Long-term Decreases in Stream Nitrate: Successional Causes Unlikely; Possible Links to DOC?

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Huntington (2005) poses the hypothesis that ''immobilization of inorganic N, in combination with region-wide recovery from past disturbances may explain the decrease in stream water nitrate in recent decades'' that we observed in 28 White Mountain, New Hampshire streams (Goodale and others 2003). We focus our response on Huntington's suggestions, and note that a range of additional factors not discussed here can have marked impacts on long-term patterns of NO_3^- loss (for example, N deposition, insect outbreaks, climate variation and extreme events such as soil frost). Below, we address Huntington's suggestion in two parts, first considering the role of region-wide recovery from historical disturbances and then considering recent changes in environmental factors that might have increased soil N immobilization through increased belowground productivity. We then introduce a hypothesis that suggests that changes in stream NO_3^- might be partly linked to observed changes in dissolved organic carbon (DOC).

We agree with Huntington that historical disturbances have had substantial impacts on forest carbon and nitrogen dynamics in the White Mountains of New Hampshire (see for example, Bormann and Likens 1979; Covington 1981; Thorne and Hamburg 1985). We have previously considered in some depth the role of the region's disturbance history as a major driver of patterns of organic matter accumulation and watershed N retention (see for example, Vitousek and Reiners 1975; Aber and Driscoll 1997; Goodale and others 2000; Goodale and Aber 2001). We agree that re-accumulation of soil organic matter in re-growing forests provides important sinks for atmospheric CO_2 and N deposition across large parts of the eastern U.S. (see for example, Huntington 1995; Hooker and Compton 2003). However, we do not believe that forest re-growth and soil re-accumulation explain the approximately 70% decrease in stream NO_3^- concentration (mean decrease of 25 µmol/L) that we observed between 1973–4 and 1996–97 (Goodale and others 2003).

First, we emphasize that we observed large decreases in stream NO_3^- concentration in both aggrading successional systems and in several old-growth watersheds that had no evidence of stand-level disturbance by historical logging or fire (see Goodale and others 2003 Figure 6; see also Martin and others 2000).

Second, the observed decreases in stream NO_3^- between the 1970s and the 1990s would require a synchronous *increase* in the rate of soil re-accumulation during this time period across all watersheds. Few successional factors could cause an increase in soil re-accumulation rate, and such factors are unlikely to occur simultaneously in both old-growth and successional watersheds.

On Huntington's suggestion that changes in climate and atmospheric CO_2 (a 10% increase) between 1973 and 1997 might have increased soil N accumulation through stimulation of belowground C production (and hence, microbial demand for N), we agree that this is a plausible hyphothesis, although it is not supported by long-term trends in aboveground C production. We agree that changes in climate and atmospheric CO_2 might be expected to have increased forest growth and N accumulation in plant and soil organic matter pools over the last several decades. However, as discussed by both Huntington and our original paper, available measurements provide no evidence for increased tree growth across the region or for increased woody biomass accumulation at Hubbard Brook (Likens and others 1996) since the 1970s. Nor do long-term satellite records suggest significant trends in net primary productivity in this region over 1982-1998 (Hicke and others 2002, and J. Hicke pers. comm.). Furthermore, model simulations suggest only small increases in watershed N retention between the 1970s and the 1990s due to observed changes in climate, CO_2, and other factors (Aber and others 2002). Because of the difficulty and scarcity of measurements of belowground processes, we are not aware of any long-term data sets available to test the hypothesis that belowground C production and N immobilization have increased over the last several decades without discernable effect on aboveground production, other than what we suggest below as one plausible driver of surface water DOC trends. As Huntington points out, N stocks in forest soils are very large and heterogeneous, and it would be nearly impossible to detect a change in the soil N pool as small as the expected change in watershed N export (for example, see, Huntington and others 1988). It is because of the large size of the soil organic N pool – and the size of N fluxes to and from it – relative to the size of changes in stream NO_3^- export that we previously speculated about the potential role of variable climate effects on soil net N mineralization relative to plant uptake as drivers of interannual variation in stream NO_3^- losses.

Here, we propose an additional hypothesis that might explain part of the unexpectedly low NO_3^- concentrations during the mid-1990s at White Mountain watersheds and elsewhere across the Northeast (Driscoll and others 2003; Stoddard and others 1999, 2003): increased N immobilization and/or denitrification driven by increased availability of terrestrial DOC.

Over the last 10–20 years, DOC concentrations have increased in lakes and streams across both the northeastern U.S. (Driscoll and others 2003; Stoddard and others 2003) and western Europe (Freemen and others 2001). In the Northeast, DOC concentrations have increased on average by approximately 0.006 mg L^{-1} y^{-1} between 1982 and 1999, amounting to a cumulative change in mean DOC concentration of about 1-2-mg/L (Driscoll and others 2003; Stoddard and others 2003). At Hubbard Brook, DOC concentrations have changed little or decreased slightly during the 1980s and 1990s (Palmer and others 2004). Unfortunately, few measurements of DOC are available for the White Mountains for the mid-1970s. Vitousek (1977) measured DOC just once (fall 973) in a subset of the White Mountain streams discussed here. Published measurements of DOC at Hubbard Brook for 1967–69 (Hobbie and Likens 1973; Fisher and Likens 1973) and for 1976–80 (Bilby and Likens 1979; McDowell and Likens 1988) fall largely before and after, respectively, the period of unusually high stream NO_3^- (1970–77; Likens and Bormann 1995).

Two hypotheses have been published as possible explanations for DOC increases observed elsewhere: (1) increased decomposition of soil organic matter in response to climate warming (Freeman and others 2001); and (2) decreased loading of acid anions from atmospheric deposition (Krug and Frink 1983; Driscoll and others 2003). Deposition of acid anions to the Northeast has decreased over the last several decades in response to decreases of sulfur dioxide emissions (Stoddard and others 1998; Driscoll and others 2001, 2003). Although NO_x emissions decreased slightly between 1990 and 2000 (Butler and others 2003), nitrogen deposition to the Northeast (as NO_3^-, NH_4^+, or total inorganic N) did not change significantly between the mid-1970s and mid-1990s (Stoddard and others 1998; Driscoll and others 2001, 2003). A third plausible explanation for increasing DOC in drainage waters – preferential stimulation of belowground C production by increased atmospheric CO_2 – would be consistent with Huntington's suggestions.

Regardless of the mechanism responsible for the observed increase in DOC, small changes in DOC concentration might indicate large, possibly non-linear effects on watershed N retention. Examining spatial patterns of chemistry in streams across the northeastern U.S., NO_3^- concentrations increase sharply with decreasing DOC concentrations (Figure 1). Inverse patterns between NO_3^- and DOC over space may reflect spatial patterns in soil C status and N immobilization capacity (Evans and others in press), or patterns of in- and near-stream denitrification. Observations of steep increases in subsurface NO_3^- and N_2O concentrations below DOC concentrations of about 2 mg/L have been
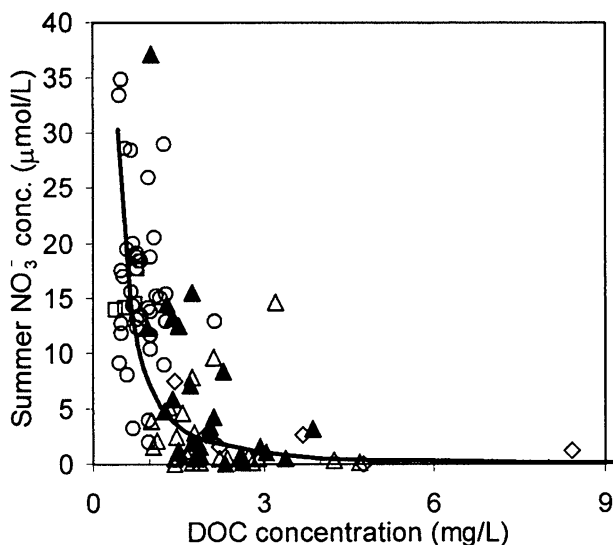
Figure 1. Relationship between nitrate and DOC concentration across 100 northeastern U.S streams, all for the mid-1990s. Stream chemistry published previously by Lovett and others (2000) for the Catskill Mountains, NY ($\bigcirc$); and by Martin and others. (2000) ($\square$), Campbell and others (2000) ($\diamond$), and Goodale and others (2000, 2003) ($\triangle$, $\blacktriangle$) for the White Mountains, NH. Line indicates best-fit: $NO_3^- = e^{1.98-1.78 \ln(DOC)}$; $R^2 = 0.46$.

interpreted as carbon limitation of denitrification below this DOC threshold (Hedin and others 1998). Experimental additions of labile DOC and litter leachate to in- and near-stream environments can result in large decreases in stream NO_3^- concentration through N immobilization by heterotrophic microbes and through denitrification (for example, see Hedin and others 1998; Strauss and Lamberti 2000, 2002; Bernhardt and Likens 2002; Sobczak and others 2003). Stream DOC can be quite refractory (McDowell and Likens 1988; Qualls and Haines 1992), and microbial processes are unlikely to increase in response to increases in recalcitrant carbon inputs (although some microbes can respond to inputs of refractory carbon; Strauss and Lamberti 2002; Findlay and others 2003). Yet, the signal of increasing stream DOC concentrations over time may simply reflect an increase in soil total DOC production and delivery of DOC to the near-stream zone, of which some is processed by microbes and the rest remains in streamwater.

Net immobilization of inorganic N by in-stream microbial biomass (see for example, Peterson and others 2001) is unlikely to explain a large amount of the NO_3^- decrease we observed, as the pool of in-stream biota its small and it turns over relatively rapidly. Furthermore, our measurements of total dissolved nitrogen ($NO_3^- + NH_4^+ +$ dissolved organic

nitrogen) concentrations in 1996-97 were far lower than concentrations of NO_3^- alone in 1973-74 (see Goodale and others 2003, Figure 6), indicating that there had not simply been a shift in the form of N export from inorganic to organic. However, DOC-fueled increases in microbial N immobilization in soils or sediments, or net removal of N by denitrification, remain as plausible explanations for the NO_3^- decrease. If NO_3^- and DOC concentrations in 1973-74 fell on the same curve as indicated in 1996-97 (Figure 1) then the decreases in NO_3^- concentration that we observed would require increases in stream DOC concentrations by an average of 0.7 mg/L (range: 0.1–2.5 mg/L), values within the range of long-term DOC increases reported elsewhere (Driscoll and others 2003; Stoddard and others 2003).

Microbial immobilization or denitrification fueled by increased loading of DOC to soils and in-and near-stream zones might be additional mechanisms to partly explain the large decrease in stream NO_3^- that we observed across a range New Hampshire streams in the mid-1990s. This proposed mechanism does not negate the importance of other factors driving temporal variation in stream NO_3^- loss, such as climate variation or disturbance events (for example, see Aber and others 2002), but would be yet another factor worth consideration. Many factors interact to affect long-term patterns of NO_3^- loss, and sorting among them remains a complicated endeavor. This hypothesis emphasizes the importance of considering coupled carbon–nitrogen dynamics in affecting long-term patterns of stream chemistry, and would benefit from increased understanding, experimentation, and analysis of controls on microbial immobilization and in- and near-stream denitrification, as well as greater understanding of the factors driving regional long-term patterns of DOC loss.

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