (C2H6)) can be used to infer for example, whether the origin of the CH4 is thermogenic, sub-seafloor, or biogenic within the water column*'. The three references we have cited (Whiticar, 1999; Pohlman et al., 2009; Lan et al., 2019) all include the analysis of additional hydrocarbons in order to provide greater contextualization for the origin of methane.

Reviewer #3
In this paper, Wilson and colleagues provide a blueprint for future research effort into constraining N2O and CH4 emissions from the marine environment. Overall the paper is well written, clear and covers the main points of interest in this research area.
Thank you for these comments

One comment that I would make, is that for a perspectives paper on a global issue, the authorship is very USA/Europe heavy. I understand this is a reflection of the OCB workshop attendees, but to ensure global collaboration on this very important issue, engagement with researchers from across the world is needed.
We thank Reviewer #3 for highlighting the international representation of the authors host countries. The composition of the authors largely derives from participation in the October 2018 workshop, which was sponsored by the US OCB program. To facilitate participation in the workshop by non-US scientists, we secured funding from the Moore Foundation and to a lesser extent, SCOR. The number of participants from non-US and non-European countries was Chile (2), Canada (3), South Africa (1), and China (2). All workshop participants were invited to contribute to the manuscript. Overall, the workshop and accompanying manuscript tried to attain a balance of male/female, early/senior, and international representation. A primary goal of this workshop and its products was to identify research priorities and strengthen collaborations across the community. We agree that the workshop and accompanying manuscript represent only a fraction of the international research community conducting CH_4 and N_2O measurements and we will seek to further engage researchers across all nations as we move forward. For example, the Standard Operating Protocols (SOPs) are currently being written and draft documents will be posted to the website https://web.whoi.edu/methane-workshop/ for community input prior to publication. Their existence will be announced via the OCB and international

partner program newsletters, websites, and social media feeds. Also, a proposal was submitted to produce consensus material for dissolved methane and nitrous oxide in 2021, which will form the basis for another intercomparison exercise. We welcome the participation of scientists from all countries in both of these capacity building endeavors.

While the processes and mechanisms controlling CH4 and N2O production and emission are reasonably well understood, the main issue is a set of SOP and certified reference material to guide the research and provide robust and inter-comparable results. Engagement with the broader research community is needed to ensure these best practice protocols are taken up. It is encouraging to read these are currently being developed, but I do wonder how reference material of significant quantities can be produced and delivered to the various labs, particularly those using equilibrator-gas analyzer set ups which are becoming the standard (as opposed to discrete samplers with GC analysis). Some details on how this issue may be overcome would be welcomed.

Reviewer #3 brings up several topics in this comment. As mentioned in response to Reviewer #1, the SOPs are being written and they will be posted to the website https://web.whoi.edu/methane-workshop/ prior to uploading to the Oceans Best Practice Network. We would like to point out to Reviewer #3 that the 'consensus material' that will be produced for CH_4 and N_2O does not meet the necessary criteria to be classified as 'reference material'. The working definition of Consensus Material is '*Material with properties of a communally agreed value better than 1%, as measured by multiple laboratories*', while reference material is '*Material whose properties are sufficiently established so that it can be used for the calibration of an instrument or the assignment of values to samples*'. Finally, the consensus material is primarily intended to help with the analysis of discrete samples, not equilibrator systems. This does not mean that calibration of equilibrator systems for CH_4 and N_2O cannot be achieved with the help of consensus material. Indeed one of the SOPs (SOP#7: Underway system) specifically mentions the evaluation of equilibrator systems using discrete samples.

These are the only minor comments I have on this paper, and I look forward to seeing it in print.

Many thanks

Ideas and perspectives: A strategic assessment of methane and nitrous oxide measurements in the marine environment

Samuel T. Wilson[1], Alia N. Al-Haj[2], Annie Bourbonnais[3], Claudia Frey[4], Robinson W. Fulweiler[2,5], John D. Kessler[6], Hannah K. Marchant[7], Jana Milucka[7], Nicholas E. Ray[5], Parv Suntharalingham[8], Brett F. Thornton[9], Robert C. Upstill-Goddard[10], Thomas S. Weber[6], Damian L. Arévalo-Martínez[11], Hermann W. Bange[11], Heather M. Benway[12], Daniele Bianchi[13], Alberto V. Borges[14], Bonnie X. Chang[15,16], Patrick M. Crill[9], Daniela A. del Valle[17], Laura Farías[18], Samantha B. Joye[19], Annette Kock[11], Jabrane Labidi[20], Cara C. Manning[21#], John W. Pohlman[22], Gregor Rehder[23], Katy J. Sparrow[24], Philippe D. Tortell[21], Tina Treude[13,20], David L. Valentine[25], Bess B. Ward[26], Simon Yang[13], Leonid N. Yurganov[27]

[1]University of Hawai'i at Manoa, Daniel K. Inouye Center for Microbial Oceanography: Research and Education (C-MORE), Hawai'i, USA

[2]Boston University, Department of Earth and Environment, Massachusetts, USA

[3]University of South Carolina, School of the Earth, Ocean and Environment, South Carolina, USA

[4]University of Basel, Department of Environmental Science, Basel, Switzerland

[5]Boston University, Department of Biology, Massachusetts, USA

[6]University of Rochester, Department of Earth and Environmental Science, New York, USA.

[7]Max Planck Institute for Marine Microbiology, Department of Biogeochemistry, Bremen, Germany

[8]University of East Anglia, School of Environmental Sciences, Norwich, UK.

[9]Stockholm University, Department of Geological Sciences and Bolin Centre for Climate Research, Stockholm, Sweden

[10]Newcastle University, School of Natural and Environmental Sciences, Newcastle upon Tyne, UK

[11]GEOMAR Helmholtz Centre for Ocean Research Kiel, Düsternbrooker Weg 20, 24105 Kiel, Germany

[12]Woods Hole Oceanographic Institution, Marine Chemistry and Geochemistry, Massachusetts, USA,

[13]University of California Los Angeles, Department of Atmospheric and Oceanic Sciences, California, USA

[14]University of Liège, Chemical Oceanography Unit, Liège, Belgium

[15]University of Washington, Joint Institute for the Study of the Atmosphere and Ocean, Washington, USA

[16] National Oceanic and Atmospheric Administration, Pacific Marine Environmental Laboratory, Washington, USA

[17]University of Southern Mississippi, Division of Marine Science, Mississippi, USA
[18]University of Concepción, Department of Oceanography and Center for Climate Research and Resilience (CR2), Concepción, Chile
[19]University of Georgia, Department of Marine Sciences, Georgia, USA
[20]University of California, Los Angeles, Department of Earth, Planetary, and Space Sciences, Los Angeles, California, USA
[21]University of British Columbia, Department of Earth, Ocean and Atmospheric Sciences, British Columbia, Vancouver, Canada
[22]U.S. Geological Survey, Woods Hole Coastal and Marine Science Center, Woods Hole, USA
[23]Leibniz Institute for Baltic Sea Research Warnemünde, Rostock, Germany
[24]Florida State University, Department of Earth, Ocean, and Atmospheric Science, Florida, USA
[25]University of California Santa Barbara, Department of Earth Science, California, USA
[26]Princeton University, Geoscience Department, New Jersey, USA
[27]University of Maryland Baltimore County, Baltimore, USA
[#]Current address: Plymouth Marine Laboratory, Plymouth, UK

Abstract. In the current era of rapid climate change, accurate characterization of climate-relevant gas dynamics - namely production, consumption and net emissions - is required for all biomes, especially those ecosystems most susceptible to the impact of change. Marine environments include regions that act as net sources or sinks for numerous climate-active trace gases including methane (CH_4) and nitrous oxide (N_2O). The temporal and spatial distributions of CH_4 and N_2O are controlled by the interaction of complex biogeochemical and physical processes. To evaluate and quantify how these mechanisms affect marine CH_4 and N_2O cycling requires a combination of traditional scientific disciplines including oceanography, microbiology, and numerical modeling. Fundamental to these efforts is ensuring that the datasets produced by independent scientists are comparable and interoperable. Equally critical is transparent communication within the research community about the technical improvements required to increase our collective understanding of marine CH_4 and N_2O. An Ocean Carbon & Biogeochemistry (OCB) sponsored workshop was organized to enhance dialogue and collaborations pertaining to marine CH_4 and N_2O. Here, we summarize the outcomes from the workshop to describe the challenges and opportunities for near-future CH_4 and N_2O research in the marine environment.

1. Background

The most abundant greenhouse gases in the troposphere, excluding water vapor, are carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Together they account for more than 80% of the total radiative forcing (IPCC, 2013) and their current tropospheric mole fractions and rates of increase are unprecedented in recent Earth history (Ciais et al., 2013; Burke et al., 2020; Fig. 1a and 1b). While CO_2 is the most abundant of the three greenhouse gases, CH_4 and N_2O both have a higher warming potential than CO_2 (Montzka et al., 2011). To accurately constrain the contribution of CH_4 and N_2O to Earth's radiation budget and their representation in predictive models requires their sources and sinks to be quantified with high resolution at the global scale.

The oceans are a fundamental component of the global climate system and are a net source of tropospheric CH_4 and N_2O at the global scale, although local to regional budgets may include both source and sink components. There are far fewer marine measurements of dissolved CH_4 and N_2O than of dissolved CO_2 and while there is substantial international coordination with regard to CO_2 analysis, calibration and data reporting, no such coordination yet exists for CH_4 and N_2O (Wilson et al. 2018). Given the increasing prominence of climate change on scientific and societal agendas, greater coordination among the marine CH_4 and N_2O scientific community to provide more targeted measurements and increase the quality and interoperability of CH_4 and N_2O observations is particularly timely.

Despite the lack of an international coordinating framework, there have been important advances in our understanding of marine CH_4 and N_2O in numerous research disciplines, ranging from cellular metabolism and model microbial systems to large-scale modeling. For example, recent work identified novel microorganisms and metabolic pathways in the production of N_2O (Trimmer et al., 2016; Caranto and Lancaster, 2017) and CH_4 (Repeta et al. 2016; Bižić et al., 2020). Earth system models now incorporate improved N_2O parameterizations to better resolve the ocean's role in the global N_2O cycle (Battaglia and Joos, 2018). New techniques enable the discrimination of ancient and modern dissolved CH_4 (Sparrow et al., 2018) and the transfer of CH_4-derived carbon to other carbon pools (Pohlman et al., 2011; Garcia-Tigreros and Kessler, 2018). Other technological and analytical advances include improved near-continuous spectroscopic analysis that yield greater sampling resolution in surface waters (e.g. Gülzow et al., 2011; Arévalo-Martínez et al., 2013; Erler et al., 2015) and the deployment of analytical devices on robotic vehicles (Nicholson et al., 2018).

These scientific advances and an improvement in the quantity and quality of CH_4 and N_2O observations are timely given that large areas of both the open and coastal ocean remain under-sampled (Fig. 1c and 1d). Limited observations contribute to uncertainty in marine CH_4 and N_2O inventories, their rates of production and consumption, and their emissions. The uncertainty associated with CH_4 and N_2O inventories is particularly problematic given that the marine environment is susceptible to an accelerating rate of anthropogenic change that will continue to modify the global cycles of carbon and nitrogen into the future. Environmental impacts on marine CH_4 and N_2O distributions include increasing seawater temperatures, decreasing concentrations of dissolved oxygen (O_2), acidification, retreat of ice and mobilization of carbon substrates from former permafrost, altering coastal run-off, and eutrophication (IPCC, 2019). These impacts will undoubtedly alter future CH_4 and N_2O exchange with the atmosphere, but the directions and magnitudes of these modified fluxes remains insufficiently understood.

The need to resolve the marine CH_4 and N_2O inventories prompted an evaluation of the collective ability of the international scientific community to accurately determine the distribution and emissions of CH_4 and N_2O, and the determining physical-biogeochemical factors. This became the focus of a marine CH_4 and N_2O workshop hosted by the Ocean Carbon and Biogeochemistry (OCB) program at Lake Arrowhead, California in October 2018. The workshop considered CH_4 and N_2O equally on the same agenda, even though nearly all field, laboratory, and modeling studies examine these trace gases separately. The rationale for this dual approach is that CH_4 and N_2O share common considerations of the physical, chemical, and microbial processes that dictate their water-column distributions (Bakker et al., 2014; Bodelier and Steenbergh, 2014). In addition, many of the analytical procedures for quantifying CH_4 and N_2O and the subsequent data quality assurances share many common requirements. The opportunity to bring a large research community together to increase dialogue and encourage the cross-fertilization of ideas was thus considered very valuable. This article articulates the workshop outcomes framed in the context of current marine CH_4 and N_2O research and explores future research opportunities and challenges.

2. Coordination of oceanic CH_4 and N_2O measurements

Our understanding of the temporal and spatial distributions of oceanic CH_4 and N_2O derives from over five decades of open ocean and coastal observations, including targeted expeditions, repeat hydrographic surveys, and time-series monitoring, each of which has been crucial to the development of our current knowledge (Fig. 2). Targeted programs have enabled invaluable insights into the role of oxygen deficient zones in N_2O cycling (Babbin et al., 2015; Bourbonnais et al., 2017; Frey et al., 2020) and the exploration of CH_4-rich seeps and vents (Foucher et al., 2009; Suess, 2010; Boetius and Wenzhöfer, 2013). Basin-scale repeat hydrographic surveys (e.g. the international GO-SHIP program) have facilitated extensive water-column mapping to identify relevant water masses and evaluate ventilation rates (Fig. 2d) (de la Paz et al., 2017). Other oceanic surveys have focused exclusively on surface sampling, using continuous equilibrator systems connected to various gas analyzers to yield high-resolution surface concentration fields of CH_4 and N_2O (Gülzow et al., 2013; Erler et al., 2015; Kodovska et al., 2016; Thornton et al., 2016a; Pohlman et al., 2017). In contrast, sustained long-term time-series measurements of CH_4 and N_2O at fixed monitoring stations are relatively few, but they span a range of latitudes and biogeochemical provinces (Fig. 2a and 2b). The time-series observations provide the contextual background for seasonal and interannual variation that allow long-term temporal trends and episodic events to be identified and evaluated (Farías et al., 2015; Wilson et al., 2017; Ma et al., 2019). Overall, the majority of measurements enable the variability in marine CH_4 and N_2O to be quantified at the mesoscale or greater (i.e. from hundreds of kilometers to ocean basins), with monthly to annual resolution, but there are substantially fewer datasets at the sub-mesoscale level (i.e. <10 km and hours to days) (Fig. 3). A major reason for the limited sampling at the sub-mesoscale level is that it necessitates high-resolution measurements to resolve the heterogeneous variability that exists at these time-space scales. Such analyses have only recently become technically feasible (discussed in more detail in Section 6).

Until recently there has been no formal coordination of observations across the CH_4 and N_2O scientific community. In response to this, a Scientific Committee on Oceanic Research (SCOR) Working Group was initiated in 2014 entitled: '*Dissolved N_2O and CH_4: Working towards a global network of ocean time series measurements*'. A major goal of the SCOR Working Group was to unite the international community in joint activities conceived to improve and inform seagoing CH_4 and N_2O analyses. An important activity was the preparation and distribution of common, combined gaseous CH_4 and N_2O standards to twelve international laboratories, with the aim of improving and standardizing calibration (Bullister et al., 2017). A subsequent inter-comparison of discrete seawater samples included the use of these standards and revealed the variability between laboratories. While there were some encouraging results from the intercomparison, such as the agreement between individual laboratories using contrasting techniques, overall a large range was observed in CH_4 and N_2O concentration data generated by the participating laboratories (Wilson et al., 2018). Such analytical discrepancies weaken our collective ability as a community to evaluate temporal-spatial variability in marine CH_4 and N_2O. The discrepancies also highlighted the need for Standard Operating Protocols (SOPs) for CH_4 and N_2O analyses to facilitate standardization of sampling, measurement, and calibration, as well as the reporting of data and accompanying metadata in common repositories. The SOPs are currently in preparation with intended publication on the Ocean Best Practices network.

A data repository for oceanic CH_4 and N_2O data known as the MarinE MEthane and NiTrous Oxide database (MEMENTO) was established in 2009 (Bange et al., 2009; Kock and Bange, 2015). MEMENTO is now sufficiently mature to support descriptions of the broad-scale surface distributions of CH_4 and N_2O (e.g. Suntharalingam et al., 2012; Zamora and Oschlies, 2014; Buitenhuis et al., 2018; Battaglia and Joos, 2018). Machine-learning mapping also recently identified the various contributions of physical and biogeochemical predictor variables for CH_4 (e.g. depth, primary production; Weber et al., 2019; Fig 4b) and N_2O distributions (e.g. chlorophyll, sea surface temperature, apparent oxygen utilization, and mixed-layer depth; Yang et al., 2020; Fig. 4a). The application of gas transfer algorithms to the extrapolated oceanic CH_4 and N_2O distributions helped decrease the uncertainty in estimates of global air-sea exchange fluxes (Fig. 4c), thereby fulfilling one of the key goals of MEMENTO (Bange et al., 2009). Net global open ocean emissions of N_2O are now similarly estimated at 3–5 Tg N yr^{-1} by both Yang et al. (2020) and the Global Nitrous Oxide Project (Tian et al., 2020). In comparison, net global ocean CH_4 emissions from machine-learning mapping were estimated at 6–12 Tg CH_4 yr^{-1} (Weber et al., 2019), compared to 9–22 Tg CH_4 yr^{-1} in the most up-to-date CH_4 synthesis (Saunois et al., 2020). However, the narrower range for machine-learning derived CH_4 emissions retains high uncertainty in regions such as the Arctic, where emissions are highly heterogeneous and compounded by seasonal ice cover. Identifying the causes for uncertainty in high emission regions will greatly aid future sampling campaigns, as is discussed in the following sections.

3. Methane in marine environments

In the surface waters of tropical and temperate oceans, a number of factors contribute to the low supersaturation of CH_4 including direct aerobic production arising from the degradation of methylated sulfur compounds by phytoplankton (Klintzsch et al., 2019) and methyl phosphonate in phosphorus-depleted waters (Karl et al. 2008, Sosa et al., 2020), indirect production via grazing (Schmale et al., 2018) and abiotic photoproduction (Li et al., 2020). A recent study demonstrated that CH_4 production by cyanobacteria is linked to general cell metabolism and does not rely on the presence of methylated precursor compounds (Bižić et al., 2020). Deep within the ocean's pelagic interior, CH_4 is weakly undersaturated reflecting depletion via microbial oxidation (Reeburgh 2007; Weber et al., 2019). Towards the coastline, CH_4 supersaturation increases by orders of magnitude (Figure 5b), reflecting terrestrial inputs (e.g. river and groundwater), increased organic matter loading (Borges et al., 2018), and CH_4 diffusion and ebullition from shallow anoxic methane rich sediments (Zhang et al., 2008; Borges et al., 2016; Upstill-Goddard and Barnes, 2016). Supersaturation of CH_4 occurs frequently in the Arctic Ocean and its relatively shallow marginal seas with the most extreme values observed in the Eurasian Arctic (e.g. Shakhova et al., 2010; Damm et al., 2015; Kosmach et al., 2015; Thornton et al, 2016a; Lorensen et al., 2016; Fenwick et al., 2017; Lapham et al., 2017). Terrestrial and subsea permafrost are potential CH_4 sources to shelf waters in addition to CH_4 hydrates that are found in marginal shelves globally (Ruppel and Kessler, 2017). Large point source CH_4 emissions, such as seafloor gas seeps can be large sources to the atmosphere in small localized areas (e.g. Thornton et al., 2020), but these sites remain particularly difficult to parameterize in models. This reflects limited observations and a poor understanding of their spatial distributions, the driving mechanisms, and the wider context within the carbon cycle. For example, the upwelling of cold, nutrient-rich water that accompanies CH_4 ascending the water column stimulates CO_2 consumption by photosynthesizing phytoplankton, rendering such CH_4 seeps an overall net sink for climate-forcing gases (Pohlman et al., 2017). Recent work using thermal infrared satellite retrievals indicates increased high-latitude oceanic CH_4 release in late autumn, coincident with pycnocline breakdown and a deepening of the ocean mixed layer depth thereby bringing deep CH_4 to the surface (Yurganov et al., 2019). This is especially notable in the Kara and Barents Seas, but the remote observations have not yet been confirmed by surface ocean measurements which are difficult and therefore rare, except during the Arctic summer.

Seabed CH_4 emissions are hypothesized to increase in a warming ocean through the decomposition of gas hydrates, the degradation of subsea permafrost under some high-latitude seas, and the increased biodegradation of sediment carbon (Romanovskii et al., 2005; Biastoch et al., 2011; Lapham et al., 2013; Ruppel and Kessler, 2017; Borges et al., 2019). Effort is thus focused on quantifying the fraction of CH_4 generated in or released from marine sediments that ultimately enters the atmosphere, particularly on shallow continental shelves and in coastal ecosystems. Natural stable isotopes have been used to inform spatial and temporal changes in dissolved CH_4 concentrations (e.g. Pack et al., 2011; Mau et al., 2012; Weinstein et al., 2016; Leonte et al., 2017; Chan et al., 2019) and incubation experiments with added stable isotopes and radiotracers have helped elucidate how oxidation (anaerobically in sediments and aerobically in the water column), ebullition (where CH_4 pore water partial pressure exceeds sediment hydrostatic pressure), and subsequent bubble dissolution in the water column interact to mitigate CH_4 emissions to air (Steinle et al., 2015; Jordan et al., 2020). The information deriving from these various approaches is inherently different but complementary. Isotope tracer incubations provide snapshots of rates specific to the methanotrophic community and CH_4 concentration at the time of sampling, whereas concentrations and isotopic gradients are used to infer *in situ* rates integrated over space and time. A recent study deployed a remotely operated vehicle to examine the isotopic fractionation of CH_4 during bubble ascent and used this to constrain the extent of bubble dissolution (Leonte et al., 2018). This work demonstrated an experimental approach established for broadly constraining water column CH_4 cycling directly from a surface research vessel.

Despite the range of analytical and experimental approaches available, determining whether the origin of the emitted CH_4 is seafloor release or aerobic production in the upper water column remains problematic. To date there is no straightforward way to routinely distinguish between seafloor derived and water column generated CH_4 for all locations. Even so, stable carbon and hydrogen isotope measurements (i.e. $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4) combined with ancillary data may provide valuable source information. For example, combining these measurements with the ratio of CH_4 to higher order hydrocarbons (e.g. ethene (C_2H_4) and ethane (C_2H_6)) can be used to infer for example, whether the origin of the CH_4 is thermogenic, sub-seafloor, or biogenic within the water column (Whiticar, 1999; Pohlman et al., 2009; Lan et al., 2019). Continuous shipboard measurement of CH_4 isotopes in surface water (e.g. Pohlman et al., 2017) and in the atmospheric boundary layer (Pankratova et al., 2019; Berchet et al., 2020) are now possible and they have been used in combination with atmospheric inversion models to characterize and discriminate marine-emitted CH_4 from other sources (Berchet et al., 2020). Application of this method to land-based monitoring stations appears promising for apportioning CH_4 emissions from various marine regions and sources (Thonat et al., 2019). Additionally, in regions where aerobic CH_4 oxidation is substantial, the resulting isotopic fractionation generates measurable vertical and/or horizontal seawater gradients that can also be used to identify contrasting biogenic CH_4 sources (Leonte et al., 2020). However, the general overlap in isotope compositions of sediment CH_4 (e.g. Thornton et al., 2016b; Sapart et al., 2017) can complicate purely isotope-based determinations of sources.

Measurements of the natural radiocarbon content of dissolved oceanic CH_4, while being highly specialized and requiring substantial amounts of ship time and processing (Kessler and Reeburgh, 2005; Sparrow and Kessler, 2017), provide valuable source information because the ^{14}C-CH_4 measurements are normalized to the same $\delta^{13}C$ value and are unaffected by the extent of oxidation. The bubbles sampled from hydrate and active seafloor seeps are largely devoid of radiocarbon (Pohlman et al., 2009; Kessler et al., 2008; Douglas et al., 2016). However, CH_4 in sediments can also be derived from more modern or recently deposited organic material and an exact determination of individual contributions is hard to achieve (Kessler et al., 2008; Sparrow et al., 2018). The powerful insights made by radiocarbon-CH_4 investigations would be further strengthened by concurrent sampling of other analytes that offer CH_4 source information, such as clumped isotopes. Isotope clumping, the co-occurrence of two or more of the less abundant isotopes in a molecule (e.g. ^{13}C and ^{2}H or ^{1}H and ^{2}H), provides unique information on marine CH_4 sources (Stolper et al., 2014; Wang et al, 2015; Douglas et al., 2017; Young et al., 2017; Labidi et al., 2020). In this approach, the isotopic deviations in samples from their random probability distributions can give insight into formation temperature and the extent of biochemical disequilibrium. However, the sample size required for a clumped isotope analysis in the oceanic environment away from areas of seafloor emission is large and exceeds the already demanding volume requirements for ^{14}C analyses by 1–2 orders of magnitude (Douglas et al., 2017). While the requirement of large sample size and lengthy measurement time currently preclude their more widespread application, clumped isotope measurements offer future promise in refining our understanding of the processes of marine CH_4 production and consumption.

4. Nitrous oxide in marine environments

The large-scale spatial distribution of N_2O in the global ocean is reasonably well-established. The highest open ocean N_2O values are in upwelling environments, where concentrations extend up to micromolar levels (Arévalo-Martínez et al., 2015) and production rates can be as high as 120 nM d^{-1} (Frey et al., 2020). The highly elevated N_2O concentrations can be proximal to regions with some of the lowest recorded N_2O concentrations, in the cores of O_2 deficient zones. This coexistence of the highest and lowest observed N_2O concentrations over vertical distances of tens of meters make upwelling regions a focal point for N_2O research, particularly since O_2 deficient ocean zones are increasing in size (Stramma et al., 2011). In contrast, in the surface waters of the expansive oligotrophic ocean gyres, N_2O is weakly supersaturated (103-105%) with respect to atmospheric equilibrium (Weiss et al., 1992; Wilson et al., 2017, Charpentier et al., 2010). Nitrous oxide becomes more highly saturated in the surface waters of equatorial upwelling regions due to the upward advection of N_2O-rich waters (Arévalo-Martínez et al., 2017). For the Arctic Ocean, the data indicate low net N_2O emissions, with some areas acting as net N_2O sources and others as N_2O sinks (Fenwick et al., 2017, Zhang et al., 2015).

Several parameters control net N_2O emissions from the ocean, including temperature, salinity, dissolved O_2, apparent oxygen utilization (AOU), nutrients, and microbial community abundance and composition. A recent modeling study trained with just three of these variables (chlorophyll, O_2, and AOU) accounted for 60% of the observed variability in oceanic N_2O concentrations (Yang et al., 2020; Fig. 5a), highlighting the importance of N_2O in productive upwelling systems. Correlations between N_2O and environmental variables provide some insight into the factors controlling its distribution, but they provide no information about the microorganisms or metabolic pathways involved. Microbial production of N_2O occurs during the metabolic processes of nitrification and denitrification (Stein and Yung, 2003). To determine which process dominates N_2O production at any given location requires the application of multiple methodological approaches, ideally in parallel.

One of the most commonly used approaches is the incubation of discrete water samples under *in situ* conditions with stable isotope (^{15}N) addition such as ^{15}N enriched NH_4^+, NO_2^- or NO_3^- to measure N_2O production rates from nitrification and denitrification (e.g. Ji et al., 2017). These approaches also provide insight into the microorganisms involved. For example, N_2O resulting from archaeal NH_4^+ oxidation is mostly formed from a combination of NH_4^+ and another N compound (e.g. NO_2^-) whereas bacteria produce N_2O from NH_4^+ alone (Santoro et al., 2011, Stieglmeier et al., 2014; Carini et al. 2018; Lancaster et al., 2018; Frey et al. 2020). Unfortunately, as with all incubation-based approaches ^{15}N techniques are subject to bottle artifacts, and the strong dependence of N_2O production and consumption on ambient O_2 increases the potential for contamination during the collection and manipulation of anoxic deep seawaters. Incubation based rate measurements are also compromised by abiotic N_2O production via chemodenitrification, specifically the reduction of NO_2^- coupled to Fe^{2+} oxidation, as observed in high Fe environments (Ostrom et al., 2016; Buchwald et al., 2016; Wankel et al., 2017). These issues highlight the need for incubation techniques that mitigate the effect of experimental artifacts (Stewart et al., 2012).

In addition to isotope addition and incubation, natural abundance water-column measurements of N_2O concentrations, isotopes, and isotopomers yield valuable rate and process information. These measurements are free from experimental artifacts and can be used to integrate over appropriate temporal and spatial scales. For example, nitrification in sunlit waters has been inferred from N_2O distributions (Dore and Karl, 1996), and N_2O production close to the ocean surface is a large contributor to the uncertainty in oceanic N_2O emissions (Ward et al., 1982; Zamora and Oeschlies, 2014). Isotopomers are isomers having the same number of each isotope of each element but differing in their structural positions. Nitrous oxide isotopomers are increasingly used, sometimes in combination with box models, to estimate the rates of different N_2O production pathways, in the upwelling systems off southern Africa (Frame et al., 2014) and Peru (Bourbonnais et al., 2017). There is however some disagreement about whether isotopomer signatures are robust indicators of the formation pathway (Yoshida and Toyoda, 2000; Sutka et al., 2006) or whether there is fractionation during production (Schmidt et al., 2004; Casciotti et al., 2018). Greater clarity is therefore required in the use of N_2O isotopes and isotopomers to infer metabolic pathways of N_2O formation. Notwithstanding this issue, field measurements of N_2O isotopes and/or isotopomers have the potential to greatly increase current experimental capabilities and robustness (Yu et al., 2020). However, the development of spectroscopic gas analysis systems that have been so advantageous to CH_4 research has been slower for N_2O. This is due to the higher costs and the increased complexity of the laser systems, although progress is being made to improve instrumental precision, and to decrease matrix effects and spectral interferences (e.g. Harris et al., 2019).

A better understanding of the microorganisms responsible for N_2O production and consumption is fundamental to deriving more accurate estimates of process rates. For example, the metabolic activity of ammonia oxidizing archaea can exceed that of ammonia oxidizing bacteria in the ocean (Santoro et al., 2010; Löscher et al., 2012; Fuchsman et al., 2017). The differing sensitivities of these archaea and bacteria to dissolved O_2 (Stahl and de la Torre, 2012; Hink et al., 2017) are a critical factor in evaluating the microbial response to changing environmental conditions, as shown for the terrestrial environment (Prosser at al., 2020). Therefore, to understand the impact of deoxygenation on oceanic N_2O emission requires a better understanding of both archaeal and bacterial metabolisms and their environmental niches. Field-based sequencing not only characterizes the community but can highlight potential metabolic pathways when they might not otherwise be inferred. For example, transcripts encoding for N_2O consumption (nosZ) have repeatedly been identified in the oxic water column, despite denitrification being an anaerobic metabolic process (Wyman et al., 2013; Sun et al., 2017). The transcription of nosZ has been also located in highly dynamic O_2 permeable coastal sediments (Marchant et al., 2017). Denitrification under aerobic conditions is attributed to fluctuations in O_2, NO_3^-, organic matter and other parameters that affect the availability of electron donors and acceptors which ultimately influences whether a coastal environment is a net source or sink of N_2O, as discussed in the next section.

5. CH_4 and N_2O in shallow marine environments

Coastal and other shallow (<50 m) marine systems are globally relevant CH_4 and N_2O source regions. However, their emission rates to the atmosphere are weakly constrained in comparison with the open ocean. Several factors contribute to the uncertainty, including the high diversity of coastal and shallow marine ecosystems and lack of consistency in adequately defining them, locally heterogeneous conditions causing strong spatial and temporal concentration gradients, highly uncertain spatial distribution of CH_4 seeps, a bias towards studies in the northern hemisphere, and incomplete or sometimes inappropriate sampling strategies (Al-Haj and Fulweiler, 2020). Until these issues are resolved it will remain difficult to adequately define the contribution from shallow marine systems to global CH_4 and N_2O budgets. An important illustration of this is reflected in the prevailing view that large geological sources (e.g. seeps, mud volcanoes, and hydrates) are the main contributors to marine CH_4 emissions (Ciais et al., 2013). The most recent modeled estimate of global marine CH_4 emissions (6–12 Tg CH_4 yr^{-1}) reported that near-shore environments (depths of 0–50 m) contribute a large and highly uncertain diffusive flux (Weber et al., 2019). A study of coastal ecosystems, in this case defined as shelf, estuarine, and tidally influenced rivers, estimated them to contribute 7 Tg CH_4 yr^{-1} (Anderson et al., 2010) while another estimated 1–7 Tg CH_4 yr^{-1} for estuaries alone (Borges and Abril, 2011). Similar uncertainties exist for N_2O. Estimates of coastal N_2O emissions (which include coastal, estuarine, and riverine sources) range from 0.1–2.9 Tg N yr^{-1} (Ciais et al., 2013), although a recent review of N_2O production across a range of estuarine habitats placed N_2O fluxes at the lower end of these estimates (0.17–0.95 Tg N yr^{-1}) (Murray et al., 2015). Based on these data, coastal systems account for around one third of total marine N_2O emissions (Yang et al., 2020).

The direct quantification of CH_4 and N_2O emissions from shallow coastal ecosystems has historically involved using gas concentrations measured in discrete water and air samples combined with a gas transfer velocity (k_w). For the coastal and open ocean, the dominant driver of gas exchange is wind speed (e.g. Nightingale et al., 2000; Wanninkhof, 2014) whereas in nearshore, shallow water environments the interaction of water, depth, and tidal current speeds may be a major contributor to near surface turbulence. Several k_w parameterizations are now in use for coastal waters (e.g. Raymond and Cole 2001; Kremer et al., 2003; Zappa et al., 2003; Borges and Abril, 2011; Ho et al. 2011; Rosentreter et al., 2017; Jeffrey et al., 2018) which increases the uncertainties associated with CH_4 and N_2O emissions. For example, a fivefold variation in CH_4 emissions from a single system occurred when applying different parameterizations to the measured gradients in CH_4 (Ferrón et al., 2007).

To constrain emissions over small areas, continuous air-sea fluxes can be measured using free-floating chambers (e.g. Bahlmann et al., 2015; Rosentreter et al., 2018; Yang et al., 2018; Murray et al., 2020), but issues related to turbulence modification may still generate flux artifacts (Upstill-Goddard, 2006). To overcome these problems in the future, a greater reliance on direct and robust continuous techniques for air-sea flux measurement, such as eddy covariance (e.g.

Podgrajsek et al., 2016), that avoid any need for k_w, will be necessary. Eddy-covariance measurements also capture both diffusive and ebullitive flux components (Thornton et al., 2020). Combining this approach with new analytical techniques such as cavity enhanced absorption spectroscopy (CEAS) and non-dispersive infrared (NDIR) should continue to improve the quality of CH_4 and N_2O flux estimates (McDermitt et al., 2011; Nemitz et al., 2018; Maher et al., 2019). Indeed, eddy flux towers aboard ships (Thornton et al., 2020) and in coastal locations (Yang et al., 2016; Gutiérrez-Loza et al., 2019) are now being equipped with CH_4 instrumentation that enables the integration of CH_4 fluxes over large areas. There are fewer N_2O flux estimates made with CEAS and NDIR and the implementation of N_2O sensors on eddy flux towers remains limited. Recently, N_2O emissions from Eastern Boundary Upwelling Systems were quantified using inversion modeling based on atmospheric measurements from coastal monitoring stations highlighting the potential of this approach to constrain N_2O emissions from remote oceanographic regions that have significant spatial and temporal heterogeneity (Ganesan et al., 2020; Babbin et al., 2020). Inverse modeling of atmospheric measurements was also recently used to constrain CH_4 emissions from the East Siberian Arctic Shelf (Tohjima et al., 2020)

Coastal measurements of CH_4 and N_2O also require the collection of ancillary data such as water-column depth, tidal motions (Rosentreter et al., 2018; Huang et al., 2019; Pfeiffer-Hebert et al., 2019), and other information relating to diel processes (Maher et al., 2016). Such data are important because for example, the magnitude of CH_4 and N_2O fluxes vary over a diel period depending on the redox environment as a result of tidal effects and changes in inorganic N and O_2 availability (Seitzinger and Kroeze, 1998; Call et al., 2015; Vieillard and Fulweiler, 2014; Maher et al., 2015; Murray et al., 2015; Foster and Fulweiler, 2019). The magnitude of CH_4 and N_2O fluxes also varies over longer temporal scales (seasonally to yearly) due to additional factors such as groundwater inputs, adjacent land-use, dissolved O_2, organic matter content and quality, and macrofaunal distributions (Barnes and Upstill-Goddard, 2011; Upstill-Goddard and Barnes, 2016; Gelesh et al., 2016; Bonaglia et al., 2017; Borges et al., 2018; Wells et al., 2018; Ray et al., 2019; Al-Haj and Fulweiler, 2020; Reading et al., 2020). To determine the contributing factors and resolve the spatial distributions, mobile sampling platforms such as small vessels (Müller et al., 2016; Brase et al., 2017; Tait et al., 2017), and autonomous vehicles (Manning et al., 2019) are essential. Recent improvements in gas sensors and in technology such as sonar and ebullition sensors will further increase our ability to measure dynamic fluxes (Maher et al., 2019; Lohrberg et al., 2020). Improvements to the quality and quantity of CH_4 and N_2O measurements in coastal systems will enable the development of iterative forecast models, further improving estimates of global coastal CH_4 and N_2O fluxes.

6. Leveraging culture studies to further our ecosystem understanding

A more complete understanding of marine CH_4 and N_2O necessitates closer integration between biogeochemistry, model requirements, and targeted microbiological studies involving both single microorganism isolates and enrichment cultures. Marine CH_4 and N_2O budgets deriving from both 'bottom-up' (e.g. emissions inventories, ocean and terrestrial process models) and 'top-down' (e.g. inverse analyses of atmospheric trace-gas measurements) approaches would greatly benefit from more highly constrained metabolic processes. Specifically, this includes rates of CH_4 or N_2O production and consumption for key model microorganisms, and the kinetic parameters associated with these metabolic rates. Reliable inventories of key microbially mediated process rates will improve the robustness of Earth System models used for predicting climate-mediated changes to marine CH_4 and N_2O emissions.

For N_2O, laboratory studies quantifying microbial process rates, such as for nitrification and denitrification, are relatively few (e.g. Frame and Casciotti 2010; Santoro et al. 2011; Löscher et al. 2012; Ji et al. 2015; Qin et al., 2017). Consequently, models largely continue to use process rates optimized using water column concentrations of N_2O, O_2, and related nitrogen cycle quantities (e.g. Battaglia and Joos, 2018; Buitenhuis et al., 2018; Landolfi et al., 2017). Future model parameterizations for N_2O will require information on the variability of microbial process yields derived from culture studies with controlled varying conditions of O_2 (Goreau et al. 1980, Frame and Casciotti 2010, Löscher et al. 2012; Ji et al., 2018), pH (Breider et al., 2019; Hopkins et al. 2020), temperature, and nutrients. Automated incubation systems have measured N_2O production kinetics and yield as functions of the concentrations of O_2 and total ammonia nitrogen (Molstad et al., 2007; Hink et al., 2017). Quantifying the physiology of relevant microorganisms and connecting them to environmental characteristics will provide insights into why, for example, some shallow marine habitats act as N_2O sinks while others are N_2O sources, or how N_2O is produced in well oxygenated open-ocean waters, as compared to oxygen deficient zones.

For CH_4, a key requirement to relate *in situ* CH_4 production with transport to atmospheric emissions is our ability to accurately determine rates of CH_4 oxidation. Fundamental issues include the challenges of cultivating methanotrophs and of replicating environmental conditions such as pressure and the chemistry of CH_4 gas bubbles. The increased emphasis on CH_4 dynamics in shallow water environments highlighted in Section 5, must be supported by culture-based measurements of CH_4 oxidation that control for temperature, O_2 and other important variables. In comparison to CH_4 oxidation, culture-based studies are used increasingly to identify organisms capable of aerobic CH_4 production and their underlying metabolic pathways (Carini et al., 2014; Klintzsch et al; 2019; Bižić et al., 2020).

Specific cellular yields and consumption rates of CH_4 and N_2O are not the sole objective of culturing experiments. Cultivation of microorganisms involved in CH_4 and N_2O production and consumption provides vital information into the physiology, metabolism, and interactions of environmentally relevant clades. When combined with genomic approaches, insights can therefore be gained into the diversity and global distribution of organisms involved in CH_4 and N_2O cycling. For CH_4 some unexpected physiologies have been revealed (Ettwig et al., 2010; Haroon et al., 2013; Ettwig et al., 2016), which has directed research into sources and sinks of CH_4 in the natural environment. Similarly, our understanding of how and when ammonia oxidizers produce N_2O has been facilitated by studies of cultured nitrifiers and detailed analysis of their biochemistry (Stahl and de la Torre, 2012; Caranto and Lancaster, 2017). Recent combinations of cultivation studies with environmental genomics, albeit largely for terrestrial systems, have revealed a variety of denitrifiers, many of which are only involved in specific denitrification steps (Ganesh et al., 2014; Lycus et al, 2017; Hallin et al, 2018; Marchant et al., 2018; Conthe et al, 2019).

7. Outlook and priorities for marine CH_4 and N_2O measurements

This perspectives article has assessed the collective ability of the scientific community to determine the spatial variability of marine CH_4 and N_2O distributions, the underlying mechanisms that determine this variability, and the resulting sea-to-air emissions. Shallow marine environments and oxygen deficient zones are widely recognized as deserving of greater attention because they have high CH_4 and N_2O concentrations with inherently high uncertainties that complicate any assessment of their emissions to air (Bange et al., 1994; Bange et al., 1996;

Bakker et al., 2014; James et al., 2016; Borges et al., 2016; Tian et al., 2020). Fortunately, recent technological advances that have increased our ability to conduct high-resolution measurements allow an optimistic outlook for making substantial progress in quantifying the CH_4 and N_2O budgets of these ecosystems. Even so, the inherent complexity of shallow marine environments clearly warrants a strategically coordinated approach to optimize the value of future studies. Issues to consider include identifying the locations of complementary sampling sites, standardizing sampling strategies and techniques, and agreeing the use of common ancillary measurements that set the broad biogeochemical context (Bange et al., 2019). In contrast to the open ocean, measurement campaigns in shallow water environments are amenable to the use of eddy covariance flux towers, and they have the potential to lever resources from existing observation networks, which in North America include the Long-Term Ecological Research network (LTER) and the National Estuarine Research Reserve (NERR) System (Novick et al., 2018). Indeed, such activities are already underway; an increasing number of flux towers are being equipped for CH_4 measurements (Torn et al., 2019) and future efforts should focus on the inclusion of N_2O (see Section 5).

We are encouraged that the Global Carbon Project with its objective of developing a complete picture of the global carbon cycle including interactions and feedbacks has expanded to include CH_4 (Saunois et al., 2020) and is now incorporating N_2O (Tian et al., 2020). These Projects compile the most recent data from peer-reviewed analyses of the sources and sinks of atmospheric CH_4 and N_2O from both natural and human activities. For example, the aquatic components of the recent Global Carbon Project N_2O budget reported emissions from the open ocean, inland waters, estuaries and coastal zones. Low-oxygen oceanic regions associated with eastern-boundary upwelling zones, and the coastal ocean were identified as key regions with significant N_2O variability requiring more detailed assessment via measurement campaigns and model analyses (Tian et al., 2020). Contribution to the Global Carbon Project and similar initiatives will identify areas of synergistic CH_4 and N_2O research for oceanographers and other Earth observation scientists (Ganesan et al., 2019). Furthermore, as highlighted in Section 6, field observations alone are insufficient to improve the robustness of Earth System models and leveraging laboratory-based microbial process studies is highly recommended.

The success of any coordinated CH_4 and N_2O research program relies heavily on having uniformly high confidence in the various resulting datasets and their interoperability, and we identify three key initiatives that are paramount to ensuring this:

(i) The first is to develop and adopt Standard Operating Protocols (SOPs) to help obtain intercomparable CH_4 and N_2O datasets of the highest possible accuracy and precision. Currently, there is no community-defined level of analytical uncertainty to characterize high quality CH_4 and N_2O measurements. However, attaining an analytical agreement between multiple laboratories of ≤1% is considered achievable for the repeat oceanographic surveys and time-series observations (Fig. 3). For context, an analytical agreement of ≤1% would permit the ocean's response to the increasing tropospheric CH_4 and N_2O mole fractions to be resolved on timescales of 10 and 5 years, respectively. These values are based on the changes in surface ocean CH_4 and N_2O concentrations that are predicted to occur due to the ongoing increase in tropospheric CH_4 and N_2O mole fractions at a seawater temperature of 20°C and a salinity of 35 g kg^{-1}, and assuming all sources and sinks remaining constant. In our recent marine CH_4 and N_2O inter comparison exercise we concluded that the diversity of analytical procedures employed by the participants was a major cause of high variability between the reported concentrations, highlighting an urgent requirement for CH_4 and N_2O SOPs (Wilson et al., 2018). Consequently, these SOPs are now being compiled, and they will be freely available via the Ocean Best Practices System.

(ii) The second is increased regularity of intercomparison exercises through the periodic distribution of consensus material, i.e. water samples in which CH_4 and N_2O concentrations are known with high confidence, obtained by pooling analyses from several laboratories with demonstrated analytical capability. These will help the scientific community to monitor data comparability and accuracy, particularly in the case of highly elevated concentrations of CH_4 and N_2O, i.e. those exceeding atmospheric equilibrium concentrations by at least an order of magnitude.

(iii) The third activity builds on the previous initiative and calls for the production of Global Data Products for dissolved CH_4 and N_2O measurements. To date, individual CH_4 and N_2O measurements are represented at the global scale by the MEMENTO database which has been very successful at compiling CH_4 and N_2O datasets and making them readily accessible to the modeling community. However, the MEMENTO database does not currently include a Global

Data Product that includes publicly accessible quality controlled dissolved CH_4 and N_2O datasets. The international marine carbon science community has widely embraced such an approach for fCO_2, by submitting data to the Surface Ocean CO_2 Atlas (SOCAT), which was initiated in response to the need for a quality controlled, publicly available, global surface CO_2 dataset (e.g. Bakker et al., 2016). Due to the fewer measurements, a similar data product for marine CH_4 and N_2O would be needed every ~5 years. We consider the production of Global Data Products for dissolved CH_4 and N_2O to be essential for supporting future global modeling efforts and to enhance field observations.

The benefits of pursuing the three activities described above have already been clearly demonstrated for carbon system measurements in the ocean. The intercomparability and high accuracy and precision of carbon system measurements was achieved by streamlining methodological approaches, universally adopting agreed SOPs, production of reference material, and following community-driven quality control procedures (Dickson et al., 2007, Dickson et al, 2010). It is encouraging to see the marine CH_4 and N_2O community beginning to move in a similar direction.

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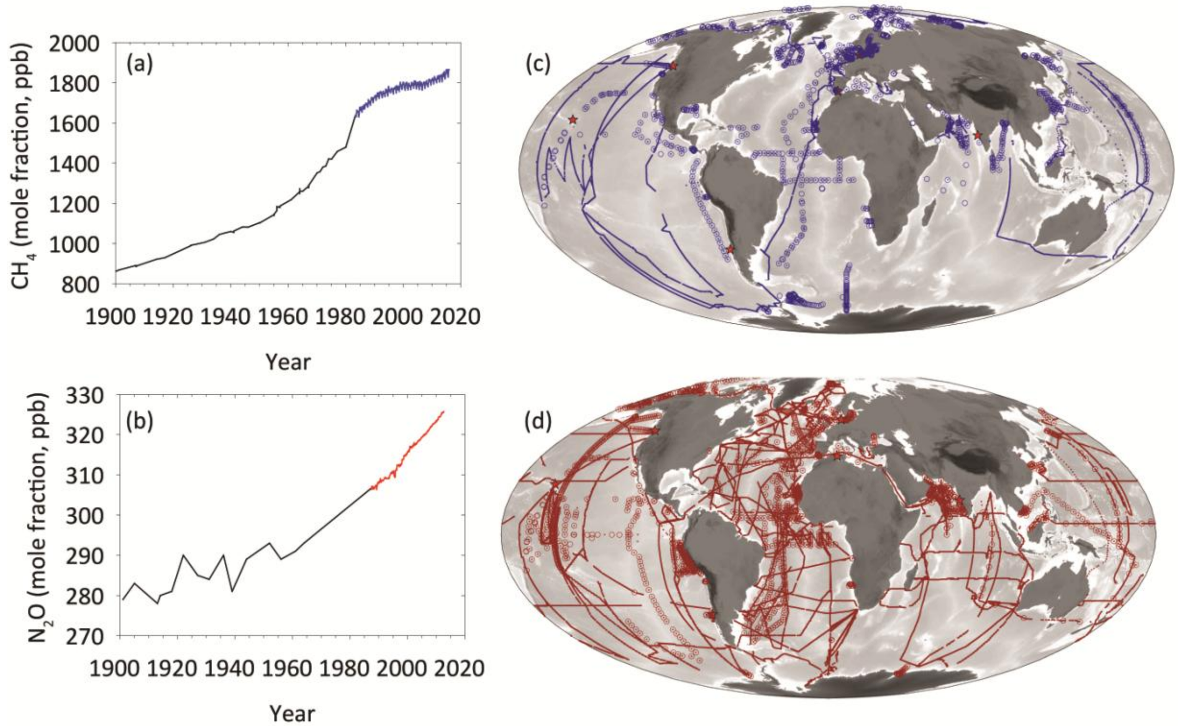

Figure 1. Atmospheric values of (a) CH_4 and (b) N_2O with the black lines reconstructed from ice-core measurements (Etheridge et al., 1998; Machida et al., 1995) and the colored lines from Mauna Loa Observatory (https://www.esrl.noaa.gov/gmd/dv/data/). Global maps of marine (c) CH_4 and (d) N_2O measurements available from the MEMENTO database (https://memento.geomar.de/). The 2018 workshop focused on the marine contribution to atmospheric CH_4 and N_2O and the underlying microbial and biogeochemical control mechanisms.

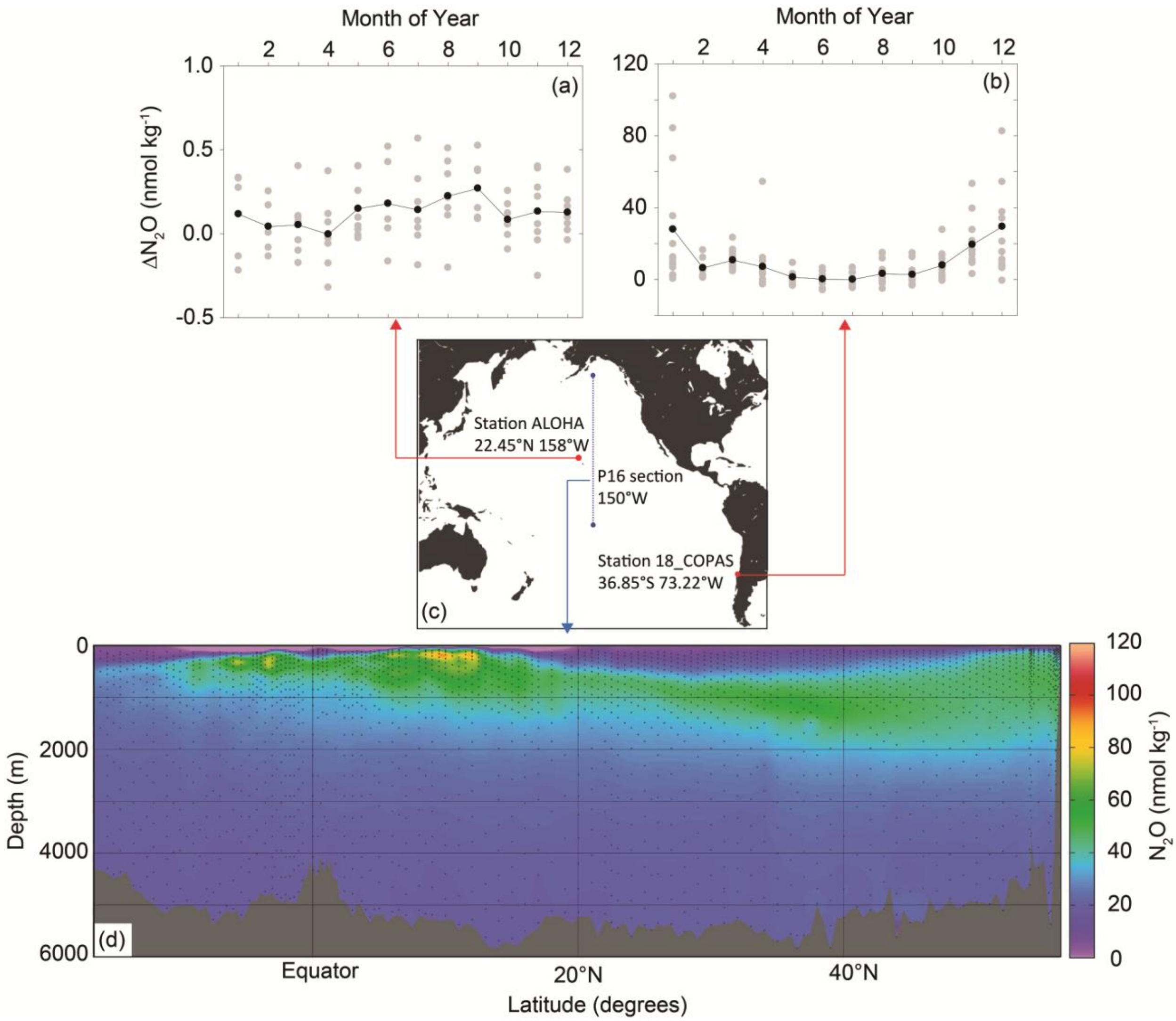

Figure 2. Repeat oceanic observations include both (a, b) fixed location time-series monitoring observations and (c,d) hydrographic surveys. Together, such field observation programs helps resolve temporal variability ranging from months to years and spatial variability at the ocean basin scale (see Fig. 3). The Station ALOHA data derive from Wilson et al. (2018), the Station 18 data derive from Farías et al. (2015), and the P16 transect was conducted in 2015 by the NOAA PMEL Tracer Group as part of the GO-SHIP program. The data shown in the plots are N_2O concentrations, either as ΔN_2O (i.e. deviation from equilibrium value) or absolute values.

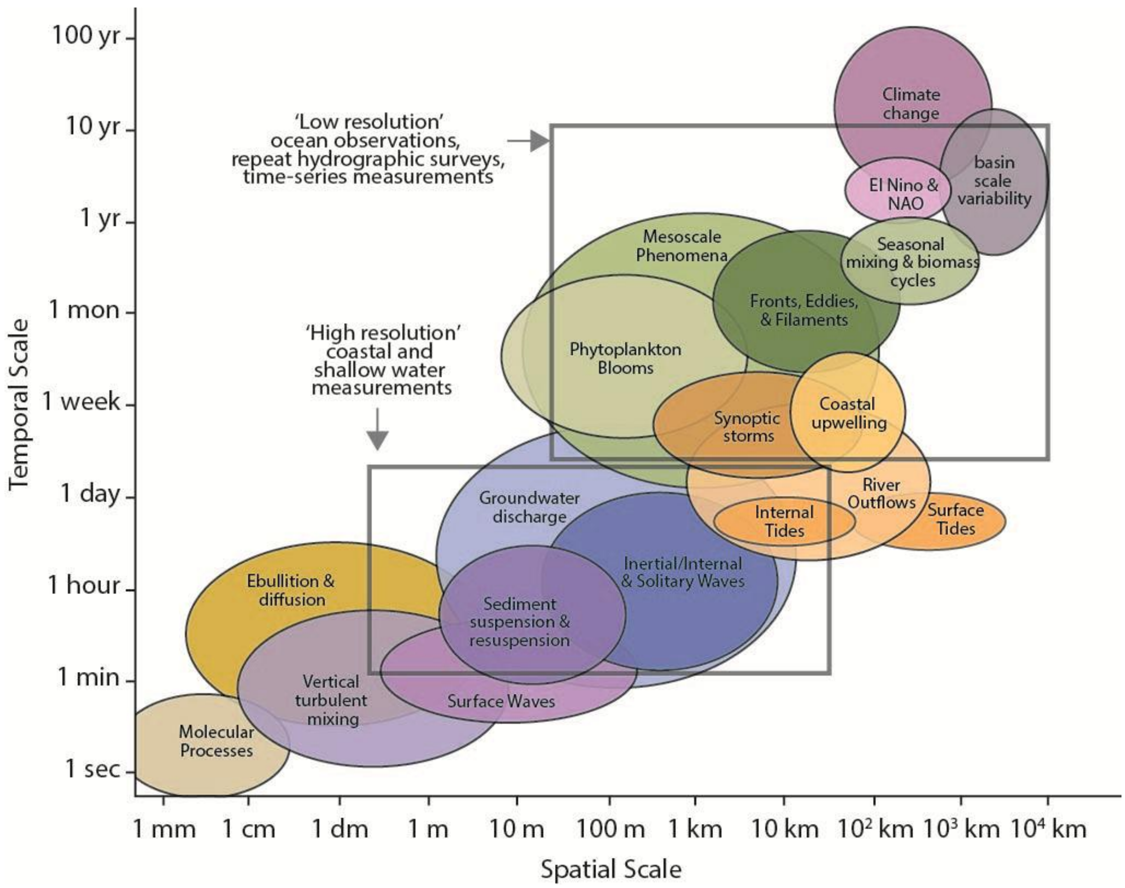

Figure 3. Time-space scale diagram illustrating various physical, biological, and climatological processes relevant to marine CH_4 and N_2O (adapted from Dickey, 2003). To date, the majority of marine CH_4 and N_2O measurements resolve variability at the mesoscale level or higher. Recent technological developments and the need to resolve concentrations and fluxes in shallow water environments will increase the number of measurements conducted at the submesoscale level (see Fig. 5). The low resolution oceanographic surveys are more likely to achieve a high level of analytical accuracy compared to high resolution coastal measurements, however this is compensated for by high temporal resolution achieved by underway sampling.

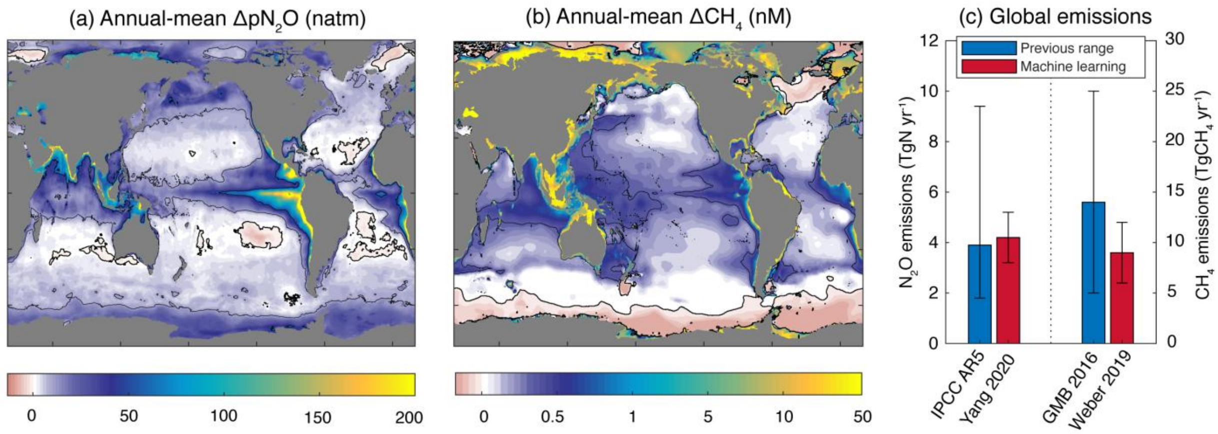

Figure 4. Distributions and emissions of marine CH_4 and N_2O, (a) Air-sea N_2O disequilibrium mapped using a Regression Forest model (adapted from Yang et al., 2020), (b) Air-sea CH_4 disequilibrium mapped using an Artificial Neural Network model (adapted from Weber et al., 2019). For consistency with the original publications, the air-sea disequilibrium is shown in different units for N_2O (partial pressure) and CH_4 (concentration). (c) A summary of global ocean CH_4 and N_2O emissions estimated by Yang et al. (2020) and Weber et al. (2019), compared to the estimates of the IPCC 5th Annual Report (IPCC AR5) and the Global Methane Budget (Saunois et al., 2016).

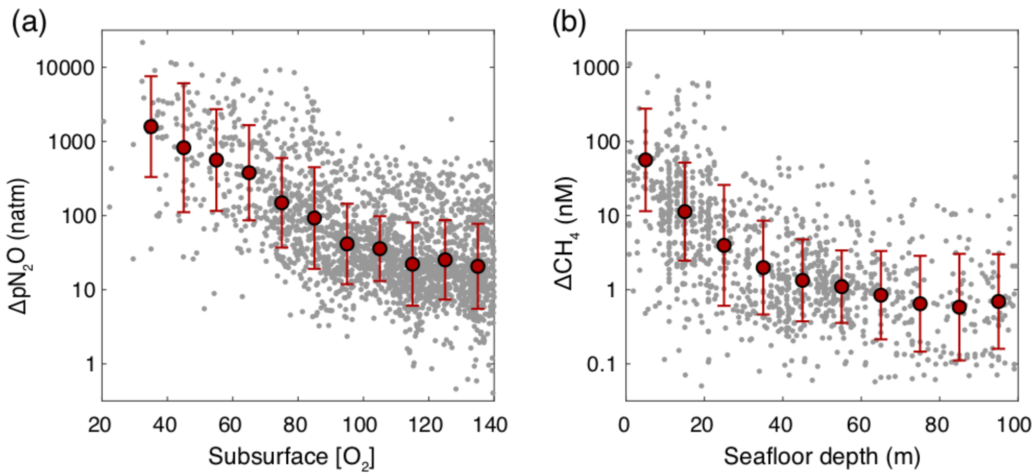

Figure 5. Key environmental predictors of surface ocean CH_4 and N_2O gradients. (a) Excess air-sea N_2O is best predicted by O_2 concentrations in the subsurface water-column (base of the mixed layer to a depth of 100 m) (adapted from Yang et al., 2020). (b) Excess CH_4 is best predicted by seafloor depth, reflecting the supply from anoxic sediments (adapted from Weber et al., 2019). The grey dots represent individual data points and the red dots with error bars represent mean ±1s.d. of binned data, using O_2 bins of 10 μM width and seafloor depth bins of 10 m width.