WHAT'S IN THE RISING TIDE?

The nitrogen cycle rarely features in the grim litany of things at risk from global warming. **Nick Lane** reports on research that might change this — with grave consequences for ocean chemistry.

Colossal bridges bestride the waters of Narragansett Bay. Towns, interstate highways and suburbs sprawl along its shores and its waves are studded by thousands of pleasure boats. Yet the estuary retains a quiet beauty that befits the pious settlers who, 350 years ago, named the islands within the bay Prudence, Hope and Patience.

Extending its briny fingers through much of Rhode Island, Narragansett Bay has long juxtaposed man and nature, pollution and purity. Industrialization in the nineteenth century led to the rapid growth of cities such as Providence, a port at the bay's north end. The area now supports about a million people, all flushing their waste into the pastoral watershed. Reactive nitrogen compounds from treated sewage, industrial waste and fertilizers have poured in for decades, but remained at a relatively constant level for the past 25 years. Nevertheless, set against this steady background, a silent microbial and biochemical transformation has occurred in the bay that could have devastating ecological effects. The cause is pollution, but of an indirect sort — the changes seem to be down to global warming.

For the past three decades, the bottom

sediments of the bay have mopped up much of the reactive nitrogen that humans have dumped into it. Although the fraction sequestered had been falling, this valuable natural sink has been protecting the bay and the coastal oceans from the effects of nitrate runoff. But last year the sediments abruptly stopped performing this service. Worse than that, they went into reverse. In a single summer, the bay switched from being a net sink to a net source of nitrates¹.

Robinson “Wally” Fulweiler, an oceanographer at Louisiana State University in Baton Rouge, and her colleagues at the University of Rhode Island in Kingston, were among the first to notice the turning environmental tide. If Narragansett

is typical of other bays, they argue, it could be the harbinger of a new threat. Shifting the effect of anthropogenic nitrogen loading beyond the immediate coastal zone could destabilize ocean ecosystems by acidifying the waters, exacerbating harmful algal blooms, killing fish and shellfish, or perhaps even powering a vicious new cycle of global warming. The studies are currently hard to interpret and some say the system is poised to rebalance itself. But if they are wrong, global warming may do

more to the oceans than make them rise.

According to Fulweiler, the root of the problem is a disconnect between life in the water column and that in the bottom sediments — the pelagic and benthic ecosystems, respectively. Under normal conditions, phytoplankton in the water column generate new organic matter through photosynthesis, some of which filters down to the bottom sediments — the benthos — where it provides food for bacteria. These benthic bacteria detoxify the water, removing excess nitrates, phosphates, and other pollutants while adding various micronutrients back to the water column. Healthy coastal ecosystems tend to have a good interchange — a tight coupling — between the pelagic and the benthic zones.

A silent switch

In Narragansett, the pelagic ecosystem is failing. Primary productivity, as measured by chlorophyll concentration, has fallen by 40% during the past 30 years, reflecting a dwindling of the spring bloom of phytoplankton.

Unlike harmful algal blooms — in which excess nutrients such as nitrates provoke a strangling growth of weed-like algae, ultimately leaving the water full of dead, rotting matter — normal seasonal blooms of phytoplankton are necessary to maintain the health of the estuary.

“Last year 17,000 tonnes of nitrate went unaccounted for in Narragansett Bay.”

SWERVE/ALAMY

The decline, Fulweiler says, could have been caused by warmer winters, either because they provide thicker cloud cover or because they allow more grazing zooplankton to flourish. Either way, rising temperatures are hitting primary productivity.

Falling productivity means a decline in the quantity and quality of organic matter reaching benthic bacteria, notably the denitrifiers. Denitrifying bacteria convert nitrates back to inert nitrogen gas. Just as organic molecules from food are reacted with oxygen to generate energy in animals, these denitrifying bacteria glean energy when organic remains react with nitrate.

The benthic denitrifiers are choosy eaters. They live on 'labile organic carbon', essentially, fresh food. A decline in primary productivity was likely to hit them hard.

What came as a shock was the switch to a completely new population — the nitrogen-fixing bacteria. These organisms take nitrogen dissolved in water and convert it into ammonia, in a process known as nitrogen fixation. This new organic nitrogen is ultimately converted into nitrates by a third group of bacteria, the nitrifiers. So the sediments not only stop mopping up excess nitrates, they start adding more to the pot (see 'The changing cycle').

What flipped the switch is unknown. The nitrifying bacteria at the end of this chain have been shown to have unpredictable population patterns². If that is the case here, then the change may not be significant. But a more troubling explanation relates to the composition of non-labile organic matter. According to Bess Ward, a biogeochemist at Princeton University in New Jersey, organic matter can become so depleted of nitrogen that it no longer provides enough sustenance for denitrifying bacteria. That stops their growth. Because nitrogen

fixers don't face this constraint, they thrive.

If Ward is right, then the switch could be both persistent and widespread. The overall equation is not trivial. Under normal circumstances, the sediments in Narragansett Bay decontaminate around one quarter of the reactive nitrogen compounds running off from farmland and sewage — something in

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— Robinson
"Wally" Fulweiler

the order of 1,000 tonnes of nitrogen, or 5,000 tonnes of nitrate, every year — making the failure of denitrification significant in its own right. Fulweiler notes that the excess nitrogen is not accumulating as dissolved nitrates in the bay, nor is it stimulating algal blooms. Presumably, she says, at least some is simply being flushed out to sea.

An unbalanced equation

In addition to this substantial flux, in the three summer months of 2006, the rate of nitrogen fixation by the thriving nitrogen fixers was estimated to be around 1.5 times greater than the total input from rivers, sewage and atmospheric pollution combined — nearly 3,000 tonnes of nitrogen converting into 12,000 tonnes of nitrate. Even allowing for more typical conditions throughout the rest of the year, this still represents 20–60% more nitrogen input annually. Last year, in Narragansett Bay, some 17,000 tonnes of nitrate

went unaccounted for. So, what's happening to it all?

A switch from denitrification to nitrogen fixation is utterly unexpected, which in itself shows just how much remains to be learned about the nitrogen cycle. Fulweiler notes that nitrogen-fixing bacteria in estuarine sediments have not been seen as important players in the nitrogen cycle before. But balancing the nitrogen cycle has been a bit of an embarrassment for years. It should be easy enough — just sum up the total nitrate inputs, from natural and anthropogenic sources, and subtract the flux back to the atmosphere as nitrogen gas. Instead, it's a giant mismatch. The calculated rate of global denitrification is twice the known inputs from fixation and anthropogenic sources. As Lou Codispoti at the University of Maryland's Horn Point Laboratory (HPL) just outside Cambridge says, either the cycle doesn't balance at all — that is, today's oceans are in some sort of a 'transient' state — or scientists have overlooked a whole lot of nitrogen fixation somewhere.

Most suspect the latter. And set against this background, Narragansett Bay might just represent a small fraction of that missing nitrogen. On the other hand, if global warming really does alter the nitrogen cycle, it could throw the global equation off balance.

Fulweiler is the first to admit that a correlation is not proof of causality. Nevertheless, she's concerned with what might be a trend. There are hints from elsewhere that nitrogen fixation is picking up. A similar uncoupling of the pelagic and benthic ecosystems was noted in the arctic last year. Jackie Grebmeier at the University of Tennessee in Knoxville, and her collaborators reported³ a 75% drop in benthic oxygen consumption (a surrogate for carbon supply) between 1988 and 2004. More recently, oceanographer Judy O'Neil at the

THE CHANGING CYCLE

When primary producers in Narragansett Bay started to dwindle, the benthic balance of bacteria shifted in favour of nitrogen-fixing bacteria.

HPL measured nitrogen fixation in tributaries to Chesapeake Bay, a few hundred miles south of Narragansett. Although she's yet to quantify their total contribution, her data incriminate cyanobacterial blooms, rather than benthic nitrogen-fixation for flipping the switch. The reason is that cyanobacterial blooms are notoriously full of toxins, which makes them unpalatable to grazing zooplankton, and the animals that eat them in turn. As a result, more carbon is flushed out in a dissolved state rather than passing down to the bottom sediments via faecal pellets.

The trend appears new according to Ward, who, working with Todd Kana and his colleagues at the HPL, looked for evidence of nitrogen fixation in the Chesapeake 5 years ago; they found no activity. Later, working with Jon Zehr and others at the University of California, Santa Cruz, Ward found copies of the genes required for fixation in the sediments there⁴. What's more, they were associated with the most unusual suspects, such as proteobacteria, which have never before been associated with nitrogen fixation. Nitrogen fixation requires a suite of 10 to 20 genes; if lying fallow, these are costly to maintain and so ought to be lost. Ward says that if they're there, they're being used.

Some like it hot

In the Chesapeake, too, the rise in nitrogen fixation probably relates to global warming, albeit for different reasons. Here there is no evidence of failing spring blooms, but rather a gradual takeover by cyanobacteria, which apparently "like it hot". Don Canfield, a geochemist at the University of Southern Denmark in Odense, says he thinks the trend is global. If he's right, nitrate export could rise substantially in a matter of a few years.

Of course verifying

the export of nitrogen hinges on balancing that stubborn nitrogen cycle equation. Paul Falkowski, a biogeochemist at Rutgers University's Institute of Marine and Coastal Sciences in New Brunswick, New Jersey, is sceptical about nitrogen export from Narragansett Bay. If ammonia and nitrates are being produced in such large quantities, he asks, then why are we seeing a steady decline in primary productivity, rather than an increase in blooms? And if the nitrates are all being flushed out into coastal waters, then the more buoyant, fresher water from the bay (with its river inputs) ought to float in the sunny surface waters above the denser saline, and we should see blooms there instead. Satellite images, he says, don't show dramatic blooms.

Fulweiler has plausible answers, which need to be tested: in the bay itself, nitrates may be swallowed up by other bacteria competing for resources with phytoplankton in the water column. If so, then the export of nitrates to the oceans would be more limited, and the problem would revert back to one of local ecology. On the other hand if more nitrates really are exported out to sea, Fulweiler argues, they wouldn't necessarily stimulate large algal blooms. The salinity gap between Narragansett Bay and the ocean is quite small, she says, so the waters emerging from the bay might not float.

In the absence of dramatic blooms, the water might instead be getting more acidic, according to Scott Doney and his collaborators at Woods Hole Oceanographic Institute in Massachusetts. Both nitrates and sulphates acidify ocean waters. The impact on the open ocean is limited, compared with the acidification caused by rising carbon dioxide levels, but Doney's

marine modelling suggests that the effects of nitrates in coastal waters may be serious. The organisms most likely to be affected by ocean acidification are those with shells or skeletons made from calcium carbonate, including many algae that would otherwise bloom⁵.

No laughing matter

Another possibility, if the waters emerging from Narragansett sink, is a bloom of denitrifying bacteria lower in the water column. Denitrification in coastal waters tends to be dominated by the classic bacterial pathway; and a major by-product of this is nitrous oxide — laughing gas. Nitrous oxide is 200–300 times more potent as a greenhouse gas than carbon dioxide.

In 2000, Wajih Naqvi and his colleagues at the National Institute of Oceanography in Goa, India, reported an alarming accumulation of nitrous oxide in the Arabian Sea, along the western Indian

continental shelf, following a monsoon washout of nitrate fertilizers⁶. The calculated emissions from the region in just 6 months accounted for as much as 5% of annual ocean emissions from a region that makes up only 0.05% of the world's oceans. Although there is much to learn about the interplay of factors controlling oceanic nitrous oxide emissions, Naqvi says that emissions are generally greatest in oxygen-minimum zones. Because these are spreading as a result of global warming (oxygen is less soluble in warmer waters) and eutrophic conditions (an increase in chemical nutrients) nitrous oxide emissions will in all probability rise.

Most observers anticipate that restrictions in the use of nitrates, along with better facilities for treating sewage and industrial waste, will reduce oceanic nitrogen contamination. But a widespread switch to nitrogen fixation, as a result of global warming, could raise nitrate levels and nitrous oxide emissions despite human intervention, driving a vicious cycle. Balancing the nitrogen cycle as the world warms suddenly looks more critical and more uncertain than ever.

Nick Lane is a science writer and honorary reader at University College London.

"Either the oceans are in some sort of transient state or scientists have overlooked a lot of nitrogen fixation."

— Lou Codispoti

Judy O'Neil samples a thick bloom of assorted algae (inset) from the Sassafras River, a tributary of Chesapeake Bay in Maryland.

1. Fulweiler, R. W., Nixon, S. W., Buckley, B. A. & Granger, S. L. *Nature* **448**, 180–182 (2007).
2. Graham, D. W. *et al.* *ISME Journal* **1**, 385–393 (2007).
3. Grebmeier, J. M. *et al.* *Science* **311**, 1461–1464 (2006).
4. Jenkins, B. D., Steward, G. F., Short, S. M., Ward, B. B. & Zehr, J. P. *Appl. Environ. Microbiol.* **70**, 1767–1776 (2004).
5. Doney, S. C. *et al.* *Proc. Natl Acad. Sci. USA* **104**, 14580–14585 (2007).
6. Naqvi, S. W. *et al.* *Nature* **408**, 346–349 (2000).