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

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**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 $N_2O$. A workshop sponsored by Ocean Carbon and Biogeochemistry (OCB) 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., 2018; Fig. 1a and b). 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). Accurately constraining 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 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 yields 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 undersampled (Fig. 1c and d). 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 remain 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

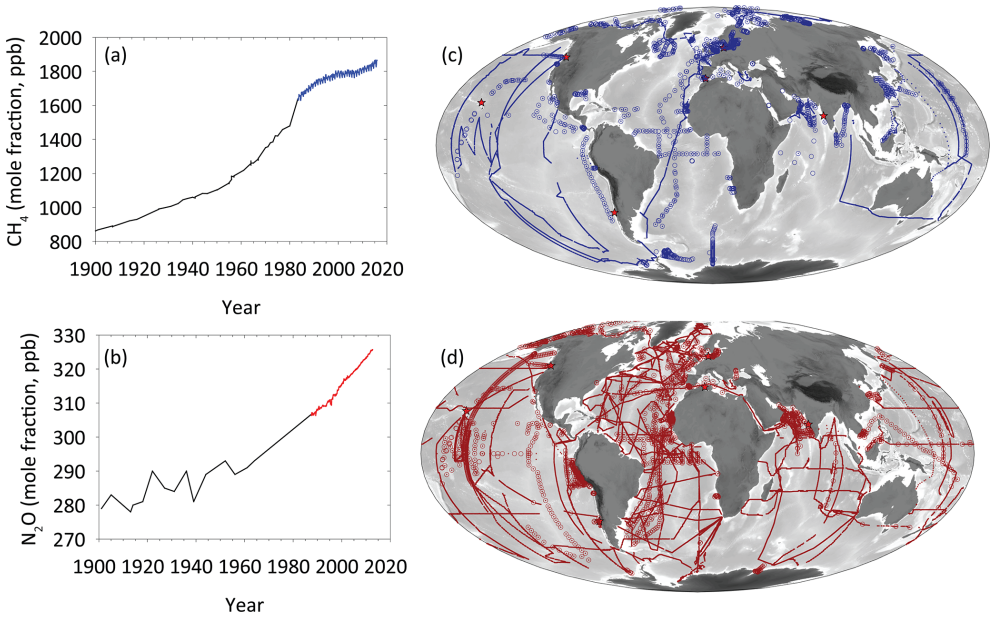


**Figure 1.** Atmospheric values of **(a)** $CH_4$ and **(b)** $N_2O$ with the black lines reconstructed from ice-core measurements (Etheridge et al., 1998; Machida et al., 1995) and the colored lines from Mauna Loa Observatory (https://www.esrl.noaa.gov/gmd/dv/data/, last access: 1 July 2020). Global maps of marine **(c)** $CH_4$ and **(d)** $N_2O$ measurements available from the MEMENTO database (https://memento.geomar.de/, last access: 1 July 2020). The 2018 workshop focused on the marine contribution to atmospheric $CH_4$ and $N_2O$ and the underlying microbial and biogeochemical control mechanisms.

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 5 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 b). 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-

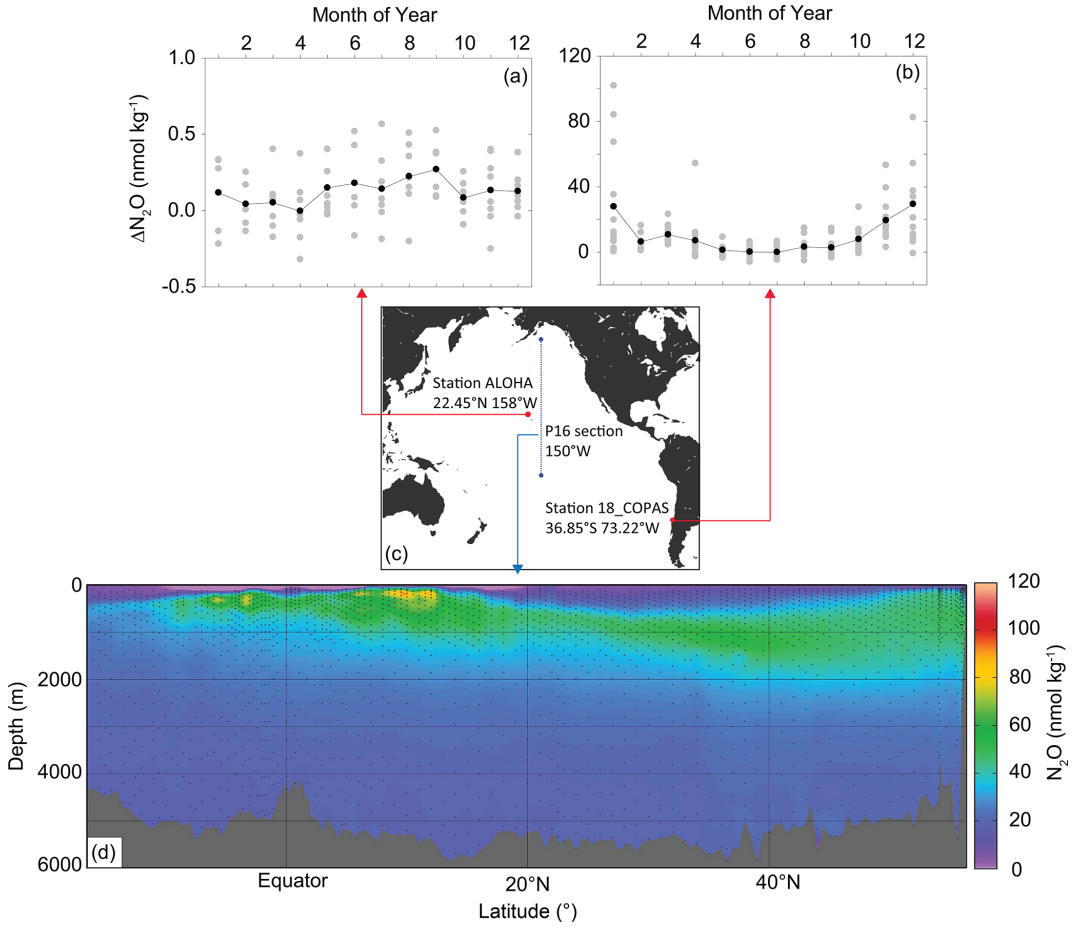


**Figure 2.** Highlights of repeat $N_2O$ observations in the Pacific Ocean including both **(a, b)** fixed-location time-series monitoring observations and **(c, d)** hydrographic surveys. Together, these observing programs help resolve temporal variability ranging from months to years and spatial variability at the ocean basin scale (see Fig. 3). The Station ALOHA data derive from Wilson et al. (2018), the Station 18 COPAS data derive from Farías et al. (2015), and the P16 transect was conducted in 2015 by the NOAA PMEL Ocean Tracer group as part of the GO-SHIP program. The $N_2O$ concentrations are shown as either $\Delta N_2O$ (i.e., deviation from equilibrium value) or absolute values.

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 Sect. 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 12 international laboratories, with the aim of improving and standardizing calibration (Bullister et al., 2017). A subsequent intercomparison 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 procedures (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.

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 broadscale surface distributions

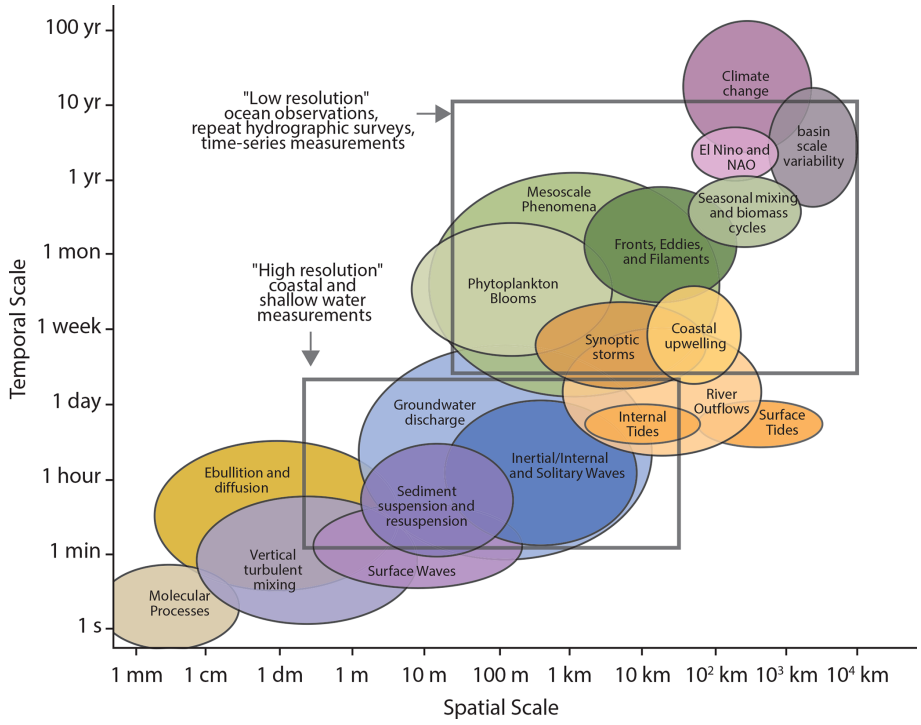


**Figure 3.** Time–space scale diagram illustrating various physical, biological, and climatological processes relevant to marine $CH_4$ and $N_2O$ (adapted from Dickey, 2003). To date, the majority of marine $CH_4$ and $N_2O$ measurements resolve variability at the mesoscale level or higher. Recent technological developments and the need to resolve concentrations and fluxes in shallow water environments will increase the number of measurements conducted at the sub-mesoscale 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.

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 (Fig. 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

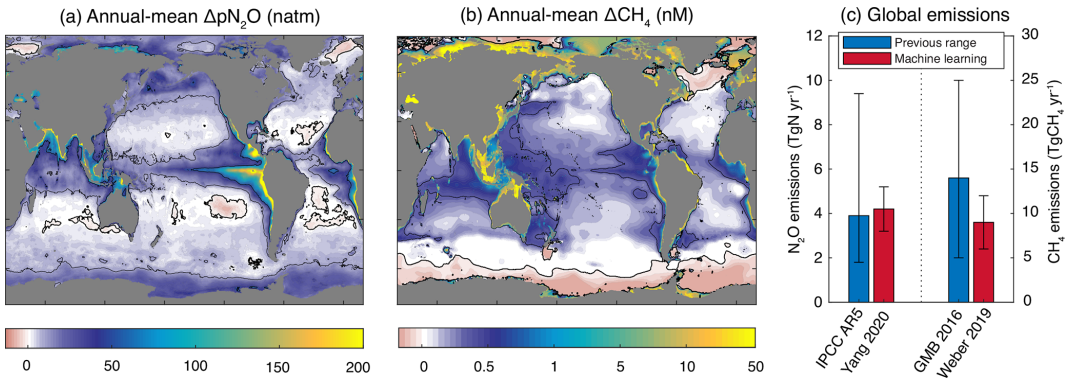


**Figure 4.** Distributions and emissions of marine $CH_4$ and $N_2O$, **(a)** air–sea $N_2O$ disequilibrium mapped using a regression forest model (adapted from Yang et al., 2020) and **(b)** air–sea $CH_4$ disequilibrium mapped using an artificial neural network model (adapted from Weber et al., 2019). 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).

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; Lorenson 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;

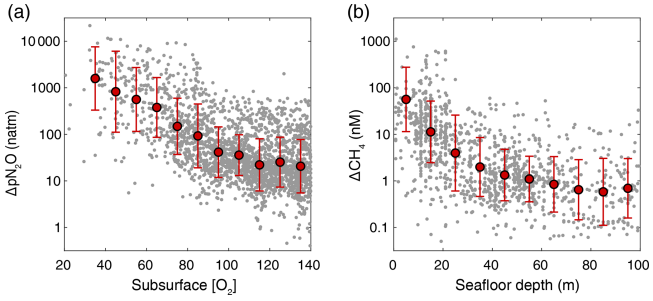


**Figure 5.** Key environmental predictors of surface ocean $CH_4$ and $N_2O$ gradients. **(a)** Excess air–sea $N_2O$ is best predicted by $O_2$ concentrations in the subsurface water column (base of the mixed layer to a depth of 100 m) (adapted from Yang et al., 2020). **(b)** Excess $CH_4$ is best 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 ±1 SD of binned data, using $O_2$ bins of 10 µM width and seafloor depth bins of 10 m width.

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 makes 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 also 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 also been 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 nearshore 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 to 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 5-fold 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) spectroscopy 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 varies 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, 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 Sect. 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 about 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 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, 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 on 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 (LTER) network 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 Sect. 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 Sect. 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 procedures (SOPs) to help obtain intercomparable $CH_4$ and $N_2O$ datasets of the highest possible accuracy and precision. Currently, there is no consensus definition of high-quality $CH_4$ and $N_2O$ measurements. However, an analytical agreement of $\leq 1\,\%$ is considered achievable for the laboratories conducting repeat oceanographic surveys and time-series observations (Fig. 3). For context, an analytical agreement of $\leq 1\,\%$ 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 $N_2O$ intercomparison exercise it was 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 by the scientific community.

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 calls for the production of global data products for dissolved $CH_4$ and $N_2O$ measurements. To date, the MEMENTO database 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 has not yet yielded 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 fewer measurements, a similar data product for marine $CH_4$ and $N_2O$ would be needed every $\sim 5$ 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 were achieved by streamlining methodological approaches, universally adopting agreed-upon 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.

*Data availability.* The atmospheric concentrations of $CH_4$ and $N_2O$ in Fig. 1 originated from the Mauna Loa Observatory (NOAA Earth System Research Laboratory). The discrete monthly averaged values are publicly available online at https://www.esrl.noaa.gov/gmd/dv/data/ (NOAA Earth System Research Laboratory, 2020). The $N_2O$ concentrations shown in Fig. 2 are available from three separate data repositories: BCO-DMO (Fig. 2a), PANGAEA (Fig. 2b), and GO-SHIP (Fig. 2d). The global reconstructed climatologies of $CH_4$ and $N_2O$ shown in Figs. 4 and 5 are adapted from Weber et al. (2019) and Yang et al. (2020). The original publications contain the specific methodologies and code, with the $CH_4$ and $N_2O$ datasets sourced from the MEMENTO database (https://memento.geomar.de/, last access: 1 August 2020).

*Video supplement.* A video supplement "Oceanic Methane and Nitrous Oxide" is attached to this publication (Hofman, 2019). The video contains conversations with participants of the 2018 OCB workshop about future research on oceanic methane and nitrous oxide. The video was commissioned by Samuel T. Wilson, produced by Thom Hoffman (producerthom@gmail.com; http://www.thomhoffman.co.uk, last access: 20 November 2020), and funded by the Moore Foundation. The video is made publicly available via the German National Library of Science and Technology (TIB) with the DOI https://doi.org/10.5446/50062 and also can be found at https://www.youtube.com/watch?v=0DyMyIVs4Qs&t=266s (last access: 20 November 2020).

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