NITROGEN CYCLE

21st-century rise in anthropogenic nitrogen deposition on a remote coral reef

Haojia Ren,[1]* Yi-Chi Chen,[1] Xingchen T. Wang,[2]† George T. F. Wong,[3,4] Anne L. Cohen,[5] Thomas M. DeCarlo,[5]‡§ Mira A. Weigand,[2] Horng-Sheng Mii,[6] Daniel M. Sigman[2]

With the rapid rise in pollution-associated nitrogen inputs to the western Pacific, it has been suggested that even the open ocean has been affected. In a coral core from Dongsha Atoll, a remote coral reef ecosystem, we observe a decline in the $^{15}N/^{14}N$ of coral skeleton–bound organic matter, which signals increased deposition of anthropogenic atmospheric N on the open ocean and its incorporation into plankton and, in turn, the atoll corals. The first clear change occurred just before 2000 CE, decades later than predicted by other work. The amplitude of change suggests that, by 2010, anthropogenic atmospheric N deposition represented 20 ± 5% of the annual N input to the surface ocean in this region, which appears to be at the lower end of other estimates.

Nitrogen is one of the essential nutrients limiting phytoplankton growth throughout much of the low-latitude surface ocean. Biologically available nitrogen, or fixed N, is primarily supplied to the surface ocean from nutrient-rich subsurface water, but it is also added by in situ biological N fixation and atmospheric deposition. Atmospheric transport and deposition of reactive nitrogen (nitrogen oxides, ammonium and/or ammonia, and N-bearing organic compounds) is an increasingly important source of fixed N to open-ocean surface waters, owing to the rapid increase in emissions from fertilizer usage and combustion of fossil fuels. Model estimates suggest that N input from the atmosphere to the open ocean has more than doubled over the past 100 years, accounting for up to one-third of the ocean's external N supply (*1*). This dramatic increase in anthropogenic atmospheric N (AAN) has been calculated to have increased ocean productivity by 3% globally (*1*) and up to 25% regionally (*2*). However, except in some nearshore environments (*3*), there is little evidence so far that anthropogenic N inputs have led to significant changes in the open ocean's N cycle and ecosystems.

The northwest Pacific Ocean is an expected hot spot for increased AAN deposition, due to rapid population growth and burgeoning industrial activity in the northeast Asian countries. Northeast Asia, especially China, has become the largest source for anthropogenic N emissions over the past 30 years (*4*, *5*). Although these growing N emissions have caused a clear increase in N deposition over land (*6*), little long-term monitoring data exist for the marine environment, especially the nutrient-limited open ocean. Model estimates and existing coastal data suggest that atmospheric N deposition accounts for 10% of the new production in the west Philippine Sea (*1*), 20% in the southeastern South China Sea (*7*), and more than one-third in the northwestern South China Sea (*1*). Observations of nutrient ratios appear to support a rise in AAN since 1980 (*8*).

Nitrogen isotopes have the potential to trace changes in N sources in this region. The $\delta^{15}N$ of shallow subsurface nitrate in the northern South China Sea is 5.0 to 5.5‰ (*9*) (fig. S2), which is higher than that for N fixation (~–1‰) (*10*) and for atmospheric N deposition in this region (~–2.7‰) (*11*). Given the low $\delta^{15}N$ of atmospheric N deposition relative to that of the subsurface nitrate that is mixed up from below, the increase in anthropogenic N emissions and deposition should cause the $\delta^{15}N$ of surface ocean N pools to decrease with time. The coral skeletal (CS)–bound organic N $\delta^{15}N$ (CS-$\delta^{15}N$) in shallow-water scleractinian corals has been shown to reflect the $\delta^{15}N$ of the N supply to reefs (*12*–*14*). Changes in $\delta^{15}N$ over time are preserved within the coral skeleton, which makes CS-$\delta^{15}N$ a powerful archive for assessing the impact of AAN on the ocean's N cycle and ecosystems.

Here we report a 45-year seasonally resolved CS-$\delta^{15}N$ record from Dongsha Atoll located at 20°40′N and 116°50′E, 340 km from land in the northern South China Sea (*15*) (Fig. 1). The proximity of Dongsha Atoll to major AAN sources combined with the relatively deep (1300-m) water that surrounds it allow Dongsha to serve as a sensitive recorder of the rise in AAN deposition without the complexities of the coastal zone. The coral core was collected from a living *Porites* sp. in June 2013 from the northern reef flat in Dongsha Atoll (filled circle in Fig. 1B), and it was sampled along the maximum growth axis [fig. S3 for age model (*15*)]. The average CS-$\delta^{15}N$ over the past 45 years is 7.2 ± 0.7‰. This is about 2‰ higher than the thermocline nitrate $\delta^{15}N$, consistent with previous findings (*13*, *14*). CS-$\delta^{15}N$ declines over time, with a 1.3‰ difference between the $\delta^{15}N$ averages of 1968–1977 and 2003–2012 (Fig. 2). The CS-$\delta^{15}N$ decline before the 21st century is subtle (0.3‰), but the rate of decline accelerates within a few years of the turn of the century. The decline is superimposed on seasonal, interannual, and decadal variation, which also appear to become slightly stronger after 1990 (Fig. 2 and fig. S4). A shorter CS-$\delta^{15}N$ record from the east end of the lagoon was generated for comparison (open circle in Fig. 1B and fig. S1). The two records, although from different reef environments, have very similar CS-$\delta^{15}N$ values and seasonal variation for the overlapping period (2009–2012) (fig. S1). Thus, the CS-$\delta^{15}N$ is best interpreted in terms of the entire atoll (*15*) (fig. S10). Although the atoll is in a single location within a vast region, lateral circulation and mixing in the ocean will tend to disperse AAN to generate a regional signal, which the atoll should capture.

The $\delta^{15}N$ decline most likely reflects a change in the N sources to the reef system. Vertical nitrate supply is the primary source of N to the waters surrounding the reef. The $\delta^{15}N$ of the subsurface nitrate in waters surrounding Dongsha Atoll is 5.5 ± 0.2‰, similar to the subsurface nitrate $\delta^{15}N$ of 5.2‰ at SEATS (South East Asian Time Series Station) in the northern South China Sea (fig. S2). We also found subsurface waters with measurable nitrate concentration within the lagoon, and these had a nitrate $\delta^{15}N$ of 5.5‰, consistent with the regional subsurface nitrate $\delta^{15}N$. Climate warming in the past decades could have stratified the surface ocean (*16*), reducing the upward mixing of nutrient-rich thermocline water and thus increasing the relative importance of ^{15}N-depleted N sources from N fixation or atmospheric N deposition. However, because of the relatively low rate of N fixation, the $\delta^{15}N$ of the N supply to the surface ocean is rather insensitive to changes in vertical nitrate supply, such that the observed CS-$\delta^{15}N$ decline would require at least 50% reduction in upward mixing of thermocline nitrate (*15*). This would cause a clear decrease in surface ocean production, but chlorophyll concentration has been remarkably stable over the past 15 years (*17*, *18*), which suggests that any increase in density stratification has been offset by other changes. In addition, on the basis of available data, the $\delta^{15}N$ of shallow subsurface (~100-m depth) nitrate at SEATS has been stable or has risen slightly from 1997 (*9*) to 2012 and 2013 (fig. S2), whereas reduced vertical mixing should allow the subsurface nitrate $\delta^{15}N$ to diverge more from underlying water; these findings argue against a significant decline in vertical mixing over time.

N fixation is one of the main external N sources in the South China Sea as a whole. Although there are no measurements of in situ N fixation

[1]Department of Geosciences, National Taiwan University, Taipei, Taiwan. [2]Department of Geosciences, Princeton University, Princeton, NJ 08544, USA. [3]Research Center for Environmental Changes, Academia Sinica, Taipei, Taiwan. [4]Department of Ocean, Earth and Atmospheric Sciences, Old Dominion University, Norfolk, VA 23529, USA. [5]Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA. [6]Department of Earth Sciences, National Taiwan Normal University, Taipei, Taiwan.
***Corresponding author. Email: abbyren@ntu.edu.tw** †Present address: Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA. ‡Present address: School of Earth Sciences and Oceans Institute, The University of Western Australia, Crawley, Western Australia, Australia. §Present address: Australian Research Council Centre of Excellence for Coral Reef Studies, The University of Western Australia, Crawley, Western Australia, Australia.

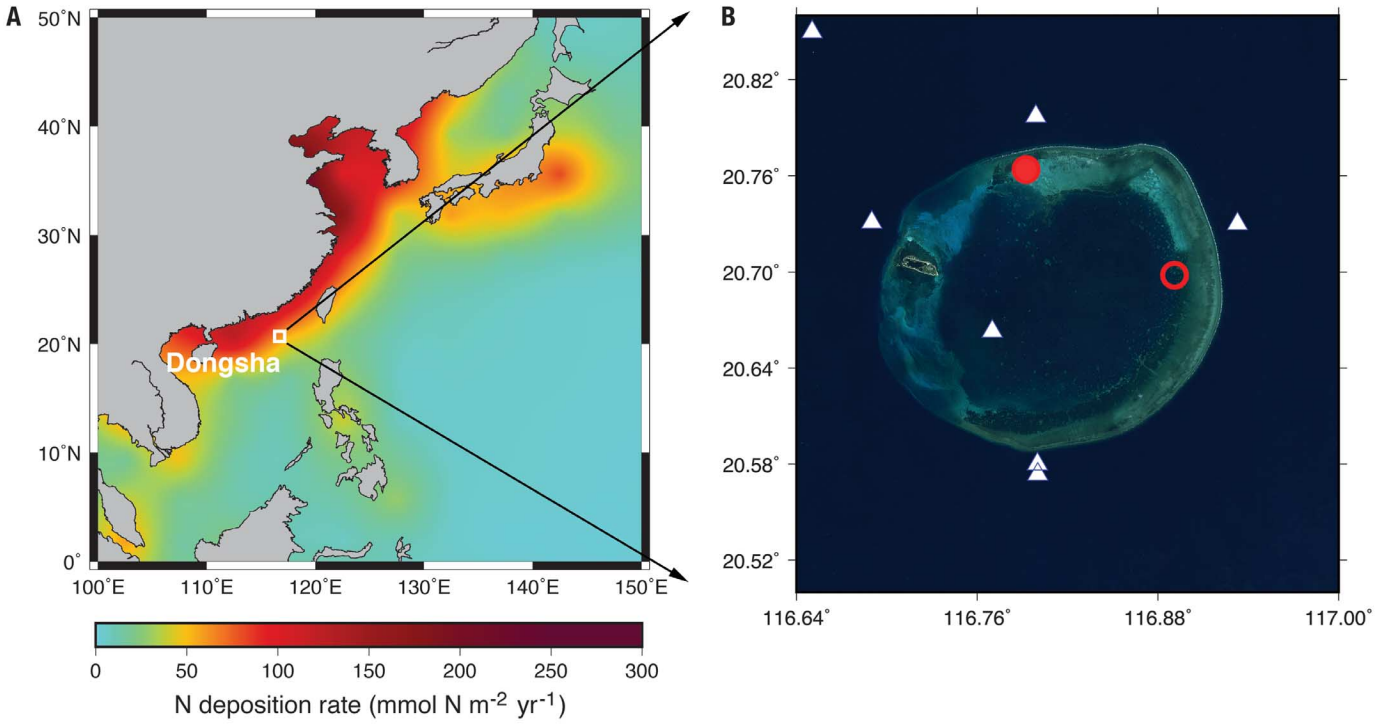

Fig. 1. Dongsha Atoll sampling sites. (**A**) Dongsha Atoll (white square) is located at 20°40′N and 116°50′E, 340 km from land in the northern South China Sea. Model-predicted atmospheric N deposition rate for 1993 (*25*) is shown in the background. (**B**) The 45-year CS-δ^{15}N record was generated using a coral core collected from the northern reef flat in Dongsha (filled red circle), and a 3-year CS-δ^{15}N record for comparison was generated from the east end of the lagoon (open red circle). Nitrate concentration and δ^{15}N were analyzed in the upper ocean both within and surrounding the atoll (white triangles) (*15*).

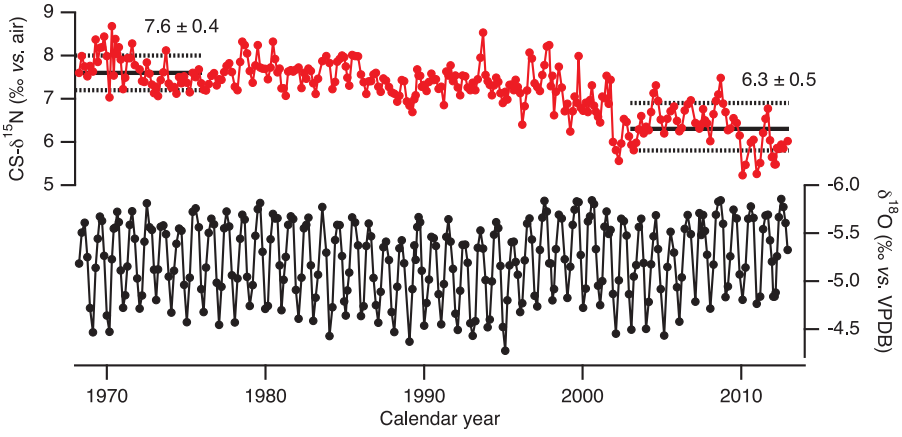

Fig. 2. The 45-year records of CS-δ^{15}N and skeletal carbonate δ^{18}O. CS-δ^{15}N declined across the record, with a 1.3‰ difference between the average δ^{15}N values from 1968–1977 and 2003–2012. The major decline in CS-δ^{15}N occurred in the 21st century. VPDB, Vienna Pee Dee Belemnite standard.

rate at Dongsha, the stability of shallow subsurface nitrate δ^{15}N argues against a basin-wide increase in this process (*9*, *19*). If N fixation alone drove the δ^{15}N decrease, it would require that the N fixation rate increased at least fivefold over this period, which is contradicted by all box model estimates and direct measurements of N fixation in the northern South China Sea (*19*, *20*). In addition, increasing AAN deposition would be expected to relax N limitation, possibly suppressing N fixation (*21*).

Therefore, the sole remaining explanation for the decline in CS-δ^{15}N over the past 45 years is as the result of increased deposition of atmospheric N to the open ocean associated with anthropogenic emissions. Increased anthropogenic N emissions since the Industrial Revolution have been invoked to explain observed declines in the δ^{15}N of nitrate in Greenland ice and of organic N in the sediments of remote lakes over the past 150 years (*22*, *23*), as well as a δ^{15}N decline in tree rings from China over the past 60 years (*24*). Located downwind of northeast Asia, the northern South China Sea is one of the open-ocean regions that could be most affected by AAN deposition associated with the rapid growth in agricultural and industrial development in China (*1*).

If one assumes the δ^{15}N for oceanic nitrate, N fixation, and atmospheric N deposition are 5.5, −1 (*10*), and −2.7‰ (*11*), respectively, the 1.3‰ decline in CS-δ^{15}N from 1968–1977 to 2003–2012 suggests that, by the latter time interval, atmospheric N input had increased to account for 20 ± 5% of the total N input to the surface of the northern South China Sea (*15*) (Fig. 3 and figs. S5 to S7). Although uncertainties in vertical nitrate input and N fixation rate are both large, the increase in atmospheric N deposition as a proportion of the total N input is robust (*15*). The greatest single source of uncertainty is whether N fixation remained constant or declined in response to the increase in atmospheric N deposition (*21*). On the basis of the CS-δ^{15}N record, we calculate for the year 2000 that atmospheric N deposition accounted for 17% or 23% of the total N flux, assuming constant N fixation or declining N fixation, respectively (Fig. 3 and figs. S5 to S7).

Although Dongsha Atoll cannot speak directly to the global pattern of AAN deposition, it provides a local test of ocean models that are tasked with producing a globally comprehensive picture. Our estimate of AAN as a proportion of fixed N

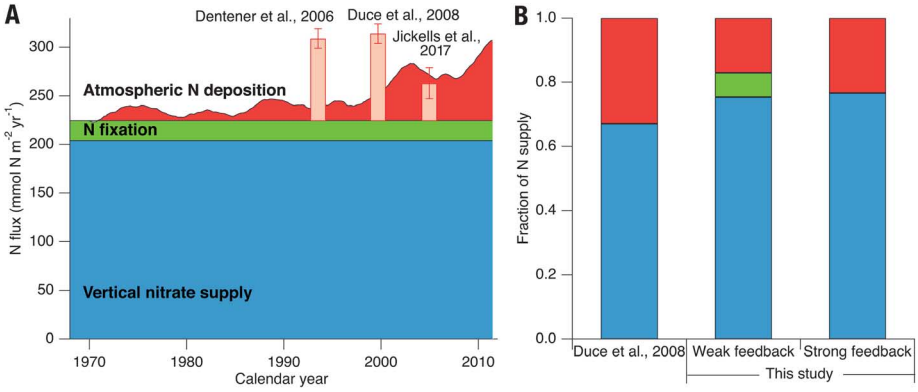

Fig. 3. Changes in atmospheric N deposition near Dongsha Atoll reconstructed from CS-δ^{15}N using an isotope mixing model. (**A**) Vertical nitrate flux (blue) and N fixation rate (green) are respectively assumed to be 204 mmol N m^{-2} yr^{-1} and 20 mmol N m^{-2} yr^{-1} (*19*, *20*) and are held constant in this version of the model. Accordingly, the recorded CS-δ^{15}N decline over the past 45 years is interpreted as atmospheric N deposition (red). A 3-year running average of the CS-δ^{15}N record is used for this calculation. Atmospheric N deposition (pink bars) from global models are shown for 1993 (*25*), 2000 (*1*), and 2005 (*26*). (**B**) Comparison of the relative fractions of different N sources calculated from the model of (*1*, *25*) and our study for the year 2000. Atmospheric N deposition contributes 17 to 23% of the total N flux in our study, depending on whether N fixation is assumed to remain constant over the study period (weak feedback) or to have declined with the rise in atmospheric N deposition (strong feedback) (*15*) (figs. S5 to S7).

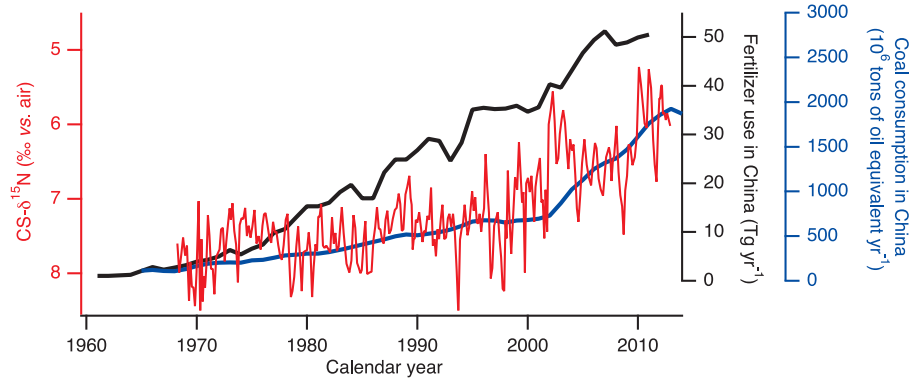

Fig. 4. Comparison of the CS-δ^{15}N decline with two contributors to anthropogenic N emissions in China. Higher values of CS-δ^{15}N (red) are plotted downward. Data on N fertilizer use (black) and coal consumption (blue) are from the Earth Policy Institute (www.earth-policy.org/data_center/). Coal consumption is shown here as a proxy for nitrogen oxide emissions, although vehicle use and associated petroleum consumption are also important sources (fig. S8).

input to the upper ocean is notably lower than an estimate of >33% in the northern South China Sea for the year 2000 from a prominent global model–based analysis (*1*, *25*) (Fig. 3 and figs. S5 to S7). Using estimates for vertical nitrate supply and N fixation of ~200 mmol N m^{-2} yr^{-1} and ~20 mmol N m^{-2} yr^{-1}, we calculate from our data an atmospheric N deposition rate of 49 ± 15 mmol N m^{-2} yr^{-1} in 2000. An analysis based on data from stations surrounding the South China Sea indicated an indistinguishable rate of 55 mmol N m^{-2} yr^{-1} for 2000–2010 (*7*). However, the study region was farther from Asia and excluded Dongsha Atoll's western margin environment, where N deposition rates are far higher (e.g., Fig. 1A). The implication is that our estimate for the same time period is again comparatively low. In contrast, our estimate is remarkably consistent with a recent model reanalysis by Jickells *et al.* (*26*), which estimates an atmospheric N input of 39 mmol N m^{-2} yr^{-1} in the region of Dongsha for year 2005 (Fig. 3). The authors note that the major driver of change in the revised fluxes is the incorporation of observational findings that a substantial fraction of gross open-ocean N deposition reflects an ocean-atmosphere N cycle rather than a net continental input (*27*). Our results thus appear to provide additional support for the importance of ocean-atmosphere cycling in the reactive N chemistry of the marine atmosphere (*28*), which complicates the quantification of AAN input from direct deposition rate measurements.

Another significant finding is that the CS-δ^{15}N decline was minor until ~2000, decades later than anthropogenic N emissions increased in China (*5*). The timing of CS-δ^{15}N change resembles the increase in the nitrogen oxide emissions associated with fossil fuel burning more than it does the ammonia emissions from food production (N fertilizer use and animal husbandry) (Fig. 4 and fig. S8). In particular, coal consumption and the number of vehicles have increased exponentially over the past decades, coinciding with the more rapid CS-δ^{15}N decline since the late 1990s. Thus, the data suggest that fossil fuel energy use has been the major driver of increasing AAN deposition in the South China Sea. This is consistent with the dominant role of energy use in the N deposition on land from the 1990s to the 2000s (*29*).

Superimposed on the decreasing trend, CS-δ^{15}N shows seasonal and decadal variations. The seasonal changes coincide with (but slightly lag) changes in δ^{18}O, indicating that low δ^{15}N values occurred in the winters and high values in the summers (Fig. 2 and figs. S1 and S4). The seasonal variation in CS-δ^{15}N is between 0.5 and 1‰, appearing stronger since the late 20th century (fig. S4). One possible driver of the seasonal variation is a seasonal cycle in atmospheric N sources. During winter, the strong northeasterly monsoon blows polluted air from northeast Asia to Dongsha, delivering more low-δ^{15}N AAN relative to the summer, when southwesterly monsoons import cleaner maritime air (*30*). Consistent with this explanation, nitrate in wet deposition in Dongsha is observed to be ~5‰ lower in winter than summer (*11*). An increase in AAN deposition since the late 20th century may thus also explain the recent increase in δ^{15}N seasonality. Further work will be required to test this interpretation. The cause of the decadal variability in CS-δ^{15}N is difficult to assess with current information; El Niño–Southern Oscillation variation may be involved (fig. S9).

Anthropogenic emissions have fundamentally changed the biogeochemical cycling of nitrogen on land and in coastal regions [e.g., (*31*, *32*)] and have been suggested to impact the open ocean, especially its nutrient-limited low-latitude regions (*1*, *33*). Our Dongsha CS-δ^{15}N record provides a multidecadal accounting of AAN deposition on the open ocean, showing that AAN has indeed increased, but the reconstructed increase falls in the lower range of prior estimates. Our findings point to energy use and vehicles as the major concern for impacts on this region of the open ocean and thus raise the prospect that reductions in nitrogen oxide emissions in East Asia achieved by upgrading combustion technology or switching to renewable energy sources could largely spare the open western North Pacific from anthropogenic N fertilization. A spatially extensive network of N isotope records from corals and similar archives from ocean islands and offshore reefs, when combined with direct measurements

and numerical models of the reactive N cycle, has great potential to clarify the evolving anthropogenic impact on the open-ocean N cycle.

REFERENCES AND NOTES

1. R. A. Duce *et al*., *Science* **320**, 893–897 (2008).
2. A. Krishnamurthy, J. K. Moore, N. Mahowald, C. Luo, C. S. Zender, *J. Geophys. Res. Biogeosci.* **115**, G01006 (2010).
3. H. W. Paerl, *Limnol. Oceanogr.* **42**, 1154–1165 (1997).
4. A. Richter, J. P. Burrows, H. Nüss, C. Granier, U. Niemeier, *Nature* **437**, 129–132 (2005).
5. X. Liu *et al*., *Nature* **494**, 459–462 (2013).
6. X. Liu *et al*., *Environ. Pollut.* **159**, 2251–2264 (2011).
7. T. W. Kim, K. Lee, R. Duce, P. Liss, *Geophys. Res. Lett.* **41**, 3156–3162 (2014).
8. I. N. Kim *et al*., *Science* **346**, 1102–1106 (2014).
9. G. T. F. Wong *et al*., *Geophys. Res. Lett.* **29**, 12-1–12-4 (2002).
10. E. Wada, M. Terazaki, Y. Kabaya, T. Nemoto, *Deep-Sea Res. A, Oceanogr. Res. Pap.* **34**, 829–841 (1987).
11. J. Y. T. Yang, S. C. Hsu, M. H. Dai, S. S. Y. Hsiao, S. J. Kao, *Biogeosciences* **11**, 1833–1846 (2014).
12. A. Yamazaki, T. Watanabe, U. Tsunogai, *Geophys. Res. Lett.* **38**, L19605 (2011).
13. X. T. Wang *et al*., *Geochim. Cosmochim. Acta* **148**, 179–190 (2015).
14. X. T. Wang *et al*., *Earth Planet. Sci. Lett.* **441**, 125–132 (2016).
15. Materials and methods are available as supplementary materials.
16. T. M. DeCarlo, K. B. Karnauskas, K. A. Davis, G. T. F. Wong, *Geophys. Res. Lett.* **42**, 831–838 (2015).
17. W. W. Gregg, M. E. Conkright, *Geophys. Res. Lett.* **29**, 20-1–20-4 (2002).
18. K. K. Liu *et al*., *Biogeosciences* **10**, 7449–7462 (2013).
19. G. T. F. Wong, C. M. Tseng, L. S. Wen, S. W. Chung, *Deep Sea Res. Part II Top. Stud. Oceanogr.* **54**, 1528–1545 (2007).
20. Y.-L. L. Chen, *Deep Sea Res. Part I Oceanogr. Res. Pap.* **52**, 319–340 (2005).
21. S. Yang, N. Gruber, *Global Biogeochem. Cycles* **30**, 1418–1440 (2016).
22. G. W. Holtgrieve *et al*., *Science* **334**, 1545–1548 (2011).
23. M. G. Hastings, J. C. Jarvis, E. J. Steig, *Science* **324**, 1288 (2009).
24. Y. Fang *et al*., *Glob. Change Biol.* **17**, 872–885 (2011).
25. F. Dentener *et al*., *Global Biogeochem. Cycles* **20**, GB4003 (2006).
26. T. D. Jickells *et al*., *Global Biogeochem. Cycles* **31**, 289–303 (2017).
27. M. G. Hastings, D. M. Sigman, F. Lipschultz, *J. Geophys. Res. Atmos.* **108**, 4790 (2003).
28. K. E. Altieri, S. E. Fawcett, A. J. Peters, D. M. Sigman, M. G. Hastings, *Proc. Natl. Acad. Sci. U.S.A.* **113**, 925–930 (2016).
29. Y. Jia *et al*., *Sci. Rep.* **6**, 19810 (2016).
30. I.-I. Lin, J.-P. Chen, G. T. F. Wong, C.-W. Huang, C.-C. Lien, *Deep Sea Res. Part II Top. Stud. Oceanogr.* **54**, 1589–1601 (2007).
31. J. J. Elser *et al*., *Science* **326**, 835–837 (2009).
32. H. W. Paerl, R. L. Dennis, D. R. Whitall, *Estuaries* **25**, 677–693 (2002).
33. B. Mouriño-Carballido, M. Pahlow, A. Oschlies, *Geophys. Res. Lett.* **39**, L05601 (2012).

ACKNOWLEDGMENTS

We thank G. P. Lohmann, K.-Y. Lee, Y.-C. Wu, L. Hou, and J.-H. Tai, for their assistance with fieldwork and coral coring in Dongsha Atoll. We also thank I. I. Lin, K. Soong, and Dongsha Atoll Research Station for their constructive input and support. Funding was provided by Ministry of Science and Technology of Taiwan (MOST) grant 105-2628-M-002-007-MY3, National Taiwan University grants NTU-SINICA-105R104513, NTU-CESRP-105R7625, and NTU-CDP-105R7719 to H.R., the Sustainability Science Research Program of the Academia Sinica to G.T.F.W. and A.L.C., Taiwan MOST grant NSC 101-2611-M-001-003-MY3 to G.T.F.W., U.S. NSF grants 1536368 and 1537338 to A.L.C. and D.M.S., the Grand Challenges Program of Princeton University to D.M.S., and an Academia Sinica Distinguished Postdoctoral Fellowship to H.R. The data reported in this work will be accessible at National Centers for Environmental Information, National Oceanic and Atmospheric Administration once the paper is published online.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/356/6339/749/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S10
References (*34*–*45*)

11 November 2016; accepted 6 April 2017
10.1126/science.aal3869

21st-century rise in anthropogenic nitrogen deposition on a remote coral reef

Haojia Ren, Yi-Chi Chen, Xingchen T. Wang, George T. F. Wong, Anne L. Cohen, Thomas M. DeCarlo, Mira A. Weigand, Horng-Sheng Mii and Daniel M. Sigman (May 18, 2017)

Science **356** (6339), 749-752. [doi: 10.1126/science.aal3869]

Editor's Summary

From air to shining sea

Nitrogen is an essential nutrient for phytoplankton growth. Nitrogen is primarily supplied to the surface ocean by mixing from below. However, as fertilizer use and combustion of fossil fuels rise, the atmosphere is expected to become an increasingly important source. Ren *et al.* measured nitrogen isotopes in organic matter from a South China Sea coral (see the Perspective by Boyle). Their findings suggest that atmospheric deposition of anthropogenic nitrogen began right at the end of the 20th century. This pathway now supplies nearly one quarter of the annual nitrogen input to the surface ocean in this region.

Science, this issue p. 749; see also p. 700