# **UCLA**

# **UCLA Previously Published Works**

## **Title**

Global reconstruction reduces the uncertainty of oceanic nitrous oxide emissions and reveals a vigorous seasonal cycle

### **Permalink**

https://escholarship.org/uc/item/5n6432kn

# **Journal**

Proceedings of the National Academy of Sciences of the United States of America, 117(22)

### **ISSN**

0027-8424

### **Authors**

Yang, Simon Chang, Bonnie X Warner, Mark J et al.

## **Publication Date**

2020-06-02

### DOI

10.1073/pnas.1921914117

Peer reviewed



# Global reconstruction reduces the uncertainty of oceanic nitrous oxide emissions and reveals a vigorous seasonal cycle

Simon Yang<sup>a</sup>, Bonnie X. Chang<sup>b,c,1</sup>, Mark J. Warner<sup>d,1</sup>, Thomas S. Weber<sup>e,1</sup>, Annie M. Bourbonnais<sup>f</sup>, Alyson E. Santoro<sup>9</sup>, Annette Kock<sup>h</sup>, Rolf E. Sonnerup<sup>b,c</sup>, John L. Bullister<sup>c,2</sup>, Samuel T. Wilson<sup>i</sup>, and Daniele Bianchi<sup>a,3</sup>

<sup>a</sup>Department of Atmospheric and Oceanic Sciences, University of California Los Angeles, CA 90095; <sup>b</sup>Joint Institute for the Study of the Atmosphere and Ocean, University of Washington, Seattle, WA 98195; <sup>c</sup>Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, Seattle, WA 98115; <sup>d</sup>School of Oceanography, University of Washington, Seattle, WA 98195; <sup>e</sup>Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627; <sup>f</sup>School of the Earth, Ocean and Environment, University of South Carolina, Columbia, SC 29208; <sup>g</sup>Department of Ecology, Evolution, and Marine Biology, University of California, Santa Barbara, CA 93106; <sup>h</sup>Chemical Oceanography Research Unit, GEOMAR Helmholtz Centre for Ocean Research Kiel, 24148 Kiel, Germany; and <sup>i</sup>Center for Microbial Oceanography: Research and Education (C-MORE), University of Hawaii, Honolulu, HI 96822

Edited by François M. M. Morel, Princeton University, Princeton, NJ, and approved April 1, 2020 (received for review December 14, 2019)

Assessment of the global budget of the greenhouse gas nitrous oxide (N2O) is limited by poor knowledge of the oceanic N2O flux to the atmosphere, of which the magnitude, spatial distribution, and temporal variability remain highly uncertain. Here, we reconstruct climatological N2O emissions from the ocean by training a supervised learning algorithm with over 158,000 N2O measurements from the surface ocean—the largest synthesis to date. The reconstruction captures observed latitudinal gradients and coastal hot spots of N2O flux and reveals a vigorous global seasonal cycle. We estimate an annual mean N2O flux of 4.2  $\pm$ 1.0 Tg  $N \cdot y^{-1}$ , 64% of which occurs in the tropics, and 20% in coastal upwelling systems that occupy less than 3% of the ocean area. This  $N_2O$  flux ranges from a low of 3.3  $\pm$  1.3 Tg  $N \cdot y^{-1}$  in the boreal spring to a high of 5.5  $\pm$  2.0 Tg N·y<sup>-1</sup> in the boreal summer. Much of the seasonal variations in global N2O emissions can be traced to seasonal upwelling in the tropical ocean and winter mixing in the Southern Ocean. The dominant contribution to seasonality by productive, low-oxygen tropical upwelling systems (>75%) suggests a sensitivity of the global N2O flux to El Niño-Southern Oscillation and anthropogenic stratification of the low latitude ocean. This ocean flux estimate is consistent with the range adopted by the Intergovernmental Panel on Climate Change, but reduces its uncertainty by more than fivefold, enabling more precise determination of other terms in the atmospheric N2O budget.

nitrous oxide  $\mid$  air–sea gas exchange  $\mid$  seasonal variability  $\mid$  nitrogen cycle  $\mid$  greenhouse gases

 $ightharpoonup^2 O$  is a greenhouse gas 300 times more potent than  $CO_2$  and the third strongest contributor to radiative forcing from anthropogenic emissions (1). It is also a primary cause of stratospheric ozone depletion (2). Recent syntheses indicate that the oceans account for a third of all natural atmospheric N<sub>2</sub>O sources (ref. 3 and *SI Appendix*, Table S1), while the remaining two-thirds are mostly sourced on land (ref. 3 and SI Appendix, Table S1). This partitioning has a substantial uncertainty, due to poorly constrained N2O emissions from both the land and the ocean. Uncertainty in the global oceanic N<sub>2</sub>O flux is particularly large, with values reported in the latest Intergovernmental Panel on Climate Change Report (IPCC Fifth Assessment Report [AR5]) ranging from 1.8 to 9.45 Tg N·y<sup>-</sup> a fivefold variation (3). While this large uncertainty reflects the historical scarcity of N2O measurements and the limitations of earlier estimates, it does not represent the recent progress and community consensus—thus calling for a revised synthesis.

 ${
m N_2O}$  is produced in the ocean interior by nitrification and denitrification, two processes linked to the remineralization of organic matter. This production is enhanced at low oxygen

concentrations and is compensated by  $N_2O$  consumption in anoxic waters and emission to the atmosphere when  $N_2O$ -laden waters emerge at the surface. Current approaches to estimate the  $N_2O$  air–sea flux couple spatial maps of  $N_2O$  disequilibrium ( $\Delta p N_2O$ , the  $N_2O$  partial pressure difference across the ocean–atmosphere interface) to wind-dependent models of gas exchange (4–8). In turn, estimates of  $\Delta p N_2O$  rely on either observational syntheses or numerical models. In observation-based approaches,  $\Delta p N_2O$  data, calculated from oceanic  $N_2O$  concentrations or partial pressures, are extrapolated to the global ocean (4, 5). Model-based approaches calculate  $\Delta p N_2O$  from coupled ocean circulation–biogeochemical models. Both methods have inherent limitations. Until recently, data coverage was sparse over much of the ocean, in particular, coastal upwelling systems, which host important  $N_2O$  air–sea fluxes (5,

#### **Significance**

 $N_2O$  is a potent greenhouse gas whose oceanic emissions are still poorly constrained. Here, we reconstruct oceanic  $N_2O$  emissions from the largest observational synthesis to date, substantially reducing the uncertainty compared to previous estimates and enabling a tightening of the global budget of this gas. We also reveal a vigorous global seasonal cycle, dominated by productive, low-oxygen tropical regions, which suggests sensitivity of the  $N_2O$  cycle to natural climate variability and anthropogenic climate change.

Author contributions: S.Y., T.S.W., and D.B. designed research; S.Y. and D.B. performed research; S.Y., B.X.C., M.J.W., A.M.B., A.E.S., A.K., R.E.S., J.L.B., and S.T.W. analyzed data; S.Y. and D.B. wrote the paper; M.J.W., A.M.B., A.E.S., A.K., R.E.S., and J.L.B. collected  $N_2O$  measurements; M.J.W. and J.L.B. provided  $N_2O$  measurements; A.M.B., A.E.S., A.K., and R.E.S. provided  $N_2O$  observations; M.J.W., T.S.W., A.M.B., A.E.S., A.K., R.E.S., J.L.B., and S.T.W. provided inputs for the paper; and S.T.W. organized the Oceanic Methane & Nitrous Oxide Workshop in October 2018, which provided impetus for this work.

The authors declare no competing interest.

This article is a PNAS Direct Submission.

Published under the PNAS license

Data deposition: The compilation of  $N_2O$  measurements, the reconstructed global  $\Delta p_{N_2O}$  climatology, and  $N_2O$  air–sea flux are available for download on the Biological & Chemical Oceanography Data Management Office (BCO-DMO) portal (https://www.bco-dmo.org/dataset/810032 (DOI: 10.26008/1912/bco-dmo.810032.1). The code used to produce these datasets can be found on a public GitHub repository at https://github.com/yangsi7/mapping-ocean-n2o (DOI: 10.5281/zenodo.3757194).

<sup>1</sup>B.X.C., M.J.W., and T.S.W. contributed equally to this work.

This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1921914117/-/DCSupplemental.

First published May 18, 2020.

<sup>&</sup>lt;sup>2</sup>Deceased June 13, 2018.

<sup>&</sup>lt;sup>3</sup>To whom correspondence may be addressed. Email: dbianchi@atmos.ucla.edu.

9, 10), and much of the polar ocean. In addition, the scarcity of repeated measurements hindered extrapolation of sparse N2O observations to seasonal timescales. The models in refs. 6-8, which have the advantage of resolving seasonal dynamics, rely on simple representations of the N<sub>2</sub>O cycle that poorly represent its sources and sinks in the ocean and are usually too coarse to capture the intense N<sub>2</sub>O supersaturation observed in coastal waters (9, 10).

Time series of N<sub>2</sub>O measurements have revealed that N<sub>2</sub>O air-sea fluxes can have a strong seasonal cycle (11), albeit with substantial regional variability. For example, an extensive survey in the Arabian Sea showed a strong monsoonal modulation of N<sub>2</sub>O outgassing (12, 13). Similarly, seasonal variations in atmo-

spheric N<sub>2</sub>O in the Southern Ocean can only be explained by seasonality in the underlying ocean circulation (14, 15). This seasonality provides important insights into the drivers of N<sub>2</sub>O emissions, but, to date, the global seasonal cycle of oceanic N<sub>2</sub>O emissions has only been crudely reconstructed and remains uncertain (4).

In this study, we train a supervised learning algorithm with a large compilation of N2O measurements to reconstruct the global distribution of N2O fluxes from well-sampled environmental variables. This reconstruction reveals a vigorous seasonal cycle and captures recently observed hot spots of coastal  $N_2O$  emission (9, 10), yielding an understanding of the factors controlling regional N2O fluxes.

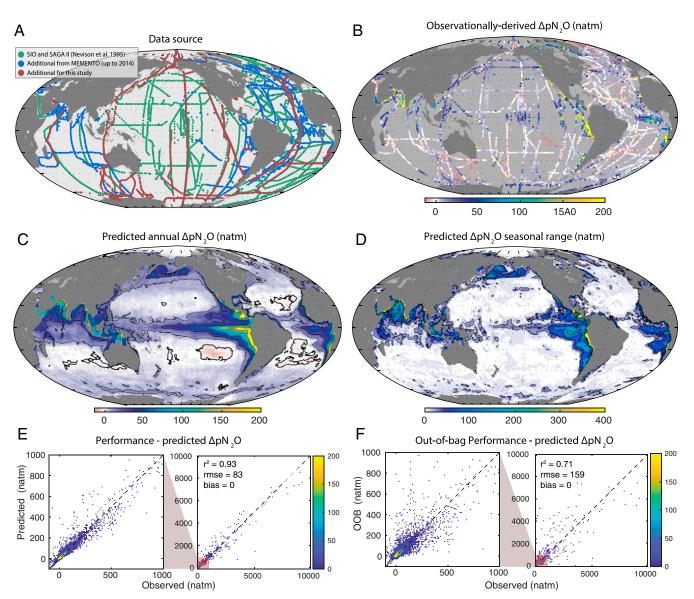


Fig. 1. Observed and reconstructed surface-ocean N2O supersaturation. (A) Location and source of the data. Green dots shows the data used in earlier N2O flux estimates (4); blue dots show the additional data in the MEMENTO database (16); and red dots are additional data compiled for this study (Dataset S1). (B) Observed N2O supersaturation averaged on a 0.25° grid and expressed as  $\Delta$ pN2O (natm). (C) Reconstructed annual N2O supersaturation. (D) Reconstructed seasonality of N2O supersaturation (natm), calculated as the seasonal range over the 12-mo period. (E) Performance of the random forest reconstruction shown as two joint distribution plots of predicted vs. observed  $\Delta pN_2O$  (colors indicate the number of grid points; note the different axis ranges). (F) Same as E, but using out-of-bag (OOB) predictions, i.e., predictions vs. observations withheld from training (SI Appendix, section S1B). Annotations in E and F show the square of the correlation coefficient ( $r^2$ ), the rmse and the global bias. Refer to SI Appendix, Fig. S1 for the monthly distribution of the data; SI Appendix, Figs. S2-S9 for model performance and uncertainty as well as regional zooms; SI Appendix, Figs. S10-S12 for seasonal maps and time series of ΔpN<sub>2</sub>O, including stereographic projections for polar regions; and Dataset S1 for a comprehensive list of the cruises included in the compilation.

### **Method Overview**

The foundation of our work is a compilation of over 158,000 observations of N2O mixing ratio, partial pressure, and concentration in the surface ocean (Dataset S1). This compilation, which builds extensively on the Marine Methane and NiTrous Oxide (MEMENTO) database (17), contains close to two times more surface measurements than previous syntheses (5), covering critical, previously undersampled regions (Fig. 1A). We estimate the N<sub>2</sub>O disequilibrium at the location of each measurement following:

$$\Delta X_{\rm N_2O} = X_{\rm ocean}^{\rm N_2O} - X_{\rm atm}^{\rm N_2O}$$
. [1]

Here,  $X_{\rm ocean}^{\rm N_2O}$  are ocean-side N<sub>2</sub>O measurements converted to mixing ratios, and  $X_{\rm atm}^{\rm N_2O}$  is the atmospheric N<sub>2</sub>O mixing ratio estimated by interpolating the National Oceanic and Atmospheric Administration (NOAA) atmospheric N<sub>2</sub>O flask dataset (18) at the latitude and time of the oceanic measurements (refer to SI Appendix, section S1 for detailed methods).

To convert sparse observations to a global climatology, we trained 100 ensembles of regressions trees (random forests) to predict  $\Delta X_{\rm N_2O}$  based on its relationship to well-sampled physical and biogeochemical predictors. Similar methods have been applied to map the distribution of chemical species in the ocean (19), including the dissolved gas methane (20). The predictors were based on hydrographic variables, nutrients, oxygen, chlorophyll concentrations, net primary production, and seafloor depth and are listed in SI Appendix, Table S2. Finally, we express the supersaturation as  $\Delta p N_2 O = \Delta X_{N_2 O} \cdot P$ , where P is the local atmospheric pressure, and calculate the N<sub>2</sub>O airsea flux as:

$$\Phi = (1 - f_{ice}) \cdot S \cdot k \cdot \Delta p N_2 O,$$
 [2]

where  $\Phi$  is the N<sub>2</sub>O flux,  $f_{ice}$  is the fractional sea ice cover, S is the  $N_2O$  solubility, and k is the piston velocity (refer to SI Appendix, section S2 for detailed methods). We estimated piston velocities using two wind-speed-dependent parameterizations: an updated version of a commonly used quadratic formulation (21, 22) and a recent formulation that explicitly accounts for the effect of bubble-mediated fluxes (23). We applied each parameterization to two high-resolution wind products (24, 25) that are available at 0.25°, 6-hourly resolution for the period from 1988 to 2017, yielding four permutations of the piston velocity (SI Appendix, section S2). In total, we obtained an ensemble of 400 global N<sub>2</sub>O air-sea flux estimates, from which we calculated a mean and uncertainty range.

### **Results and Discussion**

### $\Delta pN_20$ .

Annual mean distribution. The ensemble mean prediction reproduces  $\Delta pN_2O$  extremely faithfully ( $r^2 = 0.92$ ; SI Appendix, Fig. S2), while maintaining high generalization; observations that were withheld from the training step of the algorithm were predicted with an  $r^2$  of 0.70, an rms error (rmse) of  $\sim 159$  natm (32 natm excluding waters from the Peruvian upwelling) and a negligible global bias ( $\sim 0.01$  natm; SI Appendix, Figs. S2– S5 and S7-S9). Consistent with previous work (4, 8, 26), we found that large swaths of the surface ocean are supersaturated with N2O, including productive upwelling regions, the subpolar Pacific, and the Southern Ocean. Slight supersaturation and occasional undersaturation are predicted in the subtropical gyres (Fig. 1C). Undersaturation also characterizes the open Arctic Ocean, while its shelves, in particular, the East Siberian Shelf, are supersaturated. An aspect of our reconstruction is the ability to capture narrow bands of strong supersaturation observed in Eastern Boundary Upwelling Systems (Fig. 1 A and C), particularly along the western coast of India (27), Namibia (10), and Peru (9). There, some of the highest  $\Delta pN_2O$  ever observed, in excess of 8,000 natm, were successfully reproduced (SI Appendix, Figs. S2, S3, and S9).

We estimated the relative importance of each of the predictors by performing a recursive feature elimination for all potential predictor combinations (SI Appendix, section S1C). We found that chlorophyll, subsurface oxygen, and subsurface apparent oxygen utilization (AOU) were the features with highest predictive power for our  $\Delta p N_2 O$  dataset. A model trained with these three predictors alone can explain over 60% of the variance in observed  $\Delta pN_2O$  (SI Appendix, Fig. S6). The importance of these predictors is consistent with N<sub>2</sub>O production from nitrification and denitrification, which are enhanced in high-productivity, low- $O_2$  waters (28).

ΔpN<sub>2</sub>O seasonality and drivers. The annual mean reconstruction of  $\Delta pN_2O$  hides a dynamic seasonal cycle (Fig. 1D), with a range generally proportional to the mean saturation of the waters (Fig. 1C).

Accordingly, the largest seasonal  $\Delta pN_2O$  excursions are found over the coastal waters of Peru, the Arabian Sea, and the Costa Rica Dome, where  $\Delta pN_2O$  can change by over 500 natm over the course of the year. Significant  $\Delta pN_2O$  excursions (in excess of 200 natm) are also found in the central Arabian Sea, the Bay of Bengal, the subpolar Pacific, and the Eastern Tropical Pacific and Atlantic.

We investigated the drivers of this seasonality by analyzing the patterns of temporal correlation between  $\Delta pN_2O$  and four of its predictors: chlorophyll, subsurface AOU, mixed-layer depth, and sea-surface temperature (SST) (Fig. 2 and SI Appendix, Fig. S14). The signs of the four correlation coefficients (positive or negative), in combination, allowed us to identify four empirical regimes of  $\Delta pN_2O$  seasonality (Fig. 2). The first regime

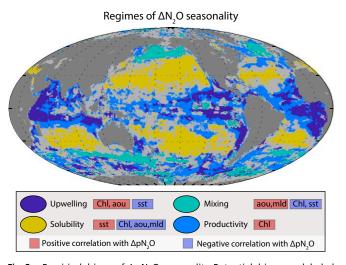


Fig. 2. Empirical drivers of  $\Delta pN_2O$  seasonality. Potential drivers are labeled based on temporal correlations between  $\Delta pN_2O$  and four environmental predictors: log(Chlorophyll) (Chl), SST, AOU, and mixed-layer depth (mld). Positive correlations are indicated by a red box and negative correlations by a blue box. Four primary regimes are identified: 1) Upwelling (navy blue), where seasonal changes in  $\Delta pN_2O$  are positively correlated with Chl and AOU, but negatively correlated with SST; 2) mixed-layer depth (turquoise), where  $\Delta p N_2 O$  is positively correlated with mld and AOU, but negatively correlated with Chl and SST; 3) solubility (yellow), where  $\Delta pN_2O$  is positively correlated with SST only; and 4) productivity (blue), which encompasses regions with positive correlations between  $\Delta pN_2O$ and ChI that do not fit in the three previous regimes. Regime (1) is constrained to a minimum annual chlorophyll concentration of 0.1 mg  $\mathrm{m}^{-3}$ to exclude parts of the subtropical gyres. See SI Appendix, section S1B for detailed methods and SI Appendix, Fig. S14 for maps of the individual correlations.

spans the majority of the tropical and northern Indian Ocean, the eastern tropical Pacific and Atlantic Oceans, and parts of the Southern Ocean (navy blue regions in Fig. 2). In these regions,  $\Delta p N_2 O$  changes are positively correlated with chlorophyll and subsurface AOU, but negatively correlated with SST, suggesting an important role for upwelling, which brings cold, nutrientrich, high-AOU waters close to the surface (Fig. 2 and SI Appendix, Fig. S14). Consistent with this interpretation,  $\Delta p N_2 O$  values in the Indian Ocean, particularly over the coastal Arabian Sea and Bay of Bengal, peak during the upwelling-favorable Southwest Monsoon in the late boreal summer (SI Appendix, Figs. S11–S13). The second regime mostly covers deep mixed-

layer systems, including the Southern Ocean Polar Front, and the subpolar Atlantic and Pacific (turquoise regions in Fig. 2). In these regions,  $\Delta p \rm N_2 O$  peaks during winter, when chlorophyll and temperature are low, and deep mixed layers expose high-AOU,  $\rm N_2 O$ -rich waters to the atmosphere (Fig. 2 and SI Appendix, Fig. S13). The third regime is found over the ocean's subtropical gyres, where the seasonality of  $\Delta p \rm N_2 O$  follows that of SST, but is in opposite phase with all other predictors (yellow regions in Fig. 2). The positive correlation with SST (average slope of 1 natm/0.13 °C) suggests that changes in  $\rm N_2 O$  solubility caused by seasonal warming or cooling drive seasonal changes in  $\Delta p \rm N_2 O$  (Fig. 2 and SI Appendix, Fig. S13), a result

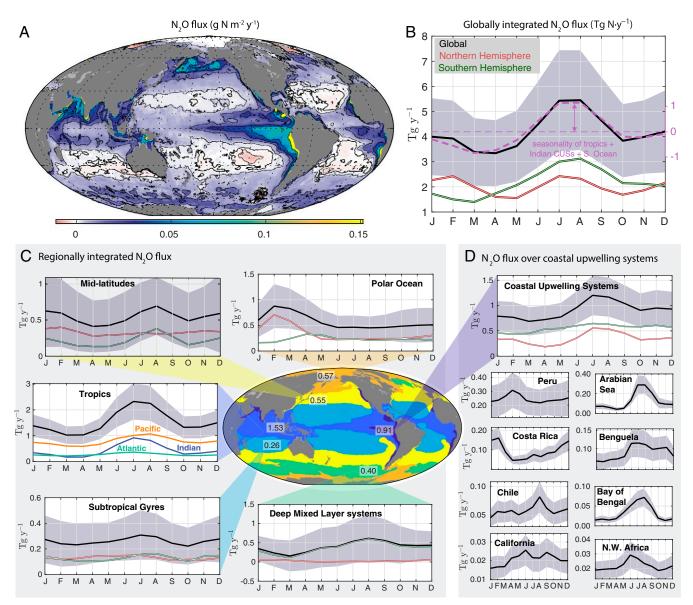


Fig. 3. Reconstructed  $N_2O$  air–sea flux. (A) Annual mean  $N_2O$  flux  $(g \cdot m^{-2} \cdot y^{-1})$ ; see also SI Appendix, Fig. S15). (B) Climatology of the  $N_2O$  flux  $(Tg \ N \cdot y^{-1})$  for the global ocean (black), the Northern Hemisphere (red), and the Southern Hemisphere (green). The purple dashed line shows the combined seasonal anomalies of the Tropical ocean biome [see C for a definition of biomes], the upwelling systems of the Arabian Sea and the Bay of Bengal (CUSs, coastal upwelling systems), and the Southern (S.) Ocean deep mixed-layer biome (vertical axis on the right, with 0 centered at value 4.2  $Tg \ N \cdot y^{-1}$  on the left axis, i.e., the global mean flux). (C and D) Climatological  $N_2O$  fluxes  $(Tg \ N \cdot y^{-1})$  for six major biomes (Tropics, Coastal Upwelling Systems, Mid-Latitudes, Subtropical Gyres, Deep Mixed-Layer Systems, and Polar Ocean; refer to SI Appendix, section S4A for detailed methods). Red and green lines show integrals over the Northern and Southern Hemispheres, respectively; orange, blue, and turquoise lines show the contribution of the Indian, Pacific, and Atlantic, respectively, to the Tropical biome. Numbers on the map show annual mean  $N_2O$  fluxes integrated over each biome. In D, climatologies for individual coastal upwelling systems are also shown (refer to SI Appendix, section S4A and Fig. S13). N.W., northwest. In B-D, envelopes around the black lines show the uncertainty.

consistent with previous findings (29). The majority of regions that are not assigned to the three previous regimes exhibited a positive correlation between seasonal cycles of  $\rm pN_2O$  and chlorophyll, suggesting that local  $\rm N_2O$  production during organic-matter cycling may control the surface disequilibrium, although this cannot be proven in the current analysis. We aggregated these waters into a fourth, productivity-driven regime (blue regions in Fig. 2), which often acts as a buffer between the upwelling, solubility, and mixed-layer regimes. Some upwelling systems also fall under the productivity-driven regime, including along Peru and California, where the seasonal cycle of chlorophyll is at least partially decoupled from that of SST and mixed-layer depth (30).

### N<sub>2</sub>O Flux.

Annual mean distribution. The reconstructed  $N_2O$  air–sea flux (Fig. 3) shows that most of the ocean is a source of  $N_2O$  to the atmosphere, in particular, in the tropics, coastal upwelling systems, and subpolar regions. These patterns closely mirror those of  $\Delta p N_2O$ , but with a relative amplification in regions of high winds, such as the mid to high latitudes. We estimated a global annual mean air–sea flux of  $N_2O$  of  $4.2 \pm 1.0$  Tg  $N \cdot y^{-1}$ . This figure is consistent with earlier data-based estimates of about 4 (1.2 to 6.8) Tg  $N \cdot y^{-1}$  (4, 5) and the IPCC range of 1.8 to 9.45 Tg  $N \cdot y^{-1}$  (3), but with a much reduced uncertainty. We trace most of the uncertainty in our estimate to the piston velocity formulation, the winds, and  $\Delta p N_2O$ , in order of importance (SI Appendix, section S2D and Fig. S18).

Despite the similarity of our global estimate to previous studies (4, 5), we reconstructed a dramatically different spatial distribution. Low latitudes (30°S to 30°N) contribute 64% of the global flux (2.7 Tg  $N \cdot y^{-1}$ ), ~60% higher than previous estimates (4, 5). We further revealed the outsize role of coastal upwelling systems, where intense outgassing drives over 20% of the global  $N_2O$  flux, despite covering only 3% of the world's oceans (Fig. 3D). Waters off the coast of Peru alone contribute nearly 0.25 Tg  $N \cdot y^{-1}$ , a magnitude consistent with the lower end of a recent regional estimate (9). They are followed by waters in the coastal Arabian Sea and off Costa Rica, which emit 0.13 and 0.09 Tg  $N \cdot y^{-1}$ , respectively. Reconstructions for the coastal Arabian Sea, Benguela, California, and Mauritanian upwelling systems fall within the range of previous observational estimates (refs. 10 and 31–33 and SI Appendix, Table S3).

The remaining 36% of the global  $\rm N_2O$  flux is distributed approximately equally between hemispheres, yielding only a 19% contribution from the Southern Ocean (south of  $\rm 30^{\circ}S$ ), about half of previous estimates (4, 5). We suggest that sampling biases are behind previous overestimates of  $\rm N_2O$  fluxes in this region. The Southern Ocean is heavily sampled in the summer and late winter, when  $\rm N_2O$  outgassing is the largest, and undersampled in the fall, when  $\rm N_2O$  outgassing rapidly drops to negligible values (ref. 5 and Fig. 3C). This result highlights the limitations of previous approaches based on direct extrapolation of sparse measurements, compared to the statistical models that we apply here.

 $N_2O$  flux seasonality and drivers. Our reconstruction revealed that the global air–sea flux of  $N_2O$  undergoes a vigorous and previously unappreciated seasonal cycle, increasing from a minimum of  $3.3 \pm 1.3$  Tg  $N \cdot y^{-1}$  in the boreal spring to a maximum of  $5.5 \pm 2.0$  Tg  $N \cdot y^{-1}$  in the boreal summer, with a secondary maximum in December  $(4.2 \pm 1.6$  Tg  $N \cdot y^{-1})$ . This global cycle emerges from nearly synchronous seasonal changes in the Indian Ocean, the tropical Pacific, and the Southern Ocean. The Indian Ocean alone contributes  $\sim 1.1$  Tg  $N \cdot y^{-1}$ , or about half of the increase in the global flux from boreal spring to summer, i.e., the Southwest Monsoon season. A large portion of this

increase originates in the Arabian Sea ( $\sim$ 0.44 Tg N·y<sup>-1</sup>), particularly near the coast ( $\sim$ 0.23 Tg N·y<sup>-1</sup>), which accounts alone for  $\sim$ 14% of the global flux increase from March to August. The tropical Pacific and the Southern Ocean contribute another  $\sim$ 23% and  $\sim$ 17%, respectively, or an increase by  $\sim$ 0.5 and  $\sim 0.4$  Tg N·y<sup>-1</sup> from the late austral summer to the austral winter, when stronger trade winds over the Pacific and deeper mixed layers in the Southern Ocean expose older, N2O-rich waters to the atmosphere (Fig. 3C). The remaining contribution mostly stems from the northern midlatitudes, where increased productivity from late spring to summer fuels excess  $N_2O$  production and release to the atmosphere (Fig. 3C). The secondary global peak in boreal winter emerges from multiple regional contributions, in particular, in the Subpolar Pacific, northern midlatitudes, and Southern Ocean. These wintertime enhancements reflect different regional drivers: deeper mixing in the North Pacific, more vigorous winds over midlatitudes, and increased summertime primary production in the Southern Ocean (Fig. 2).

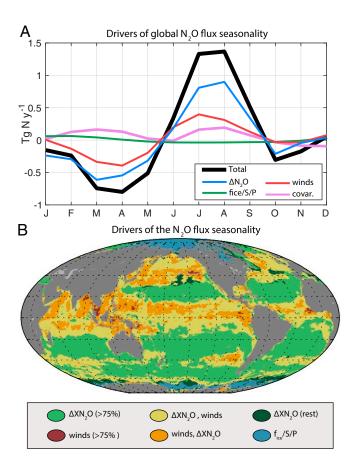


Fig. 4. Drivers of the  $N_2O$  flux seasonality. (A) Total  $N_2O$  flux deviation from the annual mean (black line) and its components (SI Appendix, Eq. S17) driven by changes in disequilibrium ( $\Delta X_{N_2O}$ ; blue line); wind spead (red line); sea-ice cover,  $N_2O$  solubility, and sea-level pressure ( $f_{ice}$ , Sa, and P; green line); and covariations (covar.) of all previous terms (pink line). See SI Appendix, section S3 and Eqs. S19 and S20 for a description of this decomposition. (B) Contribution of different drivers to  $N_2O$  flux seasonality. In dark green, regions where changes in  $\Delta X_{N_2O}$  contribute over 75%; in red, regions where changes in winds contribute over 75%; in yellow, regions where  $\Delta X_{N_2O}$  and winds are, respectively, the primary and secondary driver; in orange, regions where winds and  $\Delta X_{N_2O}$  are, respectively, the primary and secondary driver; in dark green, regions where  $\Delta X_{N_2O}$  is the primary driver, followed by a driver other than wind; and in blue, regions where  $f_{ice}$ , Sa, and P are the primary drivers. Contributions from individual drivers are shown in SI Appendix, Fig. S17.

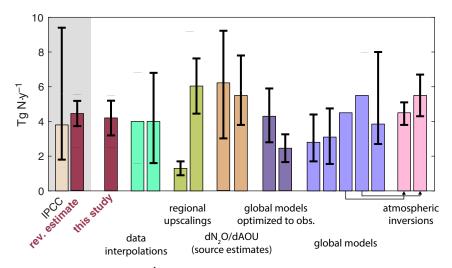


Fig. 5. Estimates of global oceanic  $N_2O$  emissions (Tg  $N \cdot y^{-1}$ ), grouped by method. Light green, data interpolations (4, 5); dark green, extrapolations of regional observations (39, 40); light brown, interior estimates based on the relationships between dissolved  $N_2O$  and AOU (28, 34); light purple, global ocean models (7, 37, 38, 41, 42); dark purple, global ocean models optimized by  $N_2O$  observations (6, 7, 8); pink, atmospheric inversions (35, 36). Black arrows connect global ocean models to atmospheric inversions that use them as priors. Our study (a databased reconstruction) is shown in brown. The revised (rev.) estimate next to the IPCC AR5 value (3) is based on an average of all categories, as discussed in the main text and *SI Appendix*.

We further investigated the seasonal modulation of N<sub>2</sub>O fluxes by decomposing flux variations into four components (SI Appendix, section S3 and Eqs. S16 and S17), respectively, driven by seasonal variations in 1) sea-ice cover, solubility, and sealevel pressure; 2) wind speed; 3) disequilibrium ( $\Delta X_{N_2O}$ ); and 4) covariations between the previous terms. We find that, on average, over two-thirds of the global flux seasonality are driven by changes in  $\Delta X_{N_2O}$ , with the remaining one-third driven by changes in wind speed (Fig. 4A). Solubility, sea-ice cover, and atmospheric pressure contribute minimally to seasonality, and covariations, while dampening seasonality in the boreal spring, enhance it in the boreal summer, resulting in a small net effect (Fig. 4A). Changes in  $\Delta X_{N_2O}$  are the primary driver of seasonality over most of the ocean, with some notable exceptions (Fig. 4B). First, in the tropics, sub-Arctic regions, and some portions of the Southern Ocean, winds are either the primary driver or a close secondary driver (Fig. 4B). Second, in the seasonal sea-ice zones around Antarctica and the Arctic coastline, N<sub>2</sub>O flux variations are mostly driven by changes in sea-ice cover (Fig. 4B).

Converging Estimates of Oceanic N<sub>2</sub>O Flux Emissions. Our global N<sub>2</sub>O emission of 4.2 Tg N·y<sup>-1</sup> is comparable to previous reconstructions based on surface-data interpolations (4, 5), although with a significantly more extensive set of observations and reduced uncertainty. It also overlaps with estimates based on N<sub>2</sub>O production in the ocean interior (28, 34), which use independent subsurface N<sub>2</sub>O observations, but cannot be constrained as tightly. Finally, it is highly consistent with atmospheric inversions (35, 36), which update prior estimates based on numerical ocean models (37, 38) to leverage the strong, independent constraint of atmospheric N<sub>2</sub>O concentrations. Combining results from all these different methods (*SI Appendix*) revises the global oceanic N<sub>2</sub>O flux to 4.4  $\pm$  0.7 Tg N·y<sup>-1</sup>—a value indistinguishable from our reconstruction and a fivefold reduction in uncertainty compared to the range (1.8 to 9.4 Tg N·y<sup>-1</sup>) adopted by the IPCC AR5 (Fig. 5).

### **Implications and Conclusions**

Our synthesis of  $N_2O$  measurements—the largest to date—reveals a vigorous seasonal cycle of oceanic  $N_2O$  emissions, with an excursion of 2.1 Tg  $N \cdot y^{-1}$ , half of the global annual

mean. Much of these emissions and their seasonal variability can be traced to tropical regions and upwelling systems, where productive waters overlay shallow oxygen minima (43). The sensitivity of tropical  $N_2O$  emissions to seasonal variations suggests a similar sensitivity to the El Niño-Southern Oscillation and the Pacific Decadal Oscillation, which modulate productivity and the depth of tropical oxygen minima on interannual to multidecadal timescales (43, 44). Reconstructing the sensitivity of oceanic  $N_2O$  emissions to these modes of natural climate variability would, in turn, shed light on their response to anthropogenic climate change, which is projected to increase thermal stratification and reduce productivity in the tropics (45). Such reconstructions would likely benefit from long-term measurements, targeting regions with large fluxes and seasonality (Figs. 2 and 3).

The reduced uncertainty of our oceanic  $N_2O$  emissions estimate and its ability to capture seasonal variations and coastal hot spots make it ideal for use as a prior in atmospheric inversions of land-based  $N_2O$  fluxes (35). This would translate into tighter estimates of other terms in the atmospheric  $N_2O$  budget, including better constraints on anthropogenic  $N_2O$  emissions.

### **Materials and Methods**

The compilation of  $N_2O$  measurements, the reconstructed global  $\Delta p_{N_2O}$  climatology, and  $N_2O$  air–sea flux are available for download on the BCO-DMO portal (https://www.bco-dmo.org/dataset/810032). The code used to produce these datasets can be found on a public GitHub repository, https://github.com/yangsi7/MappingDN2OandFlux. Refer to *SI Appendix*, section S1B and Table S2 for detailed methods, including information on published datasets used to train the random forest model and compute the flux

ACKNOWLEDGMENTS. S.Y. and D.B. were supported by NSF Grants 1635632 and 1847687 and Swiss National Science Foundation Grant PZEZPZ\_172166. This publication is partially funded by the Joint Institute for the Study of the Atmosphere and Ocean under the NOAA Cooperative Agreement NA15OAR4320063, Contribution 2019-1038 (Pacific Marine Environmental Laboratory Contribution 5047). We thank the administrators and individual contributors of all of the data products used in the manuscript, as listed in SI Appendix. We also acknowledge the Ocean Carbon and Biogeochemistry Project Office, supported by NSF Grant 1558412 and NASA Grant NNX17AB17G, for organizing the Oceanic Methane & Nitrous Oxide Workshop in October 2018, which provided impetus for this work. This work used the Extreme Science and Engineering Discovery Environment, which is supported by NSF Grant ACI-1548562.

- 1. G. Myhre et al., "Anthropogenic and natural radiative forcing in climate change 2013: The physical science basis" in Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, T. F. Stocker et al., Eds. (Cambridge University Press, Cambridge, UK, 2014), pp. 659-740.
- 2. R. W. Portmann, J. S. Daniel, A. R. Ravishankara, Stratospheric ozone depletion due to nitrous oxide: Influences of other gases. Philos. Trans. R. Soc. London. Series B, Biol. Sci. 367, 1256-1264 (2012).
- 3. P. Ciais et al., "Carbon and other biogeochemical cycles in climate change 2013— The physical science basis" in Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, T. F. Stocker et al., Eds. (Cambridge University Press, Cambridge, UK, 2014), pp. 465-570.
- 4. C. D. Nevison, R. F. Weiss, D. J. Erickson III. Global oceanic emissions of nitrous oxide. J. Geophys. Res. Oceans 100, 15809-15820 (1995).
- C. D. Nevison, T. J. Lueker, R. F. Weiss, Quantifying the nitrous oxide source from coastal upwelling. Global Biogeochem. Cycles 18, GB1018 (2004).
- G. Battaglia, F. Joos, Marine N2O emissions from nitrification and denitrification constrained by modern observations and projected in multimillennial global warming simulations. Global Biogeochem. Cycles 32, 92–121 (2018).
- 7. Q. Ji, E. Buitenhuis, P. Suntharalingam, J. L. Sarmiento, B. B. Ward, Global nitrous oxide production determined by oxygen sensitivity of nitrification and denitrification. Global Biogeochem. Cycles 32, 1790-180 (2018).
- E. T. Buitenhuis, P. Suntharalingam, C. Le Quéré, Constraints on global oceanic emissions of N2O from observations and models. Biogeosciences 15, 2161-2175
- 9. D. L. Arevalo-Martinez, A. Kock, C. R. Loscher, R. A. Schmitz, H. W. Bange, Massive nitrous oxide emissions from the tropical South Pacific Ocean. Nature Geosci 8, 530-533 (2015).
- 10. D. L. Arévalo-Martínez et al., N<sub>2</sub>O emissions from the northern Benguela upwelling system. Geophys. Res. Lett. 46, 3317-3326 (2019).
- 11. L. Farías, V. Besoain, S. García-Loyola, Presence of nitrous oxide hotspots in the coastal upwelling area off central Chile: An analysis of temporal variability based on ten years of a biogeochemical time series. Environ. Res. Lett. 10, 44017 (2015).
- S. Lal, P. K. Patra, Variabilities in the fluxes and annual emissions of nitrous oxide from the Arabian Sea. Global Biogeochem. Cycles 12, 321–327 (1998).
- 13. R. C. Upstill-Goddard, J. Barnes, N. J. P. Owens, Nitrous oxide and methane during the 1994 SW monsoon in the Arabian Sea/northwestern Indian Ocean. J. Geophys. Res. Oceans 104, 30067-30084 (1999).
- 14. X. Jin, N. Gruber, Offsetting the radiative benefit of ocean iron fertilization by enhancing N2O emissions. Geophys. Res. Lett. 30, 2249 (2003).
- 15. C. D. Nevison et al., Southern Ocean ventilation inferred from seasonal cycles of atmospheric N<sub>2</sub>O and O<sub>2</sub>/N<sub>2</sub> at Cape Grim, Tasmania. Tellus B 57, 218-229 (2005).
- 16. H. W. Bange et al., MEMENTO: A proposal to develop a database of marine nitrous oxide and methane measurements (MEMENTO database accessed via https:// memento.geomar.de in March 2019). Environ. Chem. 6, 195-197 (2009).
- 17. A. Kock, H. W. Bange, Counting the ocean's greenhouse gas emissions. Eos 96 (2015).
- 18. B. D. Hall, G. S. Dutton, J. W. Elkins, The NOAA nitrous oxide standard scale for atmospheric observations. J. Geophys. Res.: Atmospheres 112, D09305 (2007).
- 19. T. Shserwen et al., A machine-learning-based global sea-surface iodide distribution. Earth Syst. Sci. Data 11, 1239-1262 (2019).
- T. Weber, N. A. Wiseman, A. Kock, Global ocean methane emissions dominated by shallow coastal waters. Nat. Commun. 10, 4584 (2019).
- 21. R. Wanninkhof, Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res. Oceans 97, 7373-7382 (1992).
- 22. R. Wanninkhof, Relationship between wind speed and gas exchange over the ocean revisited. Limnol Oceanogr. Methods 12, 351-362 (2014).
- 23. J. H. Liang et al., Parameterizing bubble-mediated air-sea gas exchange and its effect on ocean ventilation. Global Biogeochem. Cycles 27, 894-905 (2013).

- 24. Copernicus Climate Change Service (C3S) (2017): ERA5: Fifth generation of ECMWF atmospheric reanalyses of the global climate. Copernicus Climate Change Service Climate Data Store (CDS). https://cds.climate.copernicus.eu/cdsapp#!/home. Accessed 24 February 2019.
- 25. Remote Sensing Systems Cross-Calibrated Multi-Platform (CCMP) 6-hourly ocean vector wind analysis product on 0.25 deg grid, Version 2.0. http://www.remss.com/ measurements/ccmp/. Accessed 1 May 2019.
- 26. P. Suntharalingam, J. L. Sarmiento, Factors governing the oceanic nitrous oxide distribution: Simulations with an ocean general circulation model. Global Biogeochem. Cycles 14 429-454 (2000)
- 27. H. W. Bange et al., Nitrous oxide emissions from the Arabian Sea: A synthesis. Atmos. Chem. Phys. 1, 61-71 (2001).
- 28. C. Nevison, J. H. Butler, J. W. Elkins, Global distribution of N2O and the  $\Delta N_2 O\text{-AOU}$  yield in the subsurface ocean. Global Biogeochem. Cycles 17, 1119 (2003).
- 29. S. T. Wilson, S. Ferrón, D. M. Karl, Interannual variability of methane and nitrous oxide in the North Pacific Subtropical Gyre. Geophys. Res. Lett. 44, 9885-9892
- 30. V. Echevin, O. Aumont, J. Ledesma, G. Flores, The seasonal cycle of surface chlorophyll in the Peruvian upwelling system: A modelling study. Prog. Oceanogr. 79, 167-176
- 31. S. W. A. Naqvi et al., Increased marine production of N2O due to intensifying anoxia on the Indian continental shelf. Nature 408, 346-349 (2000).
- 32. T. J. Lueker, Coastal upwelling fluxes of O2, N2O, and CO2 assessed from continuous atmospheric observations at Trinidad, California, Biogeosciences 1, 101-111 (2004).
- 33. F. Wittke, A. Kock, H. W. Bange, Nitrous oxide emissions from the upwelling area off Mauritania (NW Africa). Geophys. Res. Lett. 37, L12601 (2010).
- 34. D. Bianchi, J. P. Dunne, J. L. Sarmiento, E. D. Galbraith, Data-based estimates of suboxia, denitrification, and  $N_2O$  production in the ocean and their sensitivities to dissolved O2. Global Biogeochem. Cycles 26, GB2009 (2012).
- 35. E. Saikawa et al., Global and regional emissions estimates for N2O. Atmos. Chem. Phys. 14, 4617-4641 (2014).
- R. L. Thompson et al., Nitrous oxide emissions 1999 to 2009 from a global atmospheric inversion. Atmos. Chem. Phys. 14, 1801-1817 (2014).
- 37. S. Dutreuil, L. Bopp L., A. Tagliabue, Impact of enhanced vertical mixing on marine biogeochemistry: Lessons for geo-engineering and natural variability. Biogeosciences 6. 901-912 (2009).
- 38. M. Manizza M., R. F. Keeling R. F., C. D. Nevison C. D., On the processes controlling the seasonal cycles of the air-sea fluxes of O2 and N2O: A modelling study. Tellus Ser. B Chem. Phys. Meteorol., 10.3402/tellusb.v64i0.18429 (2012).
- 39. H. W. Bange, S. Rapsomanikis, M. O. Andreae, Nitrous oxide in coastal waters. Global Biogeochem. Cycles 10, 197-207 (1996).
- 40. T. S. Rhee, A. J. Kettle, M. O. Andreae, Methane and nitrous oxide emissions from the ocean: A reassessment using basin-wide observations in the Atlantic. J. Geophys. Res.: Atmospheres 114, D12304 (2009).
- 41. P. Suntharalingam, J. L. Sarmiento, J. R. Toggweiler, Global significance of nitrousoxide production and transport from oceanic low-oxygen zones: A modeling study. Global Biogeochem. Cycles 14, 1353-1370 (2000).
- 42. L. M. Zamora, A. Oschlies, Surface nitrification: A major uncertainty in marine N2O emissions. Geophys. Res. Lett. 41, 4247-4253 (2014).
- 43. C. Deutsch, H. Brix, T. Ito, H. Frenzel, L. Thompson, Climate-forced variability of ocean hypoxia. Science (New York, N.Y.) 333, 336-339 (2011).
- 44. S. Yang, N. Gruber, M. C. Long, M. Vogt, ENSO-driven variability of denitrification and suboxia in the Eastern Tropical Pacific Ocean. Global Biogeochem. Cycles 31,1470-1487 (2017).
- 45. L. Bopp, et al., Multiple stressors of ocean ecosystems in the 21st century: Projections with CMIP5 models. Biogeosciences 10, 6225-6245 (2013).