Using High-Frequency Sampling to Detect Effects of Atmospheric Pollutants on Stream Chemistry

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Abstract

We combined information from long-term (weekly over many years) and short-term (high-frequency during rainfall and snowmelt events) stream water sampling efforts to understand how atmospheric deposition affects stream chemistry. Water samples were collected at the Sleepers River Research Watershed, VT, a temperate upland forest site that receives elevated atmospheric deposition of pollutants such as nitrogen (N) and mercury (Hg). Our use of high-frequency sampling documents responses of nutrients and mercury in streamflow to atmospheric deposition inputs to the watershed.

Keywords: atmospheric deposition, dissolved organic matter, mercury, nitrogen, Sleepers River Research Watershed, stream chemistry

Introduction

Routine surface water sampling schemes provide baseline information to elucidate the effects of ecological disturbance. In the northeastern United States, one disturbance that affects forests is chronic atmospheric deposition of pollutants. Emissions from sources including power plants, vehicles, agriculture, and industry can be transported and dispersed over large areas to blanket even the most pristine forests (Driscoll et al. 2003, Driscoll et al. 2007). Many long-term watershed studies assess trends and the effects of ecological disturbances by measuring stream water chemistry at fixed intervals (weekly, monthly, or quarterly). Here we demonstrate that additional high-frequency sampling may yield important information that is needed to discern both short- and long-term effects of atmospheric deposition on biogeochemical transformations and solute transport in watersheds.

Surface water chemistry varies over time and space in response to complex biogeochemical and hydrological processes. In temperate forest environments, hydrological flushing of solutes along subsurface and surface flow paths during storm events links source areas of the landscape to stream chemistry (Creed et al. 1996, Boyer et al. 2000, Burns 2005). As such, atmospherically-deposited pollutants that accumulate in surficial soils may be exported from watersheds during stormflow (Sebestyen et al. 2008). This hydrological flushing of solutes is an example that highlights a need to better understand when, where, and how atmospherically-deposited pollutants cascade through biogeochemical cycles to affect solute availability and transport.

We give examples from the Sleepers River Research Watershed that highlight the importance of linking routine weekly sampling with intensive, high-frequency sampling to discern sources, transformations, and transport processes that affect the variation of stream solutes (nitrate, mercury, and dissolved organic matter) that are affected by atmospheric deposition.

Methods

Stream water samples were collected from 2002 to 2005 at watershed 9 (W-9) of the Sleepers River Research Watershed, one of five sites in the U.S. Geological Survey (USGS) Water, Energy, and Biogeochemical Budgets program (Figure 1). The 40.5-ha, steep watershed has a mixed northern forest cover and is typical of upland forests in mountains of the

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northeastern United States. The soils are derived from glacial tills that overlie metamorphic bedrock. The climate is temperate with warm humid summers and cold winters during which snow accumulates in a seasonal snowpack.
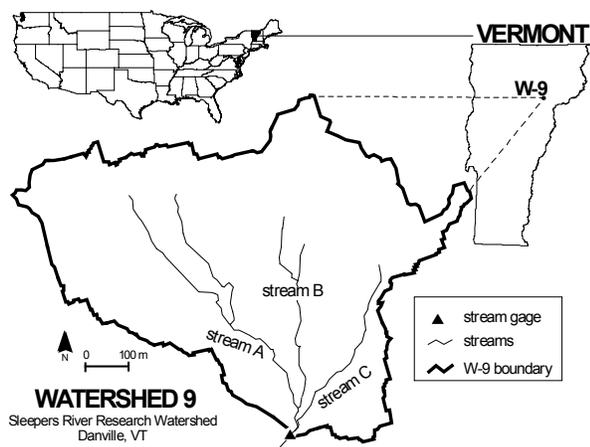
Figure 1 . The location of W-9 at the Sleepers River Research Watershed in northeastern Vermont, United States.

Stream stage was measured every five minutes at a 90° V-notch weir and streamflow was calculated from a stage-discharge relationship. Samples of W-9 stream water were collected weekly and more frequently during stormflow, often using an ISCO automatic sampler to collect samples at intervals ranging from minutes to hours to days depending upon the timing and magnitude of streamflow changes. We also measured isotopic and chemical tracers in precipitation, groundwater, and soil water on an event basis. Samples were collected, processed, and analyzed according to standard methods that are detailed elsewhere for nitrate and dissolved organic carbon (DOC) concentrations (Sebestyen et al. 2008) and total and methylmercury (Hg) concentrations (Shanley et al. 2008). We apportioned nitrate sources for a subset of the samples using hydrochemistry, isotopic tracers, and end-member mixing analysis as detailed in Sebestyen et al. (2008).

Results and Discussions

High-frequency sampling generates large numbers of samples and is both labor and resource intensive but yields insights on the effects of atmospheric deposition on ecosystem functions and stream chemistry that are not readily discerned from sparser sampling.

Throughout the northeastern United States, atmospheric N deposition has affected soil N status, biological cycling, and stream nitrate concentrations (Aber et al. 2003). At W-9, the average total N input from 1978 to 1998 of 13.2 kg ha^{-1} y^{-1} (Campbell et al. 2004) is among the highest in the nation. Understanding the direct effects of N deposition on stream chemistry is complex because biological cycling retains N in organic matter and may re-emit N species back to the atmosphere via nitrification and denitrification. Additionally, atmospheric N deposition affects soil N status which has an indirect effect when N from atmospheric sources cascades through organic matter pools is subsequently nitrified in catchment soils and is then transported to streams.
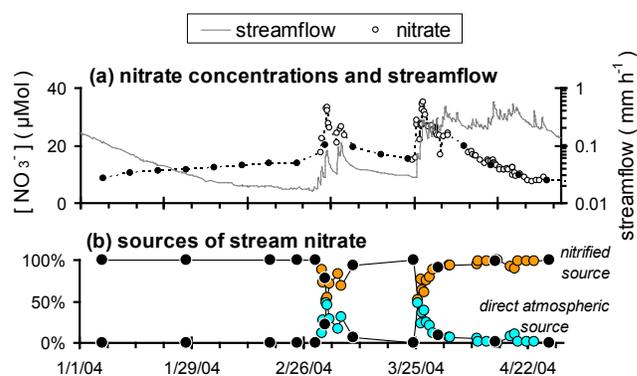
Figure 2. Stream nitrate concentrations at W-9 (A) and source apportionment (B) during winter and spring snowmelt 2004. The weekly-only samples are shown by the solid black symbols.

For atmospheric nitrate to directly affect streams, the atmospheric deposition must have a high concentration and the atmospherically-deposited nitrate must be rapidly transported through a watershed to a stream without being retained or biologically processed. High-frequency hydrochemical and isotopic data are needed to apportion how direct atmospheric sources affect stream nitrate loadings (Kendall et al. 2007). Recently, high-resolution temporal sampling has shown that the direct transport of atmospheric nitrate to the W-9 stream during spring snowmelt events has pronounced effects that were not previously quantified and that a fraction of the atmospheric nitrate inputs may be exported from watersheds without being transformed or retained by biological uptake (Ohte et al. 2004, Sebestyen et al. 2008). For example, direct atmospheric contributions as large as 49 percent at peak concentration during spring snowmelt mixed with a soil nitrified source that was flushed to the W-9 stream during stormflow (Figure 2).

During snowmelt, samples were often collected daily or at shorter intervals ranging from tens of minutes to hours. With only weekly data (solid black circles in Figure 2), the direct contribution of atmospheric nitrate to stream waters may have been missed.
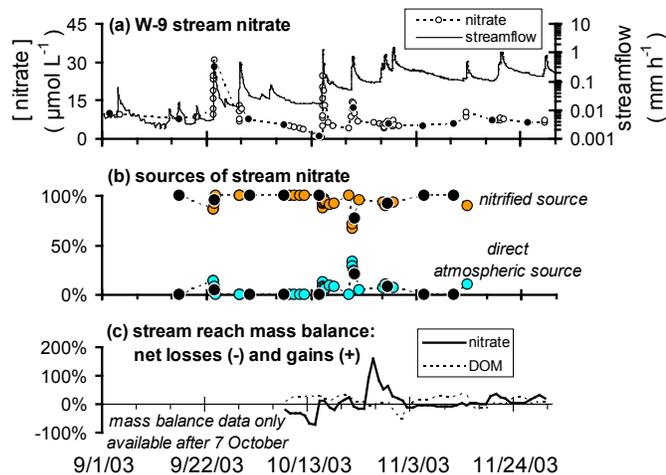

Figure 2. Nitrate concentrations (A), apportioned sources of stream nitrate (B), and nitrate and DOC losses and gains in the stream reach (C) at W-9 during autumn 2003. Weekly samples are indicated with solid black symbols.

High-frequency sampling during autumn revealed direct atmospheric contributions to the stream as large as 30 percent during stormflow (Figure 3)—another example of the effects of atmospheric deposition on stream chemistry that differs from base flow conditions. During base flow, stream nitrate originated from a nitrified source showing that the N had been microbially processed in the ecosystem (Figures 2, 3). Dynamics of nitrogen cycling may also be revealed with high-frequency samples. For example, litter inputs increase dissolved organic matter (DOM) concentrations and bioavailability in streams during autumn (Meyer et al. 1998) and should affect the cycling of stream nitrate. With daily samples, we detected transformations during base flow that were a seasonal response to the changing availability of nutrients during leaf fall. A mass balance shows up to 70 percent net retention of nitrate and the net production of dissolved organic carbon in a stream reach between the W-9 gage and the three upstream tributaries during base flow. The instream losses of nitrate and production of DOC show a "hot moment" of biogeochemical transformations that may not have been detected with weekly-only samples while the transport of atmospheric nitrate to streams shows the importance

of high-frequency sampling during short-duration stormflow events.

Large stormflow events, such as spring snowmelt, significantly contribute to the annual stream nitrate budget and the direct yield of nitrate from an atmospheric source is only a small fraction of the stream nitrate budget (Sebestyen et al. 2008). Between January and April the direct yields from atmospheric sources were 7 percent in both 2003 and 2004 (Figure 4). However, these small quantifiable yields provide an important baseline from which to assess future effects of nitrogen pollution on upland forested watersheds where atmospheric nitrogen deposition is chronic.
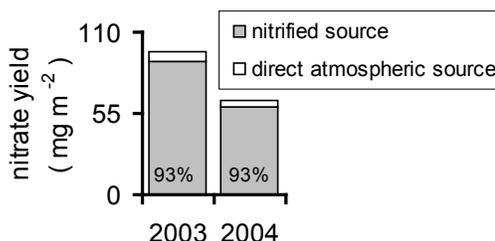

Figure 3. Isotopically apportioned nitrate yields from 1 January to 30 April show that 7 percent of the total stream nitrate originated directly from atmospheric nitrate deposition in both 2003 and 2004.

Like N deposition, the effects of Hg deposition are widespread in the northeastern United States (Driscoll et al. 2007). Mercury inputs accumulate in soils and are transported to surface waters. At Sleepers River, the average annual total Hg deposition is 25.1 $\mu g\ m^{-2}$ (Shanley et al. 2008). At W-9, Hg concentrations exponentially increase during stormflow (Schuster et al. 2008) and elevated Hg fluxes during stormflow dominate the annual budget (Shanley et al. 2008). For example, after seven weeks of dry conditions, Hg was flushed to the stream during an intense rain storm on 15 September 2002 (Figure 5). Because stream Hg concentrations consistently increase during stormflow, Hg export is highly episodic throughout the year and fluxes of total and methyl Hg would be grossly underestimated if events were ignored (Shanley et al. 2008). Furthermore, Hg export is tightly coupled with DOM export (Shanley et al. 2008) which provides another example of coupled element cycles and pollutant transport to streams.

Linkages between DOM and other solute dynamics highlight a need to quantify DOM flushing from catchment soils to streams. Throughout northern North America and northern Europe, stream DOM

concentrations and loadings have increased in many ecosystems where drivers of environmental change such as pollutant inputs via atmospheric deposition and climate change affect northern forests (Goodale et al. 2005, Monteith et al. 2007).
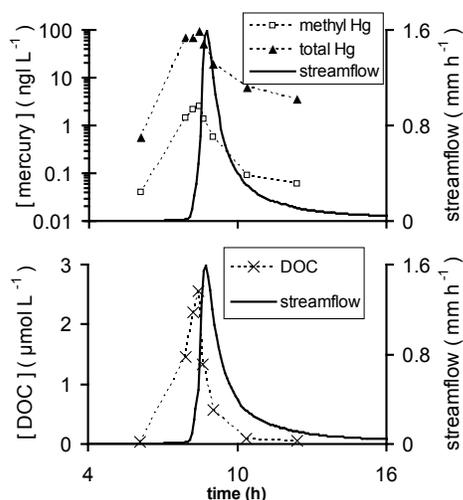

Figure 5. Increased total and methyl Hg concentrations during the 15 September 2002 storm reflect a legacy of atmospheric Hg deposition in watersheds. Note the log scale on the mercury concentrations. Increased Hg concentrations are highly associated with DOC that is flushed to streams during stormflow events.

Annual nutrient budgets show that large amounts of water, nitrate, DOM, and Hg are exported from catchments during infrequent but large stormflow events (Figure 6). This flow-stratified distribution of water and solute fluxes suggests that rapid and large magnitude transport to streams during stormflow is important.

If the climate of the northeastern United States changes consistent with projections (Hayhoe et al. 2007), we hypothesize that DOM transport to streams will increase because the frequency of large magnitude storm events is expected to increase. Because DOM is related to both nitrate and Hg, increased DOM fluxes will affect the hydrological flushing of Hg as well as the cycling, availability, and export of nitrate.

Implications for Watershed Studies

Targeted high-frequency hydrochemical sampling provides basic information that is needed to assess stream solute responses to drivers of environmental change such as atmospheric deposition and climate

change that affect forested watersheds. Examples from the Sleepers River Research Watershed illustrate how high-temporal resolution sampling in small watershed studies can be used to elucidate effects of atmospheric pollutants on stream chemistry while providing valuable information to inform land managers and environmental regulators. This sampling approach may increase our understanding of how atmospheric pollutants accumulate and flow through forested watersheds, especially as new hydrochemical and isotopic tracing techniques become available.
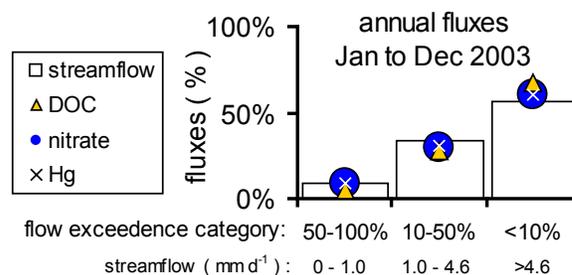

Figure 6. Large magnitude fluxes of water, nitrate, Hg, and DOC occur during short periods of high stormflow (i.e., the flows that are exceeded less than 10 percent of the time).

Acknowledgments

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