

# Out of reach

SYBIL SEITZINGER

Denitrifying bacteria and hungry plants do sterling work in disposing of the nitrates that we pump into rivers and streams. But as the excess influx goes up and up, the efficiency of removal goes down and down.

**T**hanks to human contributions — from fossil-fuel combustion, the growth of agricultural crops, and above all the fertilizers that help to keep the more than six billion humans worldwide in food<sup>1</sup> — nitrogen is entering Earth's soils at more than twice its natural rate. Much of the nitrogen from these sources goes on to enter streams, primarily as nitrates, and is transported downriver to coastal marine systems. There, it fuels excessive rates of plant growth and decay in the process known as eutrophication. This can result in hypoxia (shortage of oxygen) or, in extreme cases, anoxia (total loss of oxygen), creating the 'dead zones' seen in places such as Chesapeake Bay, the Gulf of Mexico and the Baltic Sea.

Fortunately, as Mulholland and colleagues detail in a recent paper in *Nature*, not all the extra nitrates that we pile into streams make it to coastal systems; instead, some is removed and retained by biological processes. In the short term, aquatic plants and microbes take up and store nitrogen as a nutrient. But by far the greatest part in long-term nitrogen removal is played by the denitrifying bacteria that live in anoxic sediments in a stream's bed and banks. These microbes transform the nitrogen in nitrates to gaseous forms such as molecular nitrogen ( $N_2$ ) and nitrous oxide ( $N_2O$ ), which diffuse out of river water into the air. Such denitrification is not without environmental consequences: whereas  $N_2$  is harmless (and makes up almost 80% of the atmosphere),  $N_2O$ , although only a small portion of the total gaseous nitrogen produced, is a potent greenhouse gas that has also been implicated in stratospheric ozone destruction.

Because many different methods have been used to measure rates of denitrification, comparison of the many measurements that have been made

is difficult. In addition, the physical and chemical characteristics of rivers that might affect nitrogen removal are extremely diverse, depending in part on the type and extent of human disturbance in the surrounding landscape. Developing predictive, widely applicable relationships linking river and watershed characteristics to nitrogen removal and retention rates is quite a challenge<sup>3</sup>.

Mulholland *et al.*<sup>2</sup> attacked these shortcomings with a study of unparalleled scale. They used a consistent method to quantify the fate of nitrate ( $NO_3^-$ ) in 72 small streams in pristine, urban and agricultural watersheds throughout the United States and Puerto Rico, adding trace amounts of nitrates labelled with the nitrogen isotope  $^{15}N$  to stream waters over periods of around 24 hours during spring or summer. The stable (non-radioactive) isotope  $^{15}N$  is rare in nature, occurring at less than 0.4% of the abundance of  $^{14}N$ . Using mass spectrometry, it was relatively easy to detect small decreases in  $^{15}NO_3^-$ , and increases in  $^{15}N_2$  and  $^{15}N_2O$  from denitrification. Decreases in labelled nitrates not accounted for by an increase in labelled  $N_2$  and  $N_2O$  were attributed to uptake by plants and microbes within each stream segment, or reach. This approach maintained existing conditions in the stream, and not only permitted the authors to distinguish denitrification from the temporary storage of nitrogen in biomass, but also allowed the rates of denitrification and biotic uptake to be assessed for the entire reach.

The authors found that measurable rates of nitrate removal occurred through biotic uptake and denitrification in most streams, and that absolute rates of removal generally increased as nitrate concentrations increased. But the efficiency of nitrate removal — the proportion of nitrate removed relative to the total amount present — decreased exponentially as nitrate concentrations

increased. This pattern held across nitrate concentrations that differed by six orders of magnitude in eight different biomes. As we use land ever more intensively, the effectiveness of the receiving streams in removing the additional nitrate pollution is likely to continue to diminish. Thus, looking at the results of this study, the pressure on policy-makers to reduce the load of anthropogenic nitrogen entering rivers from terrestrial systems will grow.

Of course, small streams are only one component of the filigree of flowing waters that drain a landscape. Small streams connect to middling channels, which connect to larger rivers, all of which propel water and its dissolved and particulate constituents towards coastal systems. The length of all the channels in a river system is often extensive — those within the 30,000 km<sup>2</sup> watershed of the Potomac River in the eastern United States amount to a length of some 25,000 km, equivalent to about five times the distance across the United States from coast to coast. Unsurprisingly, therefore, there are ample opportunities for nitrates to be removed on their journey from a river's headwaters to the coast that are not covered by Mulholland and colleagues' study.

To address this point, the researchers use a model to scale up their results to an entire river network. The outcome underscores the importance of river channels of all sizes, as well as the distribution of nitrate loading within the river network, in controlling the amount of nitrates reaching coastal waters. Nitrates not removed within a particular stream reach may be removed in the next, and so on down to the coast; but the relative importance of small, medium and large channels depends in part on where the nitrate concentration in a particular stream reach is on the curve of nitrate-removal efficiency. A small stream might remove most

of the nitrates quite effectively if the concentration is low; but if the local nitrate concentration increases such that nitrate-removal efficiency decreases, the capacity of downstream reaches to remove excess nitrates becomes relatively more important. And if the nitrate concentration throughout a river network continues to increase, the network's overall capacity to remove nitrates decreases. The importance of nitrogen removal across all channel sizes in a river network underlines the need for comprehensive studies such as that of Mulholland *et al.*<sup>2</sup> across a range of stream sizes and throughout the annual cycle.

Denitrification occurs not only in rivers, but in almost all environments at some time and place: nearly 80% of all reactive nitrogen is disposed of before it reaches coastal waters. Soils are generally the first receptor of the large amounts of nitrogen that we add to terrestrial systems, and the amount of denitrification in soils can substantially exceed that removed in the stream network<sup>4</sup>. Groundwater, lakes and coastal systems are also important sites of denitrification. For all these environments we urgently need advances in methods and models<sup>5</sup> that will increase our understanding of how large amounts of nitrogen move and are removed as they journey from soils to the sea.

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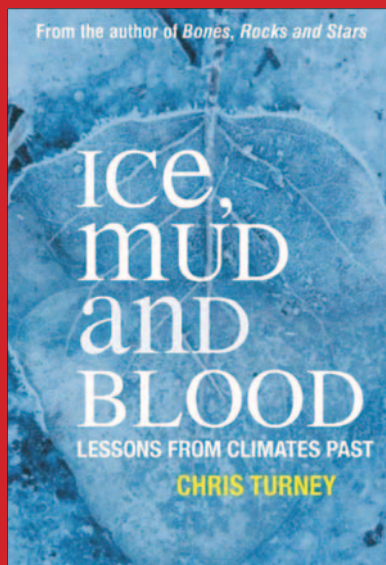
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Sybil Seitzinger is at the Institute of Marine and Coastal Sciences, Rutgers, The State University of New Jersey, Rutgers/ NOAA CMER Program.  
e-mail: sybil@marine.rutgers.edu

Article originally published in *Nature* (162–163, Vol 452, 12 March 2008).

Please refer to this for citation purposes.

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