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Nitrogen pollution knows no bounds

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Coral Nitrogen Isotope Data Reveals Increasing Anthropogenic Nitrogen Fluxes into the South China Sea

Ed Boyle

In recent decades, atmospheric chemists have alerted the scientific community to the growing magnitude of anthropogenic fixed nitrogen emissions into the environment. This nitrogen flux into the ocean may approach the magnitude of natural sources (1-3). There are many human sources, ranging from excess production and utilization of nitrogen fertilizers, ammonia emitted from animal husbandry and sewage, and nitrogen oxides created in automobiles, airplanes, and fossil fuel power plants. It is difficult to precisely specify the integrated increase over the natural sources because there is very little data when nitrogen sources were dominantly natural. Although some natural archives such as ice cores, peat bogs, and lake deposits support the premise of higher global fixed nitrogen deposition (e.g. increases of nitrate and ammonia in ice cores (4,5), organic N in remote lake sediments (6), and a $\delta^{15}\text{N}$ decline in Chinese tree rings (7)), these archives are too sparse and remote to quantify the global deposition of anthropogenic nitrogen emissions into the ocean. In the paper by Ren et al. in this volume, a half-century record of increasing anthropogenic fixed nitrogen emissions is derived from measurements of the nitrogen isotope composition of proteins trapped in the aragonite skeletons of an annual banded coral from Dongsha Atoll, just off of China in the South China Sea.

Nitrogen isotope measurements are helpful in resolving processes that transport fixed nitrogen through the ocean. The major source of fixed nitrogen to open-ocean phytoplankton is the upwelling and upward mixing from the reservoir of nitrate ion dissolved in the deep ocean waters. Below the uppermost layers, nitrate ion in the deep sea shows a relatively narrow range in the $^{15}\text{N}/^{14}\text{N}$ ratio (+5.0 to +5.5‰ within the South China Sea) because the residence time of oceanic nitrate is greater than the mixing time of the ocean. The ocean is slightly depleted in the lighter isotope relative to the ultimate source (atmospheric gaseous nitrogen, the 0‰ reference point) because of preferential removal of the lighter isotope during water column denitrification (the conversion of nitrate to N_2O or N_2 gas which is lost from the ocean). In the warm stratified ocean, nitrate that mixes up to the surface is almost completely consumed by phytoplankton and eventually converted into sinking biological organic matter that balances the upward flux, having the same nitrogen isotope ratio as the upward mixing deep ocean water. Although phytoplankton at any instant preferentially take up the lighter isotope from nitrate in solution, mass balance requires the isotopic composition of upwelling nitrate to equal the flux of nitrogen in sinking biologically-derived particulate matter. Organic matter derived from this flux (such as the proteins trapped in coral skeletons) reflects the isotopic composition of the total flux.

In the modern era, there are three sources of fixed (biologically utilizable) nitrogen to the surface ocean that have isotope compositions that are lighter than

that of deep ocean nitrate, two of which are naturally-occurring. Lightning provides relatively minor inputs of fixed nitrogen with an isotopic composition that is only slightly fractionated relative to atmospheric N₂. The larger pre-anthropogenically dominant source is from biological nitrogen fixation – the conversion of N₂ gas to biologically utilizable forms of nitrogen- that occurs both on the continents by commensal bacteria on plant roots within soils, some of which can be transported to the ocean by rivers and atmospheric dust, and within the marine phytoplankton community by organisms such as *Trichodesmium* that use solar energy to convert dissolved N₂ gas into biologically-available forms. Biologically fixed nitrogen is about -1‰ relative to the atmosphere. Finally, in the modern era nitrogen is fixed by many human activities, either deliberately during the Haber-Bosch production of nitrogen fertilizers, or inadvertently during high temperature combustion in power plants, automobile engines, and airplanes. These anthropogenic mechanisms produce fixed nitrogen that is about -2.7‰ relative to atmospheric N₂, in contrast to the ~+5‰ in the oceanic nitrate reservoir.

The use of organic matter in corals as an indicator of the nitrogen isotope composition of nitrogen sources to the surface ocean is based on the premise that the trace proteins that are incorporated into the coral aragonite calcium carbonate skeleton have an isotopic composition that is offset from that of the source fixed nitrogen by a fixed value (about +2‰). This assumption is supported by data on the nitrogen isotopic composition of corals (8).

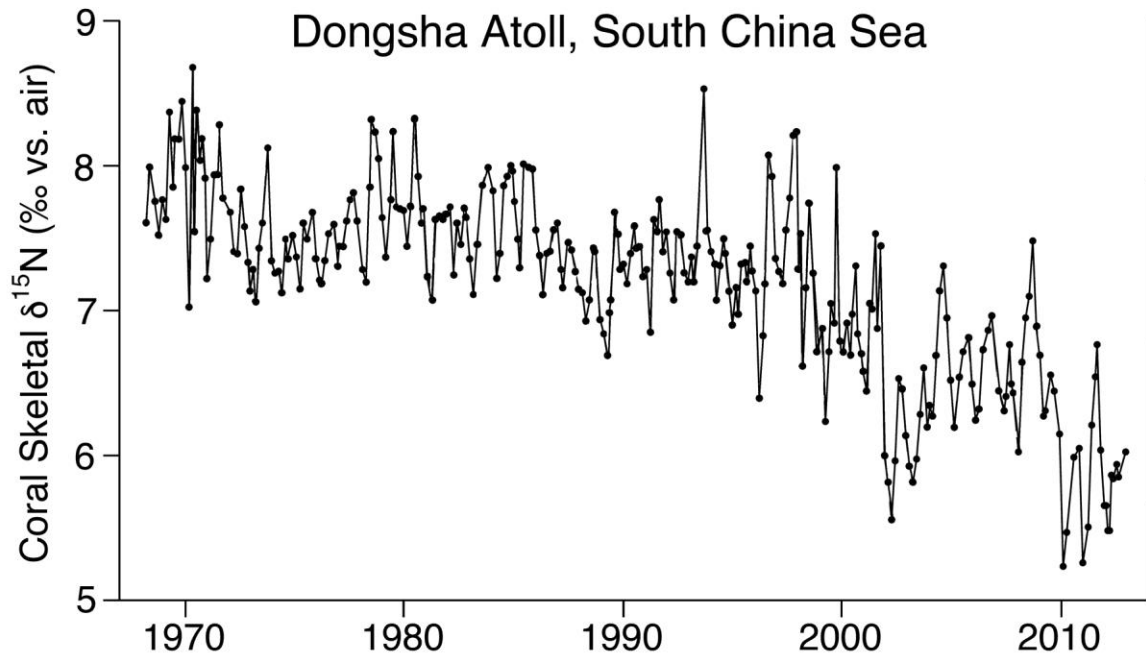
The observation that the Dongsha Atoll coral has lighter organic skeletal nitrogen now than the previous half century could be caused by either (a) relatively large reductions in the upward mixing of thermocline nitrate in this, (b) an increase in biological nitrogen fixation within the ocean, or (c) an increase in the anthropogenic fixed nitrogen sources. Reduced upward mixing is inconsistent with long-term observations of a relatively stable chlorophyll concentration in this region. Historical marine nitrogen fixation measurements do not support such an increase in regional nitrogen fixation. Hence Sun et al. conclude that the lighter of coral-bound organic nitrogen is due to an increase in the deposition of light anthropogenic nitrogen in this region.

The Dongsha Atoll data imply that anthropogenic nitrogen enhancement (~20% compared to the regional natural flux from upmixing) mainly has occurred during the past two decades. Although significant, this estimate is near the lower end of the range of previous anthropogenic enhancement estimates from atmospheric measurements. The timing of the Dongsha coral increase also is later than anticipated from the history of many Chinese anthropogenic fixed nitrogen sources such as agriculture and fertilizer production. The late rise however is coincident with a major increase in coal consumption and vehicles (9), suggesting that these fossil fuel induced sources may account for the increased anthropogenic nitrogen flux into the South China Sea.

One consequence of the recognition of significant anthropogenic additions of isotopically light **fixed nitrogen** is that some of the light upper ocean nitrate - which has been attributed solely to natural biological nitrogen fixation in the ocean - is actually anthropogenic. In order to better understand and model the integrated rates of biological nitrogen fixation in the ocean, we need to have a clearer quantification of the anthropogenic sources throughout the ocean (10).

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Skeletal-bound organic nitrogen isotope variability in a 50 year record from a coral in the South China Sea (Ren et al., this issue)