CellPress

One Earth

Commentary

Non-CO_2 greenhouse gases (N_2O, CH_4, CO) and the ocean

Hermann W. Bange[1,*]
[1]Marine Biogeochemistry, GEOMAR Helmholtz Centre for Ocean Research Kiel, Düsternbrooker Weg 20, 24105 Kiel, Germany
*Correspondence: hbange@geomar.de
https://doi.org/10.1016/j.oneear.2022.11.011

Oceanic non-CO_2 greenhouse gases (GHGs: N_2O, CH_4, and CO) require more attention in a new and wider context that is relevant for ocean and climate sciences. In order to gain a better understanding of their cycling and emissions, it is essential to establish a global ocean observing network.

It is widely known that the world's ocean has long been a great ally in the fight against climate change, absorbing around one-quarter of all carbon dioxide (CO_2) emissions and capturing the vast majority of the associated excess heat.[1] What is lesser known is that open and coastal ocean waters also play an important role as sources of non-CO_2 greenhouse gases (GHGs). These include nitrous oxide (N_2O), methane (CH_4), and carbon monoxide (CO), which, while lower in concentration relative to CO_2, still have a significant impact on atmospheric warming (see Table 1). However, our knowledge about the production and consumption pathways of these non-CO_2 GHGs as well as the major drivers that cause their release from the ocean is rudimentary at best, and estimates of their oceanic emissions are still associated with a high degree of uncertainty.

Following CO_2, N_2O, CH_4, and CO are the most important natural GHGs.[4] CO is an indirect GHG; a series of atmospheric reactions of CO increase the atmospheric mole fractions of other GHGs such as CO_2, CH_4, and ozone, resulting in an effective radiative forcing that is comparable to N_2O (see Table 1). Moreover, N_2O and CH_4 are involved in stratospheric ozone depletion (the "ozone whole").[5] N_2O, in view of the ongoing atmospheric decrease of the chlorofluorocarbons, is expected to become the most important ozone-depleting compound of the 21st century.[6] When it comes to what we know of the ocean as a source of these gases, our knowledge is patchy and uncertainty ranges are significant.

While the open ocean (water depths > 200 m) is usually classified as a natural source of atmospheric non-CO_2 GHGs, emissions from coastal oceans (water depths < 200 m) are strongly affected by anthropogenic activities such as increasing inputs of nitrogenous nutrients via agricultural practices, which can result in the eutrophication of coastal waters. Oceanic N_2O emission estimates for the period from 2007 to 2016 indicate that the open and coastal oceans (including coastal zones, estuaries, rivers, and inland waters) may contribute as much as 25% of the natural and anthropogenic N_2O sources combined (Table 1).[4] This indicates that the ocean is second only to soils as the world biggest source of atmospheric N_2O. However, the estimates range from 13%–44% and are thus highly uncertain. Estimates of oceanic CH_4 and CO emissions similarly suffer from significant uncertainties; although the ocean could contribute a minor, but still significant, 1% of global CH_4 and CO emissions (Table 1), uncertainties are in the range of at least ±50%.[4,2,3,7] In view of declining anthropogenic CO sources,[4] the importance of the oceanic source of CO might increase in the future. These uncertainties are mainly caused by the low number of available oceanic measurements, as compared to, for example, CO_2, and the lack of information on (1) seasonal and inter-annual variability and (2) land-ocean gradients.

Our understanding of the processes underlying oceanic non-CO_2 GHG formation has also been recently challenged. Traditionally, it has been thought that oceanic emissions of N_2O, CH_4, and CO are largely determined by the balance of microbial (N_2O and CH_4) or photochemical (CO) production and consumption processes (see Table 1). In the case of CH_4 and CO, microbial consumption is thought to be very effective and thus consumes a large fraction (approximately up to 90%) of the gases produced *in situ*, allowing only a small fraction to escape into the atmosphere. The surplus emissions from oceanic N_2O production are, however, much larger, since the only known N_2O microbial consumption process (Table 1) depends on anoxic (i.e., oxygen-free) environments, which are found only at a few sites in the ocean (eastern tropical Pacific Ocean and Arabian Sea) and in the sediments. However, recently published findings have questioned this conventional thinking. There is, for example, increasing evidence that N_2O can be consumed in the oxic ocean surface layer. Although the processes responsible for N_2O consumption in the ocean surface and its spatial and temporal extent remain largely unknown, this would effectively turn the surface ocean into temporary regional sink of N_2O.[8,9] It has also been shown that a decreasing pH (i.e., through ocean acidification) can affect N_2O production via nitrification. Results from studies are, however, ambiguous with respect to whether this would increase or decrease oceanic N_2O production, introducing further uncertainty.[10,11] There is also the "methane paradox" to contend with—the unexpected supersaturation of the upper ocean with methane with respect to the atmosphere—which, despite a bundle of potential explanations, remains enigmatic. Furthermore, microbial and chemical processes that take place in the surface microlayer (SML) (i.e., the uppermost 1 mm of the ocean) have been shown to significantly affect the exchange of gases across the ocean/atmosphere interface[12] but are usually not accounted for in emission

Table 1. Overview of the climate relevance and the major oceanic processes of N_2O, CH_4 and CO.

	N_2O	CH_4	CO
Atmospheric lifetime	109 years	9 years	1–4 months
Climate effects	direct	direct	indirect
Effective radiative forcing[a], W m^2	0.24	1.2	0.44[b]
Atmospheric chemistry effects	strat. O_3 depletion	strat. O_3 depletion, oxidative capacity	oxidative capacity
Oceanic contribution to atm. budget, %	25 (13–44)	0.8 (0.8–4.1)	<1[c]
Major formation processes[d]	nitrification, denitrification	methanogenesis, other processes[e]	photochemistry
Major consumption processes[d]	denitrification	aerobic/anaerobic oxidation	microbial consumption

[a]Emissions-based estimates for the period 1750–2019.
[b]Includes non-methane volatile organic compounds.
[c]See Zheng et al.[2] and Conte et al.[3]
[d]Combined open and coastal oceans (including water column and sediments).
[e]"Other processes" stands for processes potentially explaining the "oceanic CH_4 paradox," such as methanogenesis in anoxic micro niches (in sinking organic particles and in zooplankton guts), microbial production from methylated precursors, and release by cyanobacteria and phytoplankton. Moreover, a photochemical production of CH_4 has been suggested recently as an alternative, non-biological, production pathway in the ocean.

estimates of non-CO_2 GHGs. And the role of phytoplankton as a source of non-CO_2 GHGs and the molecular mechanisms associated with the photochemical production of CO remain unclear and require further evaluation.[13,14] In addition to these persistent gaps in knowledge, ongoing environmental changes such as ocean warming (and associated changes in stratification and ice coverage), decreasing pH (i.e., acidification), loss of dissolved oxygen (i.e., deoxygenation), and eutrophication due to increasing anthropogenic inputs of nutrients via rivers and atmospheric deposition of aerosols might significantly alter the production and consumption of non-CO_2 GHGs, their distribution patterns, and, ultimately, their release to the atmosphere.

We can thus conclude that our knowledge of the production, consumption, and emissions of non-CO_2 GHGs from the ocean is still far from complete. As a consequence, ocean biogeochemical models fail to provide an adequate representation of reality, which in turn affects projections of oceanic non-CO_2 GHG distributions and emissions under future scenarios of ocean warming, acidification, deoxygenation, and eutrophication. For example, model projections that account for ocean warming and atmospheric nitrogen deposition show a net decrease in future global oceanic N_2O emissions during the 21st century, but projections range between 4% and 24%.[15] An inability to reasonably simulate non-CO_2 GHG distribution and the associated oceanic emissions compromises our ability to accurately verify the potential effects of mitigating actions (e.g., the reduction of eutrophication in coastal areas). Additionally, the large degree of uncertainty in future emission projections also results from the limitations of existing concentration data used in model parameterizations and validation. Where data do exist, datasets are not yet cross-calibrated and are biased by poor spatial and temporal coverage of the ocean.

These shortcomings are not going unnoticed. Communities are rallying to improve data coverage and standardize measurements. MEMENTO, a database for marine CH_4 and N_2O measurements, was launched in 2009. The database currently contains about 120,000 surface and depth profile measurements of N_2O and more than 20,000 measurements for CH_4. Unfortunately, MEMENTO does not yet include data or protocols for CO. In 2013, working group 143 of the Scientific Committee on Oceanographic Research (SCOR) was established to develop standard measurement protocols for N_2O and CH_4. The importance of additional, routine oceanic N_2O measurements has been recognized by the Global Ocean Observing System (GOOS) program, which recently added N_2O to its list of Essential Ocean Variables (EOV) (see www.goosocean.org). Building on these efforts, in 2019, the Global N_2O Ocean Observation Network (N2O-ON) was proposed (Figure 1).[15] The objectives of N2O-ON are multiple: (1) reduce uncertainties in current global N_2O oceanic emission estimates, (2) better constrain and understand temporal and spatial variability, (3) verify that measures to mitigate N_2O emissions are effective, and (4) improve future projections of N_2O concentrations and emissions in a changing ocean. To achieve these goals, N2O-ON will make use of established (e.g., research vessels, repeat hydrographic line and time series stations, and voluntary observing ships) and new (e.g., moorings with underwater trace gas sensors, when technically mature) observation platforms to improve the characterization of spatial and temporal variability in oceanic N_2O concentrations. Although N2O-ON was originally designed for N_2O only, adding measurements of CH_4 and CO will be facilitated by deploying instruments on the basis of the same technique used for N_2O measurements (i.e., cavity-enhanced absorption spectroscopy). While necessary, the objectives of N2O-ON are ambitious, and its successful development and execution will depend strongl y on available international and national funding sources and may take up to 15 to 20 years to complete.

Although these advances will enable us to measure oceanic non-CO_2 GHG emissions with greater accuracy, they only tackle part of the problem. If we are to successfully address existing knowledge gaps and fully decipher the production and consumption pathways of N_2O, CH_4, and CO in a changing ocean, complementary approaches to a global observation network are needed. Such joint process studies should be established in open ocean sites in all major ocean basins and coastal ocean regions with high

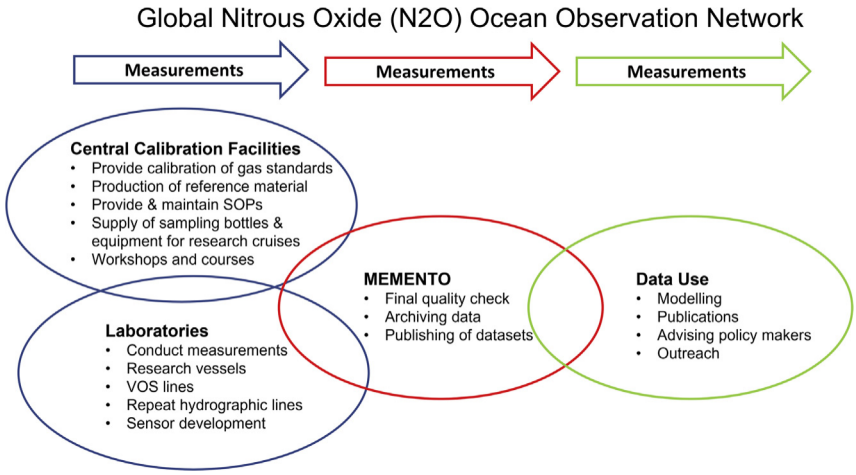

Figure 1. Proposed scheme for the Global N_2O Ocean Observation Network (N2O-ON)
MEMENTO, marine methane and nitrous oxide database: https://memento.geomar.de. The figure is taken from Bange et al.[15]

biological productivity and/or anthropogenic influence, conducted across multiple seasons and years, and designed holistically, combining microbial, molecular biological, and biogeochemical methods (including measurements' isotopic signatures). Only through such a comprehensive, coordinated, and interdisciplinary approach will we generate the data necessary to identify the relevant microbe/phytoplankton communities, quantify the rates of ocean non-CO_2 GHG production/consumption, and comprehend their major drivers.

There remains much to learn about the biogeochemistry of the oceans. Without this knowledge, the picture of greenhouse gas emissions remains incomplete.

ACKNOWLEDGMENTS

This commentary arose from discussions at meetings made possible by the Scientific Committee on Ocean Research (SCOR) working group 143 "Dissolved N_2O and CH_4 measurements: working toward a global network of ocean time series measurements of N_2O and CH_4." We thank SCOR for its generous support of WG 143 activities, which were funded, in part, by a grant from the U.S. National Science Foundation (grant OCE-1840868) to SCOR. This commentary contributes to the science plan of the Surface Ocean-Lower Atmosphere Study (SOLAS), which is also supported by the U.S. National Science Foundation via SCOR.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Friedlingstein, P., O'Sullivan, M., Jones, M.W., Andrew, R.M., Gregor, L., Hauck, J., Le Quere, C., Luijkx, I.T., Olsen, A., Peters, G.P., et al. (2022). Global carbon budget 2022. Earth Syst. Sci. Data *14*, 4811–4900. https://doi.org/10.5194/essd-14-4811-2022.
2. Zheng, B., Chevallier, F., Yin, Y., Ciais, P., Fortems-Cheiney, A., Deeter, M.N., Parker, R.J., Wang, Y., Worden, H.M., Zhao, Y., et al. (2019). Global atmospheric carbon monoxide budget 2000–2017 inferred from multi-species atmospheric inversions. Earth Syst. Sci. Data *11*, 1411–1436. https://doi.org/10.5194/essd-11-1411-2019.
3. Conte, L., Szopa, S., Séférian, R., and Bopp, L. (2019). The oceanic cycle of carbon monoxide and its emissions to the atmosphere. Biogeosciences *16*, 881–902. https://doi.org/10.5194/bg-16-881-2019.
4. IPCC (2021). Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change (Cambridge, UK and New York, NY, USA: Cambridge University Press), p. 2391.
5. WMO (2018). Scientific assessment of ozone depletion: 2018 (Geneva, Switzerland: World Meteorological Organization), p. 588.
6. Ravishankara, A.R., Daniel, J.S., and Portmann, R.W. (2009). Nitrous oxide (N_2O): The dominant ozone-depleting substance emitted in the 21st century. Science *326*, 123–125. https://doi.org/10.1126/science.1176985.
7. Rosentreter, J.A., Borges, A.V., Deemer, B.R., Holgerson, M.A., Liu, S., Song, C., Melack, J., Raymond, P.A., Duarte, C.M., Allen, G.H., Olefeldt, D., Poulter, B., Battin, T.I., and Eyre, B.D. (2021). Half of global methane emissions come from highly variable aquatic ecosystem sources. Nat. Geosci. *14*, 225–230. https://doi.org/10.1038/s41561-021-00715-2.
8. Farías, L., Faúndez, J., Fernandèz, C., Cornejo, M., Sanhueza, S., and Carrasco, C. (2013). Biological N2O Fixation in the Eastern South Pacific Ocean and Marine Cyanobacterial Cultures. PLoS One *8*, e63956. https://doi.org/10.1371/journal.pone.0063956.
9. Sun, X., Jayakumar, A., Tracey, J.C., Wallace, E., Kelly, C.L., Casciotti, K.L., and Ward, B.B. (2021). Microbial N2O consumption in and above marine N2O production hotspots. ISME J. *15*, 1434–1444. https://doi.org/10.1038/s41396-020-00861-2.
10. Rees, A.P., Brown, I.J., Jayakumar, A., and Ward, B.B. (2016). The inhibition of N2O production by ocean acidification in cold temperate and polar waters. Deep-Sea Research Part II-Topical Studies in Oceanography *127*, 93–101. https://doi.org/10.1016/j.dsr2.2015.12.006.
11. Breider, F., Yoshikawa, C., Makabe, A., Toyoda, S., Wakita, M., Matsui, Y., Kawagucci, S., Fujiki, T., Harada, N., and Yoshida, N. (2019). Response of N_2O production rate to ocean acidification in the western North Pacific. Nat. Clim. Change *9*, 954–958. https://doi.org/10.1038/s41558-019-0605-7.
12. Engel, A., Bange, H.W., Cunliffe, M., Burrows, S.M., Friedrichs, G., Galgani, L., Herrmann, H., Hertkorn, N., Johnson, M., Liss, P.S., Quinn, P.K., Schartau, M., Soloviev, A., Stolle, C., Upstill-Goddard, R.C., van Pinxteren, M., and Zancker, B. (2017). The Ocean's Vital Skin: Toward an Integrated Understanding of the Sea Surface Microlayer. Front. Mar. Sci. *4*, 165. https://doi.org/10.3389/fmars.2017.00165.
13. McLeod, A.R., Brand, T., Campbell, C.N., Davidson, K., and Hatton, A.D. (2021). Ultraviolet Radiation Drives Emission of Climate-Relevant Gases From Marine Phytoplankton. J. Geophys. Res.: Biogeosciences *126*, e2021JG006345. https://doi.org/10.1029/2021jg006345.
14. Ossola, R., Gruseck, R., Houska, J., Manfrin, A., Vallieres, M., and McNeill, K. (2022). Photochemical Production of Carbon Monoxide from Dissolved Organic Matter: Role of Lignin Methoxyarene Functional Groups. Environmental Science & Technology *56*, 13449–13460. https://doi.org/10.1021/acs.est.2c03762.
15. Bange, H.W., Arévalo-Martínez, D.L., de la Paz, M., Farías, L., Kaiser, J., Kock, A., Law, C.S., Rees, A.P., Rehder, G., Tortell, P.D., Upstill-Goddard, R.C., and Wilson, S.T. (2019). A harmonized nitrous oxide (N_2O) ocean observation network for the 21st century. Front. Mar. Sci. *6*, 157. https://doi.org/10.3389/fmars.2019.00157.