Nitrogen oxide ($N_2O$) is a powerful greenhouse gas and a major cause of stratospheric ozone depletion, yet its sources and sinks remain poorly quantified in the oceans. We used isotope tracers to directly measure $N_2O$ reduction rates in the eastern tropical North Pacific. Because of incomplete denitrification, $N_2O$ cycling rates are an order of magnitude higher than predicted by current models in suboxic regions, and the spatial distribution suggests strong dependence on both organic carbon and dissolved oxygen concentrations. Furthermore, $N_2O$ turnover is 20 times higher than the net atmospheric efflux. The rapid rate of this cycling coupled to an expected expansion of suboxic ocean waters implies future increases in $N_2O$ emissions.

Anthropogenically derived atmospheric $N_2O$ concentrations increased over the past century (1–3), but the natural marine sources and sinks of $N_2O$ have been difficult to quantify. Because of the paucity of direct measurements of $N_2O$ production and consumption in the ocean, current rate estimates and predictions of how the $N_2O$ budget will respond to a changing climate remain uncertain (4). The most concentrated oceanic sources of $N_2O$ to the atmosphere are the suboxic (0 to 20 μmol l$^{-1}$) waters overlying the oxygen minimum zones (OMZs), based on measurements and models of super-saturated $N_2O$ concentrations (5, 6). Furthermore, $N_2O$ is produced by both nitrification and denitrification, but the overall importance of each process is uncertain. Nitrification, the oxidation of ammonium to nitrite and further to nitrate, exhibits maximum rates just below the well-lit surface layer, where remineralization rates supplying ammonium are highest. Nitrification generates an $N_2O$ by-product (7) whose yield is enhanced by suboxic concentrations—the yield of $N_2O$ from a fraction of nitrite production, can be as high as 10% in culture (8, 9) and 0.4% in the environment (10, 11). However, at very low (less than a few micromolar) oxygen concentrations, nitrification ceases (12), and no $N_2O$ can be produced via this pathway.

Denitrification, the stepwise reductions of nitrate and nitrite through NO and $N_2O$ to nitrogen gas, occurs in the ocean only when molecular oxygen is sufficiently low (less than 3 μmol l$^{-1}$) (13). This anaerobic process results in local $N_2O$ minima within the OMZ core but has the potential to be a major $N_2O$ source at the suboxic-anoxic interface (the oxycline) at the top of the OMZ. Over this narrow depth interval, $N_2O$ consumption by the nitrous oxide reductase enzyme is inhibited by $O_2$ at an extent greater than its production in the denitrification sequence (14).

Further, because the denitrification steps are predominantly heterotrophic, the rates are enhanced at shallow depths, where the supply of newly produced labile organic matter from the surface (15) is greater. Incomplete denitrification (reduction of NO$\sb{3}$ to $N_2O$ rather than to $N_2$) may account for a flux that is ignored or not explicitly represented in most biogeochemical ocean and climate models. Indeed, in culture experiments (14, 15) and sediment incubations (16) at suboxic but nonzero $O_2$ concentrations, denitrification activity decreased as expected with increasing $O_2$ concentrations, but the $N_2O$ yield (i.e., the proportion of denitrification halting at $N_2O$) increased to ~50% (15).

We directly measured the production of $N_2O$ to dinitrogen gas by using labeled isotopic ($^{15}N$)$N_2O$ tracer incubation experiments at three stations in the eastern tropical North Pacific (ETNP), the largest suboxic zone (17) and a major site of $N_2O$ production (18, 19). $N_2O$ production is the only major biological $N_2O$ consumption process; because production occurs via multiple pathways, in situ production rates via isotopic tracer techniques cannot be directly constrained (20).

The transect across the ETNP (fig. S1) showed the characteristic features associated with OMZs, namely a $N_2O$ concentration peak (~100 nmol l$^{-1}$) at the base of a steep oxygen gradient and an $N_2O$ concentration minimum in the core of the OMZ. All three sites displayed similar alignments of oxygen, $N_2O$, and nitrite maxima and minima (Fig. 1A), indicating similar mechanisms affecting the biogeochemistry across the region. The similarity between the $N_2O$ profile at the offshore station 2 and data from a nearby site measured 12 years prior (19) (Fig. 1B) indicates long-term stability in the shape and peak magnitudes of the $N_2O$ profiles.

$N_2O$ consumption rates (Fig. 2) measured across all three profiles were up to 35 nmol l$^{-1}$ day$^{-1}$, indicating residence times as low as 1 day (calculated from the concentration divided by the biological rate). This fast turnover was observed throughout the OMZ core, presumably because of tight coupling of sequential denitrification steps. Within the oxycline, the $N_2O$ residence times increased and the reduction rates decreased sharply as $O_2$ increased. This synchronism is consistent with oxygen poisoning of the nitrous oxide reductase enzyme above the OMZ. Moreover, and of greater consequence to atmospheric $N_2O$ emissions, an estimate of the rate of production based on a one-dimensional (1D) transport-reaction balance (fig. S3) was systematically larger than that of consumption near the base of the oxycline. This 1D estimate is likely to be conservative, because the inclusion of horizontal transport terms, which act to erode the $N_2O$ peak, would require an increase in the $N_2O$ source to maintain the balance (table S2 and supplementary text). The observed near-shore (station 1) rates of $N_2O$ reduction and production decreased with depth (Fig. 2), resembling the depth-dependent power law decay of organic carbon supply (13). This organic carbon dependence of $N_2O$ cycling was also apparent from the occurrence of the highest rates near shore, where the greatest primary production occurs. These measurements highlight the large spatial heterogeneity of $N_2O$ cycling dependent on organic carbon export in the ETNP.

We investigated the broader implications of such rapid $N_2O$ cycling with a mechanistic, 1D model of OMZ biogeochemistry (supplementary materials) built on parameterizations widely adopted in ocean biogeochemical models, including biological $N_2O$ production via nitrification, enhanced at suboxic concentrations (4, 6, 21, 22), and consumption via denitrification (19). Following previous parameterizations (21), we defined an oxygen threshold of 2 μmol l$^{-1}$, above which $N_2O$ was produced and below which, consumed. However, this 1D model with $N_2O$ production from nitrification alone generated a production rate (maximum of 0.3 nmol l$^{-1}$ day$^{-1}$) that was a fraction of the net production rate calculated from the measured consumption (Fig. 3A). The observed $N_2O$ concentration peaks measured here at >100 nmol l$^{-1}$ (Fig. 1) are likely not reproduced in models (22), including our 1D version (which only achieves a maximum of 70 nmol l$^{-1}$), because they do not include explicit production by incomplete denitrification. The importance of denitrification to $N_2O$ production has been implicated by measurements across all three major OMZs: the ETNP (18, 23), the eastern tropical South Pacific (ETSP) (24), and the Arabian Sea (20, 25).

We expanded the 1D model to separate the $N_2O$ production and consumption terms of denitrification and allow for $O_2$-dependent denitrification (26). With this change, denitrification became a major $N_2O$ source in the low-$O_2$ waters directly overlying the OMZ (9.3 μmol m$^{-2}$ day$^{-1}$) and was comparable in size to the source from nitrification (9.1 μmol m$^{-2}$ day$^{-1}$). Furthermore, the maximum modeled net $N_2O$ production rate of 0.6 nmol l$^{-1}$ day$^{-1}$ is consistent with our observations (Fig. 3B), with a peak concentration of >110 nmol l$^{-1}$. Such agreement could not be achieved with production via nitrification alone and suggests that denitrification constitutes a major and largely overlooked source of $N_2O$. This conclusion also holds for a range of model parameters and formulations, including a simple...
Fig. 1. Biogeochemical measurements. (A) Depth profiles of N$_2$O (open circles), O$_2$ (solid gray line), and NO$_2^-$ (dashed line) concentrations at the three stations included in this study. (B) Comparison of N$_2$O concentration data (open circles) from station 2 collected in April 2012 with those from a previous study (19) (solid circles) of a nearby location (16°N 107°W) in spring 2000.

representation of lateral transports, as shown by a series of sensitivity studies (fig. S2, table S2, and supplementary text).

Similar to the model results, a conservative average from offshore measurements at the base of the oxycline indicates a net production rate on order of ~1 nmol l$^{-1}$ day$^{-1}$. Based on the measured rates and the observed extent of the suboxic layer at the base of the oxycline of the three profiles, production exceeds consumption across a thickness of ~10 ± 4 m (SD) immediately overlying the anoxic layer. A 1 nmol l$^{-1}$ day$^{-1}$ imbalance integrated over 10 m equates to an air-sea N$_2$O flux of 10 μmol m$^{-2}$day$^{-1}$, which is comparable (30 to 100%) to the fluxes estimated in the analogous suboxic ETSP (24). Our model including a denitrification N$_2$O source produced a similar atmospheric efflux of 13 μmol m$^{-2}$ day$^{-1}$. An order-of-magnitude estimate, integrating a 10 μmol m$^{-2}$ day$^{-1}$ flux horizontally over the extent of the suboxic ETNP (25.7 × 10$^{12}$ ± 1.5 × 10$^{12}$ m$^2$) yields a net atmospheric N$_2$O flux out of the ETNP OMZ of 13 ± 0.1 Tg of N year$^{-1}$. Furthermore, if we conservatively estimate the average reduction rate based on our measurements within the ETNP OMZ (2 nmol l$^{-1}$ day$^{-1}$) and integrate over the full volume of the anoxic ETNP OMZ (1.2 × 10$^{15}$ ± 0.5 × 10$^{15}$ m$^3$), the total cycling rate through N$_2$O is 25 ± 10 Tg of N year$^{-1}$, or 20 times higher than the net flux. This gross rate of N$_2$O generation is comparable to previous estimates of denitrification rates from the ETNP (27–30). Because the net outgassing of N$_2$O to the atmosphere results from the residual between large production and reduction rates, it could change greatly in response to even a small decoupling of production and consumption, caused, for example, by more frequent O$_2$ injections (31) or changes in the volume and geometry of suboxic zones (32, 33).

Our results show that the net accumulation of N$_2$O in the OMZs on the multiyear time scales dictated by ocean circulation hides the delicate balance between production and consumption that proceeds on time scales at least one order of magnitude faster. Over long time scales into the future, expanding and shoaling OMZs resulting from changes in physical circulation, widespread ocean deoxygenation (34), and increased fertilizer runoff stimulating phytoplankton blooms could exacerbate marine N$_2$O accumulation and outgassing (4, 35). This increase would be especially important given the rapid biological rates measured in the ETNP. The rapid turnover of N$_2$O in OMZs also implies that shorter time scale variations influence N$_2$O production and consumption.
flux, as reported for the Arabian Sea’s annual monsoons (35). El Niño–Southern Oscillation strongly affects the mixed layer and thermocline depths and surface productivity in the eastern tropical Pacific. Via this natural variability, the OMZs (33, 35, 37). If we assume that the three major OMZs are approximately equivalent, the N2O production rates predicted here would account for ~4 Tg of N year−1 from the OMZs alone. This is a conservative analysis, limited to the offshore sites and ignoring the coastal region with higher rates and imbalances (Fig. 2). Inclusion of coastal sites could substantially increase this estimate. Further, models parameterizing N2O production via only nitrification require tuning by some additional suboxic process to produce N2O in the OMZs and better simulate concentration distributions (4, 22, 38). The directly measured rates and simple model presented in this paper show that these tunings do not capture the dynamics necessary to represent accurately marine N2O cycling.

REFERENCES AND NOTES


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SUPPLEMENTARY MATERIALS

www.sciencemag.org/cgi/content/348/6239/1129/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S3
Tables S1 to S3
References (39–53)
Supplementary Data
12 February 2015; accepted 28 April 2015
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Rapid nitrous oxide cycling in the suboxic ocean
Andrew R. Babbin, Daniele Bianchi, Amal Jayakumar and Bess B. Ward

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More N₂O is no laughing matter
Because N₂O is a potent greenhouse gas, tracking its sources and sinks—including those from natural processes—is imperative. Babbin et al. developed an isotopic tracer method to measure biological N₂O reduction rates directly in the Eastern Tropical North Pacific Ocean. Incomplete denitrification results in the rapid cycling and net accumulation of N₂O. As oxygen minimum zones expand in the global ocean, more N₂O may enter the atmosphere than previously expected.

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