A Harmonized Nitrous Oxide (N₂O) Ocean Observation Network for the 21st Century

Hermann W. Bange[1]*, Damian L. Arévalo-Martínez[1†], Mercedes de la Paz[2‡], Laura Farías[3§], Jan Kaiser[4‖], Annette Kock[1¶], Cliff S. Law[5,6#], Andrew P. Rees[7Δ], Gregor Rehder[8◇], Philippe D. Tortell[9], Robert C. Upstill-Goddard[10↓] and Samuel T. Wilson[11↑]

[1] GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany, [2] Instituto Español de Oceanografía (IEO), Centro Oceanográfico de A Coruña, A Coruña, Spain, [3] Department of Oceanography, Center for Climate and Resilience Research (CR2), University of Concepción, Concepción, Chile, [4] Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, United Kingdom, [5] National Institute of Water and Atmospheric Research, Wellington, New Zealand, [6] Department of Chemistry, University of Otago, Dunedin, New Zealand, [7] Plymouth Marine Laboratory, Plymouth, United Kingdom, [8] Department of Marine Chemistry, Leibniz Institute for Baltic Sea Research Warnemünde, Rostock, Germany, [9] Department of Earth, Ocean and Atmospheric Sciences – Department of Botany, The University of British Columbia, Vancouver, BC, Canada, [10] School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, United Kingdom, [11] Daniel K. Inouye Center for Microbial Oceanography: Research and Education, University of Hawai'i at Mānoa, Honolulu, HI, United States

Nitrous oxide (N₂O) is an important atmospheric trace gas involved in tropospheric warming and stratospheric ozone depletion. Estimates of the global ocean contribution to N₂O emissions average 21% (range: 10 to 53%). Ongoing environmental changes such as warming, deoxygenation and acidification are affecting oceanic N₂O cycling and emissions to the atmosphere. International activities over the last decades aimed at improving estimates of global N₂O emissions, including (i) the MarinE MethanE and NiTrous Oxide database (MEMENTO) for archiving of quality-controlled data, and (ii) a recent large-scale inter-laboratory comparison by Working Group 143 of the Scientific Committee on Ocean Research (SCOR). To reduce uncertainties in oceanic N₂O emission estimates and to characterize the spatial and temporal variability in N₂O distributions in a changing ocean, we propose the establishment of a harmonized N₂O Observation Network (N2O-ON) combining discrete and continuous data from various platforms. The network will integrate observations obtained by calibrated techniques, using time series measurements at fixed stations and repeated hydrographic sections on voluntary observing ships and research vessels. In addition to exploiting existing oceanographic infrastructure, we propose the establishment of central calibration facilities in selected international laboratories to improve accuracy, and ensure standardization and comparability of N₂O measurements. Final data products will include a harmonized global N₂O concentration and emission fields for use in model validation and projections of future oceanic N₂O emissions, to inform the global research community and policy makers.

Keywords: nitrous oxide, observation network, oceanic distribution, oceanic emissions, calibration

INTRODUCTION

Nitrous oxide (N$_2$O; laughing gas) is an atmospheric trace gas, which accounts for 6% of tropospheric warming by greenhouse gasses, and is a major ozone-depleting compound in the stratosphere (Ravishankara et al., 2009; IPCC, 2013; WMO, 2014). Emission estimates indicate that the oceans may contribute 10 to 53% of combined natural and anthropogenic N$_2$O sources (Anderson et al., 2010; Ciais et al., 2013). N$_2$O has been measured in the water column of all major ocean basins, in most marginal seas and in numerous estuaries (Kock and Bange, 2015; Murray et al., 2015), with measurements from the surface mixed layer down to 9800 m in the deep Izu-Ogasawara Trench (Kawagucci et al., 2018). These and other studies show that N$_2$O concentrations may vary over three orders of magnitude from the open ocean to coastal shelves and semi-enclosed basins. Concentrations range from <1 nmol L^{-1} in the permanently anoxic deep basin waters of the Black Sea and Cariaco Trench (Hashimoto et al., 1983; Westley et al., 2006) to ≈1000 nmol L^{-1} in coastal near-surface waters off Peru (Arévalo-Martínez et al., 2015) and ≈1500 nmol L^{-1} in the suboxic deep waters of the Baltic Sea (Rönner, 1983). Some estuaries may reach similarly high concentrations (Barnes and Upstill-Goddard, 2011).

While the oceans are clearly a major natural contributor to atmospheric N$_2$O, quantitative estimates remain highly uncertain (Buitenhuis et al., 2018). This uncertainty reflects the low number of marine N$_2$O measurements to date, as compared to, for example, CO$_2$ [see e.g., (Bakker et al., 2016)], and the lack of information on (i) seasonal and inter-annual variability, (ii) land-ocean gradients, (iii) the effects of small scale/mesoscale features (Grundle et al., 2017) and (iv) extreme events such as storms (Naik et al., 2008). There is also uncertainty in the relative importance of the various biological processes driving the production and consumption of N$_2$O in oceanic waters, and their potential responses to changing oceanic conditions (Bange et al., 2010). Likewise, the influence of sea ice on N$_2$O emissions from high-latitude ecosystems is currently unknown (Vancoppenolle et al., 2013). Randall et al. (2012), for instance, showed that sea ice formation and melting cycles can reverse the direction of the N$_2$O fluxes across the ocean/atmosphere interface. Yet, the overall impact of these processes on the annual cycle is still unclear.

Oceanic N$_2$O production and consumption principally occurs in subsurface and deep waters. Microbial nitrification (N$_2$O is a by-product of ammonia oxidation to nitrite), partial denitrification (reduction of nitrate to N$_2$O), and nitrifier-denitrification (i.e., nitrifier switching to nitrite reduction under low O$_2$ conditions) are considered to be the main oceanic N$_2$O production pathways, whereas, the main N$_2$O sink is via reduction to N$_2$ by denitrification in anoxic waters (Bange et al., 2010). Extreme accumulation of N$_2$O resulting from nitrification and/or denitrification has been found at oxic/anoxic boundaries within oxygen minimum zones (OMZ) of the eastern tropical North/South Pacific Ocean and the Arabian Sea, and also in coastal shelf waters (Bange et al., 2010). In addition, several studies indicate N$_2$O production via nitrification in surface waters of the open ocean (Dore and Karl, 1996; Law and Ling, 2001; Morell et al., 2001) and in estuaries (Barnes and Upstill-Goddard, 2011), as well as its possible consumption during microbial N$_2$O fixation (Farías et al., 2013; Cornejo et al., 2015).

Environmental changes such as ocean warming (and associated changes in stratification and ice coverage), acidification, deoxygenation, and eutrophication due to increasing anthropogenic inputs of nutrients (via rivers and atmospheric deposition), may significantly alter N$_2$O production and consumption, its distribution patterns and, ultimately, its release to the atmosphere (Kroeze et al., 2005; Zhang et al., 2010; Suntharalingam et al., 2012; Rees et al., 2016; Myllykangas et al., 2017). Indeed, model projections that account for ocean warming and atmospheric nitrogen deposition show a net decrease of 4 to 24% in future global oceanic N$_2$O emissions during the 21st century (Martinez-Rey et al., 2015; Landolfi et al., 2017; Battaglia and Joos, 2018). One model projection suggests that the decrease of N$_2$O emissions in the 21st century might be followed by a substantial increase of the N$_2$O emissions in the 22nd century (Battaglia and Joos, 2018). The large degree of uncertainty in future N$_2$O emission projections results partly from the limitations of existing N$_2$O concentration data used in model parameterizations and validation. These current data sets are not yet cross-calibrated (their comparability is limited due to missing standard measurement protocols), and are biased by poor spatio-temporal coverage of the ocean (Kock and Bange, 2015).

The importance of additional, routine oceanic N$_2$O measurements is recognized by the Global Ocean Observing System (GOOS) program, which recently added N$_2$O to its list of Essential Ocean Variables (EOV)[1].

To reduce uncertainties in current global N$_2$O marine emission estimates, better constrain and understand temporal and spatial variability, and improve future projections of N$_2$O concentrations in a changing ocean, we propose the establishment of a harmonized Global N$_2$O Ocean Observation Network (N2O-ON).

OBSERVATION NETWORK COMPONENTS

Measurement Techniques

The analysis of N$_2$O at the sea surface and in the ocean interior differs in both measurement approach and the required analytical precision. While water column N$_2$O concentrations are usually determined using discrete seawater samples, state-of-the-art surface water measurements increasingly use air-water equilibration systems coupled to optical sensors in a continuous mode. In this section we briefly review the development of marine N$_2$O observations, discuss a coordinated approach to method calibration, and identify emerging technologies that should contribute to improved data quality and spatio-temporal coverage within N2O-ON.

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[1]www.goosocean.org

Discrete Measurements

The first study of oceanic N$_2$O distributions took place nearly 60 years ago in the South Pacific Ocean (Craig and Gordon, 1963), and was followed by measurements in the North Atlantic Ocean during the late 1960s/early 1970s (Junge and Hahn, 1971). A later study in the Sargasso and Caribbean Seas introduced the concept of "Δ(N$_2$O)" [$= c_{\text{measured}}$(N$_2$O) $- c_{\text{equilibrium}}$(N$_2$O)], to quantify the difference between the observed and air equilibrium concentration of dissolved N$_2$O, and thus examine net N$_2$O production/consumption (Yoshinari, 1976). The development of a rigorously calibrated electron capture detector (ECD) coupled with gas chromatography (GC) facilitated precise and reliable N$_2$O measurements (Rasmussen et al., 1976; Cohen, 1977; Elkins, 1980; Weiss et al., 1981). Since those pioneering studies, the increasing availability and comparatively low cost of such instrumentation facilitated a significant increase in data availability.

An important next step was the fundamental work on N$_2$O solubility in seawater (Weiss and Price, 1980), which promoted the development of equilibration techniques for high-resolution surveys of the surface ocean (Weiss et al., 1992) (see section "Continuous Surface Measurements") and water column N$_2$O (Butler et al., 1989; Butler and Elkins, 1991). Today, GC-ECD analysis, coupled to headspace equilibration or purge-and-trap techniques, is used by the majority of laboratories worldwide for quantifying dissolved N$_2$O in discrete seawater samples (Wilson et al., 2018). Even so, mass spectrometric analysis of N$_2$O is becoming increasingly wide-spread (Capelle et al., 2015; Babbin et al., 2017; Bourbonnais et al., 2017) and may become increasingly important in the future.

An inter-laboratory comparison of oceanic N$_2$O measurements was recently conducted by the Scientific Committee on Oceanic Research (SCOR) international Working Group (WG) 143[2]. Discrete water samples from the subtropical Pacific Ocean and the Baltic Sea were distributed to participating laboratories (Wilson et al., 2018) for a comparison of accuracy and precision. The samples represented a range of N$_2$O concentrations, from low concentrations in the oligotrophic open ocean to high concentrations in highly productive and suboxic coastal waters. Recommendations arising from the inter-comparison include (Wilson et al., 2018):

 (i) calibration of working gas standards against primary standards,
 (ii) incorporation of internal controls (i.e., air-equilibrated seawater) alongside routine sample analysis, and
(iii) the production of high and low N$_2$O concentration reference seawater for calibrating N$_2$O measurements across the full range of seawater N$_2$O concentrations.

Primary gas standard mixtures obtained from atmospheric monitoring agencies will ensure consistency between ocean observations and global atmospheric monitoring networks such as NOAA's Earth System Research Laboratory/Global Monitoring Division (ESRL/GMD[3]), NASA's Advanced Global Atmospheric Gasses Experiment (AGAGE[4]) and the European Integrated Carbon Observing System (ICOS[5]). With accompanying guidelines for discrete measurements in preparation, these recommendations should lead to significant advances in precision and accuracy, thereby improving the inter-comparability of dissolved N$_2$O measurements and facilitating the detection of seasonal and inter-annual N$_2$O variability in the near future. Detecting inter-annual N$_2$O signals is a major goal of N2O-ON, and will require a precision of better than 0.02 nmol L^{-1} (<0.2%). This value is derived from the expected change in N$_2$O solubility due to an annual surface ocean warming of 0.01°C, and an annual increase of 1 nmol mol^{-1} (ppb) in the atmospheric N$_2$O dry mole fraction, setting the salinity to 35 assuming no changes in oceanic N$_2$O sources and sinks.

Continuous Surface Measurements

In addition to the discrete analysis of N$_2$O, measurements are also conducted by continuous sampling from the shipboard underway seawater supply. Such measurements are made at a fixed depth (generally between 2 and 10 m below the sea surface) and are often accompanied by atmospheric measurements. These underway measurements have benefited from recent technological advances in cavity-enhanced absorption spectroscopy (CEAS), which facilitate rapid and precise N$_2$O detection at very low atmospheric mole fractions (i.e., in the sub-ppb range). CEAS analyzers coupled to continuous seawater/gas equilibrators (Arévalo-Martínez et al., 2013; Grefe and Kaiser, 2014; Erler et al., 2015; Zhan et al., 2018) are now frequently used to determine N$_2$O temporal and spatial variability in surface layers of open and coastal oceans, see e.g., (Arévalo-Martínez et al., 2015; Brase et al., 2017; Grefe et al., 2018; Wells et al., 2018). In addition to CEAS, Fourier Transform Infrared (FTIR) analysis coupled to continuous seawater/gas equilibration (Müller D. et al., 2016) has been developed. A ship-board comparison of five analytical systems (incl. four CEAS systems and one FTIR system) for continuous dissolved N$_2$O measurements was conducted in the Baltic Sea as part of the activities of SCOR WG 143, demonstrating good agreement between measurements obtained from the different systems. Only recently, a Pumped Profiling System (PPS), connected with a liquid degassing membrane coupled with CEAS has allowed real-time, high-resolution, vertically resolved measurements of sub-surface N$_2$O (Troncoso et al., 2018). N2O-ON will encourage the wider use of these and emerging new technologies where they can contribute to improvements to data quality, measurement frequency and spatial resolution.

Measurements in the Marine Boundary Layer

Accurate estimates of N$_2$O flux densities across the ocean/atmosphere interface require measurements of the N$_2$O mole fraction in the atmospheric boundary layer above the ocean, as well as ocean surface N$_2$O concentrations.

[2]https://scor-int.org/group/143/
[3]www.esrl.noaa.gov/gmd

[4]https://agage.mit.edu
[5]https://www.icos-ri.eu

Atmospheric dry mole fraction can be converted into seawater saturation concentration as a function of seawater temperature, salinity and ambient pressure using an established solubility equation (Weiss and Price, 1980). Atmospheric N$_2$O dry mole fractions are often measured in parallel with continuous underway measurements on research vessels and on vessels of opportunity (VOS: also often referred to as "Voluntary Observing Ship" routes) (Arévalo-Martínez et al., 2013). As for seawater measurements, N2O-ON advocates the routine rigorous calibration and quality control of accompanying atmospheric data.

The relatively inert nature of the N$_2$O molecule results in a long tropospheric residence time, leading to well-mixed and regionally invariant global mole fractions (Prather et al., 2015). Consequently, where high quality ship-based atmospheric measurements are unavailable, N2O-ON will encourage use of high quality data from land-based global atmospheric monitoring networks; for example tropospheric N$_2$O dry mole fractions from ESRL/GMD (see text footnote 3) or AGAGE (see text footnote 4). This will enable the extrapolation of individual campaign results to regional or global scales. Satellite-based N$_2$O measurements show promise to augment atmospheric data collection at land-based monitoring stations, but these remote sensing observations currently have intrinsically large measurement errors, making them unsuitable for quantifying air-sea N$_2$O exchange (Xiong et al., 2014; Bernath et al., 2017). With further improvements, however, such approaches have the potential to inform N2O-ON in the future.

Future Enhancements

New CEAS-based instruments allow high quality N$_2$O isotopolog measurements (Harris et al., 2013). N2O-ON will identify an observational framework that will facilitate deployment of these instruments on selected sustained observation lines to provide additional constraints on the global atmospheric N$_2$O budget (Rahn and Wahlen, 2000; Bernard et al., 2006; Park et al., 2012), and to potentially provide greater insight into the mechanisms of oceanic N$_2$O production and consumption (Sutka et al., 2006; Yamagishi et al., 2007).

Although the development of CEAS can considerably improve N$_2$O monitoring capabilities (see above), the estimation of sea/air N$_2$O flux densities remains challenging because of the intrinsic temporal and spatial variability in surface ocean N$_2$O concentrations, and the variability of existing gas exchange parameterizations (Garbe et al., 2014), which reflect the complexity in environmental controls of air-sea gas exchange. Unraveling this complexity, and thereby refining gas exchange parameterizations, is the focus of considerable ongoing research beyond the scope of N2O-ON. However, techniques such as the eddy covariance (EC) method that directly evaluate air-sea fluxes circumvent the need for such parameterizations (Businger, 1986). Going forward, the use of direct flux techniques such as EC in combination with N$_2$O analysis by CEAS will be encouraged by N2O-ON as a means of enhancing our understanding of N$_2$O fluxes across the sea surface on a range of temporal and spatial scales.

Observation Platforms

N2O-ON will exploit established and new observation platforms to improve the characterization of spatial and temporal variability in oceanic N$_2$O concentrations.

Research Vessels

To date, the majority of surface and water column N$_2$O data have been obtained on board research vessels from discrete samples collected in Niskin bottles on a CTD Rosette (see section "Discrete Measurements"), or from underway surface measurements via a continuous seawater supply (see section "Continuous Surface Measurements"). While the significant contribution of research vessels is beyond question and will be supported by N2O-ON, such vessels have a limited spatial and temporal footprint, with most sampling campaigns not repeated regularly and mainly occurring during the summer. N2O-ON will address this limitation by promoting the use of additional measurement platforms and sustained observational campaigns.

Repeat Hydrographic Lines and Time-Series Stations

Repeat hydrographic sampling programs are important in evaluating variability at the ocean-basin scale and for establishing variability on timescales from seasonal to decadal. For example, N$_2$O has been measured biannually since 2012 in repeat hydrographic/geochemistry surveys on GO-SHIP[6] section A25 between Portugal and Greenland (de la Paz et al., 2017). The Atlantic Meridional Transect[7] is an example of an annually repeated cruise on which N$_2$O measurements have been made over two decades (Forster et al., 2009; Rhee et al., 2009; Grefe and Kaiser, 2014). N$_2$O has been repeatedly measured during the annual Chinese Arctic and Antarctic Expeditions (CHINARE) to the Arctic and Southern Oceans, see e.g., (Zhan and Chen, 2009; Zhan et al., 2015, 2017). Beside these examples, there are few published time-series measurements of open ocean water column N$_2$O distributions from repeat hydrographic sections (Nevison et al., 1995; Fenwick and Tortell, 2018). Extending and optimizing the distribution and sampling frequency of repeat hydrographic lines is an important future aspiration for N2O-ON, both for open-ocean and coastal regimes.

Temporal variability is also investigated through regular data collection at a small number of fixed time-series stations, which are usually located close to land. Examples include stations off Goa (India), in Saanich Inlet (Vancouver Island, British Columbia), off central Chile, off Hawai'i in the North Pacific subtropical gyre, in the Eckernförde Bay (southwestern Baltic Sea) and in the Strait of Gibraltar (Naqvi et al., 2010; de la Paz et al., 2015; Farías et al., 2015; Capelle and Tortell, 2016; Wilson et al., 2017; Capelle et al., 2018). Considering the important role of coastal regions in the global N$_2$O cycle (Bange, 2006; Anderson et al., 2010; Ciais et al., 2013), extending the spatial coverage of fixed time-series stations within a coordinated network is a major aspiration of N2O-ON.

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[6]www.go-ship.org/

[7]www.amt-uk.org/

VOS Lines

Autonomous measurement systems on established, regular international VOS routes are restricted to near-surface measurements, and thus do not provide depth-resolved N$_2$O data. Nevertheless, they do have the potential to deliver a comprehensive picture of the temporal and (limited) spatial variability in surface water N$_2$O distributions. A pilot VOS line N$_2$O study in the North Atlantic Ocean between Liverpool, United Kingdom, and Halifax, Canada, was conducted in January 2017 by GEOMAR for the EU InGOS program[8]. The EU BONUS INTEGRAL program[9] will establish N$_2$O surface measurements on two VOS lines in the Baltic Sea between Lübeck/Travemünde (Germany) and Helsinki (Finland) as well as to Kemi (Finland) at the northern tip of the Baltic Sea. The successful long-term operation of CEAS-based measurements of dissolved non-CO$_2$ greenhouse gasses has already been demonstrated for methane in the Baltic Sea (Gülzow et al., 2011, 2013). Nevertheless, autonomously monitoring of N$_2$O on VOS lines requires a clean and maintained seawater supply, the oversight of analytical and emergency systems, and rapid instrument turnaround and cleaning during port calls. Although this is logistically challenging, particularly in remote ocean regions, the increased spatio-temporal coverage offered by measurement of near-surface N$_2$O on VOS routes should be encouraged as a component of N2O-ON.

Other Sampling Platforms

To date, there are no autonomous underwater sensors available for long-term in-situ N$_2$O monitoring in either the open or coastal ocean. Addressing this gap will require small, robust (resistant to high-pressure, hydrogen sulfide and biofouling) rapid response sensors with low power requirements for long-term deployment. Once developed, these sensors have the capability to decipher oceanic N$_2$O distributions with unprecedented spatio-temporal resolution. Potential sensor platforms include Bio-Argo floats[10], gliders, coastal/deep sea moorings and mooring arrays, cabled observatories, drifting buoys and lander systems. We advocate a strong focus on the future development of such sensors and their subsequent integration into N2O-ON.

Data Management
MEMENTO

MEMENTO (The MarinE MethanE and NiTrous Oxide database[11]), launched in 2009 (Bange et al., 2009), archives quality-controlled N$_2$O data from the open and coastal oceans (including estuaries, fjords etc.) (Kock and Bange, 2015). MEMENTO also publishes N$_2$O data sets, making them publicly and freely available. Regular updates include new datasets, additional meta-information, and the implementation of improved data quality control. As MEMENTO expands,

it will adopt best practices for quality control according to the recommendations resulting from inter-comparison exercises (Wilson et al., 2018) and in accordance to existing databases such as the Surface Ocean CO$_2$ Atlas (SOCAT[12]) and the Global Ocean Data Analysis Project for Carbon (GLODAP[13]). N2O-ON and MEMENTO are clearly complementary and the routine archiving of quality-controlled data in MEMENTO is an intrinsic requirement of N2O-ON.

Ancillary Data

To evaluate the N$_2$O data derived from N2O-ON, additional standard hydrographic data (i.e., water temperature, salinity, depth) are important. In addition, chemical (i.e., dissolved O$_2$ and nutrient concentrations, and pH) and meteorological (i.e., air temperature, pressure, wind speed) data should ideally be collected. Most, if not all, of these variables are measured on a routine basis during research cruises, at some time-series stations and on some repeat hydrographic lines (see section "Observation Platforms"). VOS lines could be equipped with continuously operating systems such as the FerryBox[14]. N2O-ON will formally identify a suite of mandatory ancillary measurements and recommend appropriate measurement and/or sample collection alongside N$_2$O where possible.

BASELINE MEASUREMENTS

Resource constraints (both financial and personnel) preclude the extensive monitoring of N$_2$O concentrations across the entire global ocean. For this reason, a primary goal of N2O-ON is to develop a highly strategic sampling approach. In **Figure 1**, N$_2$O seasonal distributions derived from MEMENTO clearly show severe under-sampling of many ocean regions during various seasons, and it is precisely these regions that should be the target of near-term sampling efforts within N2O-ON. The following regions were specifically identified:

- the North Atlantic during December – February,
- the South Atlantic Ocean during March – August,
- the North Pacific Ocean during September – February,
- the South Pacific Ocean during all seasons,
- the North and South Indian Ocean during all seasons,
- the Southern and Arctic Oceans during all seasons, and
- selected marginal seas and major estuaries.

N2O-ON will coordinate N$_2$O baseline measurements on VOS, establishing these along major international shipping routes crossing the gyres of the major basins of the Atlantic, Pacific and Indian Oceans (**Figure 2**). We propose the establishment of repeat hydrographic lines using research vessels and/or VOS lines to measure N$_2$O in the surface waters and water column of the Eastern Boundary Upwelling Systems (EBUS) and the Arabian Sea. This could exploit VOS lines transiting
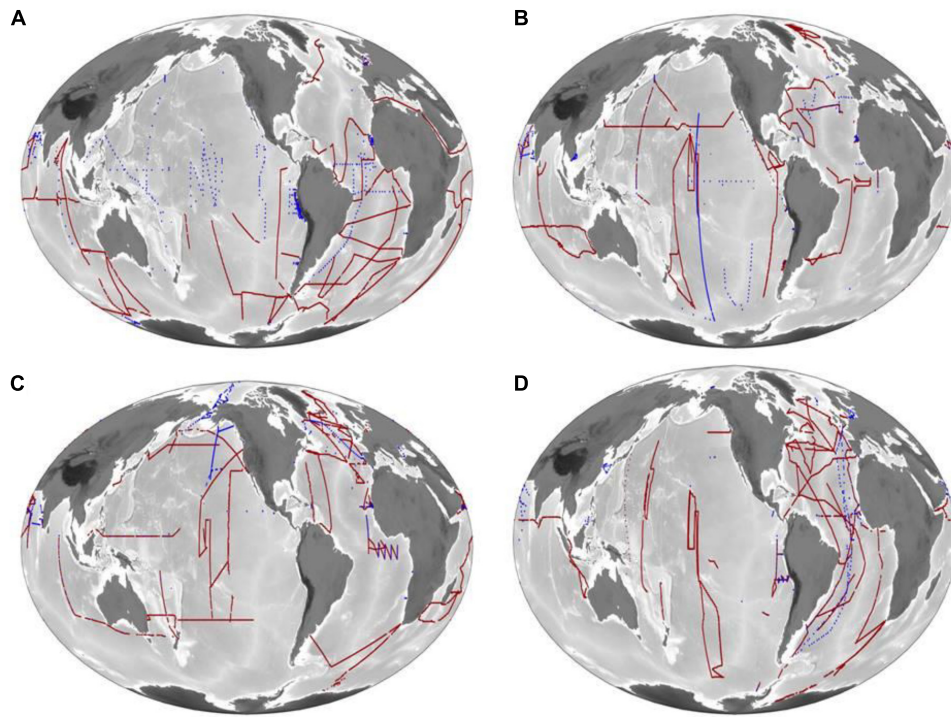

FIGURE 1 | Maps of the distribution of N$_2$O measurements in **(A)** December, January, February; **(B)** March, April, May; **(C)** June, July, August and **(D)** September, October, November. Red lines indicate continuous surface measurements. Blue dots indicate locations of N$_2$O depth profiles. Data are from MEMENTO as of October 04, 2018 (https://memento.geomar.de/de).
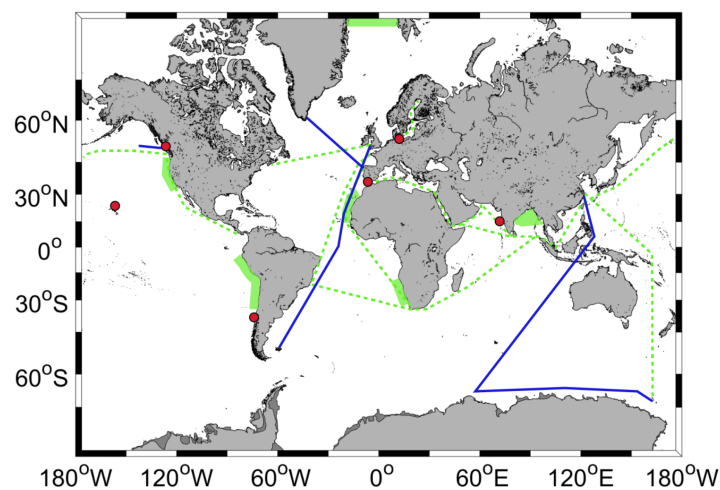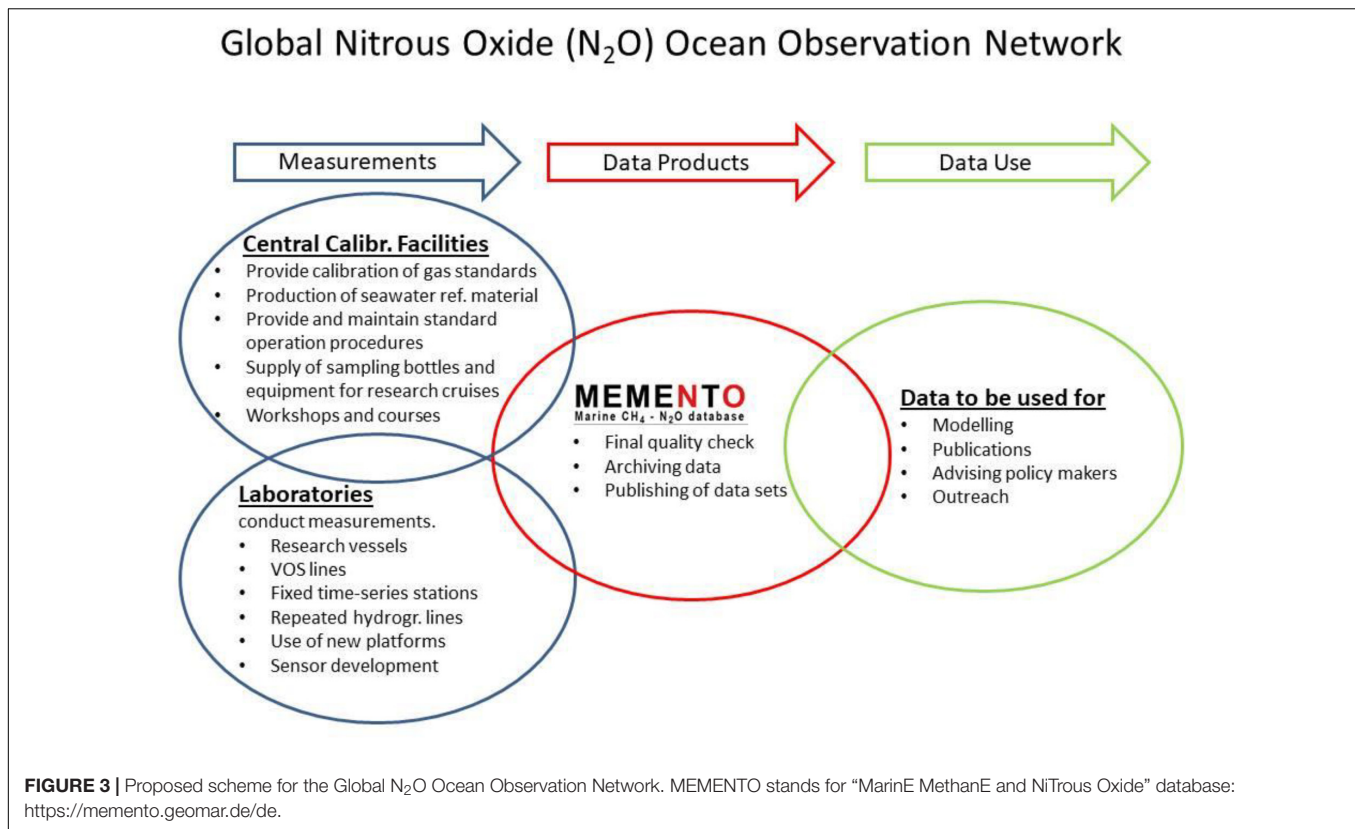

FIGURE 2 | N$_2$O baseline measurements proposed for N2O-ON. Blue lines/red points indicate currently active repeated oceanographic sections/fixed time-series stations (see text). Dashed green lines indicate prospective VOS lines to be equipped with systems for continuous measurements. Green shaded areas mark key regions for the establishment of new time-series stations.

international shipping routes along the west coasts of North and South America, northwest and southwest Africa, and in the Arabian Sea. Moreover, routine N$_2$O measurements should be incorporated into the FRAM Ocean Observing System (Soltwedel et al., 2013) in order to close some of the large data gaps in the Arctic Ocean (**Figure 2**).

Incorporating N$_2$O into the suite of measurements of some established repeat hydrographic sections, such as GO-SHIP[15] or GEOTRACES[16], could provide a basin-scale approach to resolve

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[15]www.goship.org
[16]www.geotraces.org/

FIGURE 3 | Proposed scheme for the Global N_2O Ocean Observation Network. MEMENTO stands for "MarinE MethanE and NiTrous Oxide" database: https://memento.geomar.de/de.

N_2O variability in the ocean interior, thus forming an important N2O-ON collaborative activity. N2O-ON will also encourage the regular monitoring of N_2O in shelf areas and estuaries, which are prone to changes in redox-sensitive biogeochemistry due to enhanced anthropogenic and climatic impacts. Such activities would ideally be managed by local oceanographic institutes and/or relevant universities.

Established N_2O time-series (see Section "VOS Lines") at fixed station sites need to be continued. N2O-ON will identify additional sites to be established in the EBUS off Oregon/California, Peru, Mauritania and Namibia, in the northeast Indian Ocean (Bay of Bengal), and at some strategic coastal and enclosed basin sites to form a comprehensive and coordinated network. In addition to being important N_2O sources to the atmosphere, these regions benefit from proximity to the necessary infrastructure provided by local/regional oceanographic institutes.

SUMMARY AND OUTLINE OF N₂O-ON

Surface N_2O concentration data can now be obtained with unprecedented precision. The inherent error in the CEAS technique is small relative to error in associated measurements (e.g., temperature correction to the seawater supply, non-steady state in the equilibration chamber, etc.). Even so, a harmonized data set requires a mechanism for

inter-calibration, mutual agreement on metadata information and standard post-processing operations, as has been established for the global ocean surface CO_2 network SOCAT (Pfeil et al., 2013). Enhancing the accuracy and consistency of discrete dissolved N_2O concentration measurements requires the availability of liquid standards derived from strict preparation protocols, for example by the equilibration of seawater with air at known temperatures and salinity (Capelle et al., 2015; Wilson et al., 2018), or through the distribution of certified reference materials covering the range of concentrations expected in the oceanic environment (Wilson et al., 2018). The availability of a suitable reference material has been crucial in quantifying the oceanic carbon system (Dickson et al., 2007) with the required precision and accuracy to detect and evaluate long-term trends [e.g., (Müller J. D. et al., 2016)].

To improve and harmonize N_2O measurements in a changing ocean, we suggest establishing a Global N_2O Ocean Observation Network (N2O-ON) as outlined in **Figure 3**. In addition to exploiting existing oceanographic infrastructure (research vessels, VOS/repeat hydrographic lines etc.), we propose to establish central calibration facilities (CCF) in selected laboratories around the world to secure the comparability of N_2O measurements, and provide data sets with maximum accuracy. The CCF will: (1) enable the precise calibration of N_2O gas standards; (2) produce certified seawater reference material; (3) provide and maintain standard operating procedures for

both surface and water column measurements; and (4) supply sampling bottles and equipment for research campaigns. Moreover, the N2O-ON calibration facilities will conduct regular internal comparison exercises to ensure long-term and high-level calibration performance. MEMENTO will archive all N_2O data and make them publicly available following stringent quality checks. MEMENTO will also publish the N_2O data sets with digital object identifiers (doi's) to ensure appropriate referencing and tracking. Final N2O-ON data products, such as global N_2O concentration maps, emissions, budgets and trends, will be used in modeling studies for projections of future trends in oceanic N_2O emissions and advising policy makers and global climate assessments (Ciais et al., 2013). We advocate the establishment of regular workshops and courses to support all of these activities and to train the additional next generation of researchers who will be required to help realize the goals of N2O-ON.

DATA AVAILABILITY

No datasets were generated or analyzed for this study.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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