Watershed hydrology and dissolved organic matter export across time scales: minute to millennium

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Abstract: Ecological theory emphasizes headwater streams and wetlands as hotspots for metabolism of terrestrially derived organic matter and biogeochemical transformations. Growing evidence indicates that freshwater ecosystems may be as important as terrestrial and marine environments in the annual flux of CO_2 to the atmosphere. The National Ecological Observatory Network (NEON) and the Stream Ecological Observatory Network (STREON) offer the opportunity to collect and analyze data related to these processes at spatial scales ranging from local to continental and at temporal scales from minutes to millennia. These data can be used to understand how global climate change and subsequent shifts in terrestrial plant communities and precipitation regimes will influence the export and composition of dissolved organic matter (DOM) to headwater streams, downstream freshwater ecosystems, and coastal environments. Moreover, temporal scaling of DOM export among watersheds is an underexploited frontier research area throughout the earth sciences. Long-term, high-frequency fluorometry and discharge data sets collected at NEON and STREON observatories could be linked to evaluate, quantify, and forecast DOM export among watersheds and across time scales ranging from individual hydrologic events to decadal changes in precipitation regimes.

Key words: NEON, STREON, organic matter export, fluorometry

Watershed-scale hydrological events trigger releases of terrestrial dissolved organic matter (DOM) into headwater streams and drainage networks, thereby mobilizing DOM to downstream ecosystems geographically removed from its source of origin. Terrestrial DOM exported from forested headwaters can govern heterotrophic activity in receiving lakes, rivers, reservoirs, and estuaries, and release nutrients that stimulate aquatic primary production (Vannote et al. 1980, Findlay and Sinsabaugh 2003, Tank et al. 2010). Terrestrial DOM export is controlled in part by annual precipitation, episodic hydrologic events, soil properties, and forest community composition (Mulholland 1997, McClain et al. 2003, Roberts et al. 2007). Thus, DOM export from temperate and boreal region watersheds may be especially sensitive to global climate change (Campbell et al. 2009, Pellerin et al. 2012, Grimm et al. 2013).

Watershed DOM export and biogeochemistry also have important implications for applied freshwater science. Terrestrially derived DOM affects the efficiency of drinking-water treatment, and its presence can lead to the formation of potentially harmful by-products of disinfection (Garvey and Tobiason 2003, Volk et al. 2005). Complexation reactions with terrestrial DOM influence the fate and transport of a variety of hazardous pollutants, such as hydrous aluminum. DOM concentration and geochemistry also influence stream-water pH, light absorbance, and photoreactions, and the cycling of Hg (Wetzel 2001). Knowledge of the mechanisms that control the flux and composition of terrestrial DOM is requisite to managing public water supplies and accompanying watersheds (Kaplan et al. 2006).

The Achilles' heel of DOM-export science has long been inadequate temporal resolution in measurements of DOM concentration and composition relative to estimates of stream discharge. The mismatch in data resolution and duration between stream DOM chemistry and discharge

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often has relegated quantification of DOM export to an exercise in hydrology. However, DOM export is a biogeochemical variable that may become more precise, quantitative, and useful with advances in fluorescent DOM (fDOM) probe technology. These advances already are transforming the study of DOM export in flashy headwater streams by extending and resolving traditional storm sampler data and greatly increasing the number of storm events that can be characterized (Sebestyen et al. 2009, Pellerin et al. 2012, Wilson et al. 2013). Recent advances in high-frequency stream-probe technology now enable DOM concentration to be estimated continuously and accessed remotely in a manner analogous to stream discharge.

The overarching objective for this article is to highlight emerging research opportunities in the quantification and application of watershed DOM export offered by the National Ecological Observatory Network (NEON) and the Stream Ecological Observatory Network (STREON) (see also Goodman et al. 2015, McDowell et al. 2015). Here we share ideas and lessons learned from a case study of a small, forested watershed to show the utility and value of sustained, high-resolution fluorometrically detected DOM (fDOM) export data for a diversity of environmental research areas. More broadly, we envision how a growing network of watershed DOM export stations can be used collectively to help document, quantify, and understand regional and continental responses to global climate change.

BIGELOW BROOK WATERSHED: CASE STUDY

We begin by describing a site-specific study to illustrate immediate and potential long-term scientific benefits of establishing a DOM export station and record. Bigelow Brook is a tributary of the East Branch of the Swift River that drains into the Quabbin Reservoir, the public water supply for ~2.5 million Boston-area residents. Bigelow Brook drains a small, forested watershed in north-central Massachusetts and has served as an ecological proving ground for estimating DOM export (see Wilson et al. 2013). Its biota, geomorphology, and riparian zone are described elsewhere (Collins et al. 2007, Willacker et al. 2009). The watershed's upland forest contains diverse late-successional deciduous species, and the riparian zone is dominated by eastern hemlock (*Tsuga canadensis* L.) that has old-growth characteristics (D'Amato et al. 2006). Bigelow Brook was the first Core Aquatic NEON site to enter operations, largely because of the long-term forest eddy–flux and plot experiments at the surrounding Harvard Forest Long-Term Ecological Research (LTER) site. Eddy–flux towers in or near the watershed record atmospheric H_2O vapor and CO_2 exchange hourly, and a >20-y record of forest–atmosphere C and H_2O flux already exists for this site.

We used high-frequency fluorescence and discharge data (15-min intervals) from a single station and additional water-chemistry data to quantify annual DOM export from Bigelow Brook and to hypothesize mechanisms that could account for seasonal and hydrologic-event variation in export (Wilson et al. 2013). Quantification of annual DOM export from the Bigelow Brook watershed provided missing forest C-budget data and revealed ecologically relevant patterns in discharge and DOM: 1) DOM concentration was as flashy as discharge, but was rarely in phase with discharge; 2) seasonal patterns of DOM concentration and discharge were independent; 3) DOM concentration spikes were not muted by successive storms; 4) annual DOM export was characterized by surprisingly short time intervals of high discharge coupled with high DOM concentration, and 5) the relative strength of this additive effect varied with season (Wilson et al. 2013). We also found evidence for watershed-specific relationships between DOM and bioavailability (estimated in bioassays), and DOM and dissolved organic N. Thus, improved estimates of DOM flux could yield information on DOM lability and composition.

As with any case study, our ability to generalize based on our site-specific annual DOM export patterns is inherently limited. However, the Bigelow Brook case study is an example of how synchronized, high-resolution DOM export and discharge can reveal previously unseen watershed hydrology and ecosystem properties. The full potential scientific value of the Bigelow Brook DOM export record will be realized only within the context of a network of watersheds that vary in their geographical, physical, and ecological properties.

CHALLENGES AND OPPORTUNITIES PROVIDED BY NEON AND STREON

Methods and global networking

NEON and STREON offer the opportunity to create a continental network of sites with the instrumentation capable of providing high-frequency measurements of fluorometrically detected DOM (fDOM) over a long time period, but this opportunity comes with challenges. High-frequency measurements of fDOM require appreciable instrument oversight and calibration if the data are to be converted to reliable, continuous DOM concentrations (Osburn et al. 2013). Moreover, the relationship between fDOM and traditional DOM (i.e., measured with high-temperature combustion) can shift seasonally and during hydrologic events. Thus, accurate measurement of DOM fluxes requires routine and storm-derived collections of grab samples (see appendix 1 supplemental material by Wilson et al. 2013). Other dissolved and suspended constituents can interfere with fluorescence measurements and must be accounted for in certain ecosystems (Saraceno et al. 2009, Cohen et al. 2013), and many probes are temperature sensitive and require temperature calibration (Downing et al. 2012, Wilson et al. 2013). Last, use of fDOM rather than ultraviolet (UV)-detected DOM (CDOM) in Bigelow Brook improved estimates of low DOM concentrations, but many DOM molecules are undetected by both approaches. Moreover, quality control of fDOM measurements and reliable transformation to DOM (analogous to the laborious construction of stage height vs empirical discharge rating curves) is a major challenge for the freshwater sciences.

Rapid advances in optical-probe technology offer promising new tools for freshwater and watershed scientists. However, effective use of these probes requires investment in ancillary research and knowledge of the ecosystem in which they are deployed (Fellman et al. 2010). A poignant quote from the organic geochemist George Aiken that should be emblazoned on every environmental DOM-probe is "know your system" (see Osburn et al. 2013). Based on our personal experiences at Harvard Forest, the new generation of aquatic probes complement, but do not replace, traditional grab-sample methods. Thus, establishment of fixed monitoring locations will require guiding objectives, sustained commitment, and explicit data-management and -sharing plans (Lovett et al. 2007). Standardized methods, strategic site coordination and networking, and excellent scientific leadership are paramount to establishing a useful global network of long-term DOM-export stations (Spencer et al. 2013, Weathers et al. 2013, LINX Collaborators 2014, McDowell 2015).

Scientists working with NEON, in conjunction with those at other more established networks (e.g., Arctic Great Rivers Observatory, US Geological Survey Water Resources, Global Lake Ecological Observatory Network), can play an integral role in this enterprise by championing several tenets for advancing global environmental science: 1) build inclusive national and international collaborations (Weathers et al. 2013), 2) promote multidisciplinary interaction and scientific team-building (Likens 1998), 3) contribute to standard method development (Osburn et al. 2013), 4) seek collaboration and cross-fertilization with computer scientists and statisticians advancing 'big data' analysis and management (Soranno and Schimel 2014), and 5) foster strategic education and training opportunities for graduate students, early career scientists, and professional communities (LINX Collaborators 2014).

DOM export and temporal scaling

Freshwater scientists face the challenge of identifying the appropriate spatial and temporal scales at which to address research questions (Goodman et al. 2015). Watershed hydrologists and biogeochemists conduct research at a wide range of spatial scales ranging from soil cores to continents. This spatial scaling has been central to the rapid maturation of these disciplines (e.g., Mulholland et al. 2008, Schlesinger and Bernhardt 2013), and freshwater ecologists have made important theoretical and empirical advances in understanding watershed organic C cycling across this range of spatial scales (e.g., Vannote et al. 1980, Fisher et al. 1998, Tank et al. 2010). Watershed scientists also have long valued temporal perspective (e.g., Likens and Bormann 1995, Hobbie et al. 2003, Williamson et al. 2009, LINX Collaborators 2014), and noteworthy advances in stream disturbance ecology (Stanley et al. 2010), stream biogeochemistry–climate change research (Campbell et al. 2009), watershed–stream metabolism (Roberts et al. 2007), Arctic-river biogeochemistry (Holmes et al. 2008), and global lake environmental monitoring (Weathers et al. 2013) unequivocally show the critical importance of temporal scaling to understanding watershed C cycling. However, we contend that watershed science has not yet achieved the level of maturation across temporal scales ranging from minutes to millennium as the level reached across comparable spatial scales.

Stream optical-sensor technology, combined with traditional stream discharge, provides an opportunity for watershed scientists to better resolve, quantify, and forecast DOM export at a wide range of time scales and will support research among diverse disciplines (e.g., hydrology, terrestrial ecology, stream biogeochemistry). Like stream-discharge data, DOM-export data collected and analyzed at the hydrologic-event, seasonal, annual, and decadal time scales will be useful to many basic and applied environmental scientists. High-quality DOM-export data could be used to address many questions including: 1) How does variation in the intensity, duration, and timing of major hydrologic events (e.g., hurricanes) influence watershed DOM export? 2) What watershed properties and land uses dampen, accelerate, and geochemically modify DOM export? 3) How will the acceleration of permafrost melt contribute DOM to Arctic streams, lakes, and rivers? 4) How can public water supplies be managed optimally in regard to watershed protection and water transfers to minimize DOM concentration and undesirable compositional attributes?

POTENTIAL USES OF WATERSHED-SCALE DOM EXPORT DATA

Watershed-scale DOM export is an underexploited integrative metric. We provide specific examples to illustrate how DOM export data could be used to inform disparate questions in watershed science at a range of time scales from minutes to decades (Fig. 1A–C). The main purposes of this discussion are to: 1) help those new to these data sets better appreciate the varied temporal frames that could be applied to a variety of problems and questions in environmental science, and 2) spark ideas for creative, strategic, and more widespread application of these data sets throughout the freshwater science community. A temporal continuum of DOM export provides tremendous flexibility and, thus, enables watershed managers and scientists to explore patterns and parcel data to best address individual research needs (Fig. 1A–C).

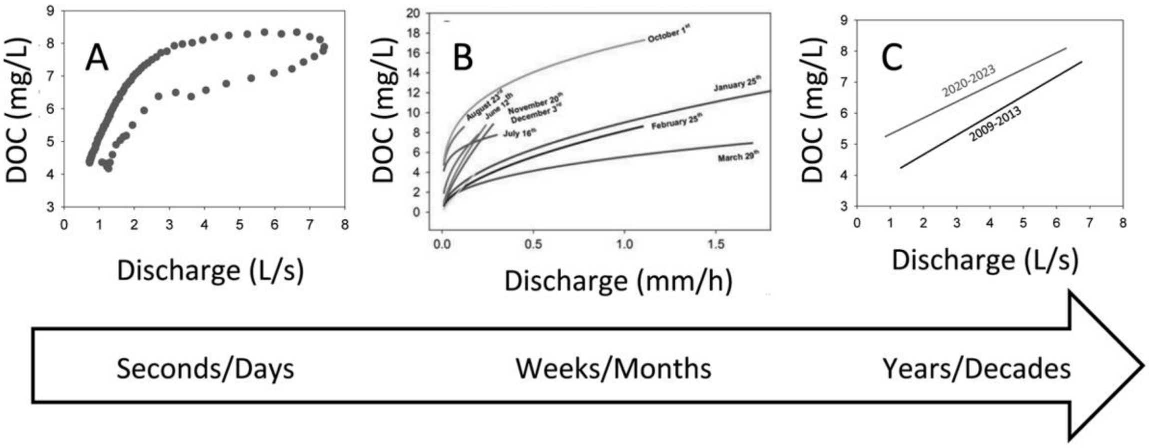

Figure 1. General conceptual model to illustrate how continuous, high-frequency dissolved organic C (DOC) concentration and discharge estimates may be used to inform disparate watershed-science questions at time scales ranging from minutes to decades. Here we provide 3 examples of research questions that are conducted at disparate time scales: A.—How does stream dissolved organic C (DOC) concentration vary during a single precipitation event? B.—Are there seasonal differences in how forests export DOC? C.—Do shifts in forest community composition in response to global climate change alter watershed DOC export?

DOM export can inform terrestrial ecology

Net ecosystem metabolism (NEM) of many terrestrial ecosystems is often close to being balanced at annual and decadal time scales. Therefore, fluvial loss of materials to streams may be an important, but overlooked, term in estimates of terrestrial organic matter and nutrient stocks (Cole et al. 2007). N lost from N-limited forests can be dominated by dissolved organic N and sensitive to high-discharge events (Hedin et al. 1995, Neff et al. 2003, Martin and Harrison 2011). This situation highlights the importance of quantifying and understanding dissolved organic matter export from many watersheds. Climate change and accompanying shifts in regional precipitation patterns are predicted to alter temperate forest NEM, growth, and fire frequency, but these changes will be heterogeneous and will occur over decadal time frames (Grimm et al. 2013). DOM export may be a sensitive and integrative metric for documenting climate-induced changes and could serve as a diagnostic tool to help interpret long-term changes in forest NEM, nutrient limitation, and fire resilience. From this perspective, stream DOM export and biogeochemistry provide information on basic terrestrial ecology that cannot be generated readily from plant-community surveys, experimental-plot studies, or soil-core analyses (see Likens and Bormann 1995, Menge et al. 2009).

Many terrestrial ecosystems have experienced loss of plant diversity, including foundational species, because of the spread of invasive pests and pathogens worldwide (Ellison et al. 2005, Lovett et al. 2006). Climate change is increasing the susceptibility of several North American biomes to invasive species; and, in some cases, these invasions may become key drivers of terrestrial ecosystem processes over the next several decades (Grimm et al. 2013). Eastern North American forests provide an example of foundational species loss caused by an invasive pest. A dominant conifer, eastern hemlock (*Tsuga canadensis*), is being killed by an exotic insect (hemlock-woolly adelgid) and replaced by deciduous trees (Orwig et al. 2011). These regional forest community changes occur over decadal time scales and affect soil decomposition and biogeochemistry (Stadler et al. 2006). More broadly, plant litter decomposition is a fundamental ecosystem process that is sensitive to exotic species invasions and accompanying shifts in plant communities and invertebrate consumers (Gessner et al. 2010, Lecerf et al. 2011). Thus, DOM export may serve as a valuable tool to help quantify and forecast terrestrial ecosystem responses to invasive species.

DOM export responds to episodic hydrologic events

Previous investigators have documented a rise in DOM concentration in streams and rivers with snowmelt (e.g., Boyer et al. 1997, Holmes et al. 2008) and have established the important influence of episodic hydrologic events on annual DOM export (Ciaio and McDiffett 1990, Inamdar et al. 2011). Global climate-change models predict acceleration of the hydrologic cycle and a shift to more large events (Palmer and Räisänen 2002, IPCC 2013). Empirical evidence is mounting that this shift is already underway in parts of the planet (Groisman et al. 2004, Raymond et al. 2008). Authors of recent studies have stressed the important effects of intense hydrologic events on DOM export and have suggested that terrestrial DOM export may be increasing in parts of the eastern USA (Sebestyen et al. 2009, Yoon and Raymond 2012). Thus, land-derived DOM subsidies to freshwater and coastal ocean ecosystems may strengthen under anticipated global climate changes to temperate-zone weather patterns (IPCC 2013). A secondary climate control on temperate-watershed DOM transfers is annual increase in temperature. In several studies from temperate regions, DOM concentrations were higher during warmer seasons, even after controlling for discharge (Raymond and Saiers 2010, Strohmeier et al. 2013, Wilson et al. 2013). The underlying mechanisms for this relationship are unclear, and probably include a combination of biogeochemical (e.g., higher rate of dissolution) and forest-ecosystem responses to higher temperature (e.g., extension of growing season, increased decomposition, and changes in leaf-litter dynamics). These recent findings suggest that increased temperature might interact positively with changes in intensity of hydrologic events to further accelerate continental DOM transfers to oceans. Watershed-DOM export studies (both empirical and modeling) that integrate variable and dynamic hydrological, biogeochemical, and ecological processes at a range of spatial (sensu Mulholland et al. 2008) and temporal scales (sensu Roberts et al. 2007) should be promoted throughout the environmental sciences.

Increases in terrestrial DOM export to fluvial networks and coastal zones probably will be accompanied by significant compositional changes (Spencer et al. 2013). For example, DOM aromaticity and humic content increase with DOM concentration (Fellman et al. 2010, Inamdar et al. 2011), potentially resulting in a greater photoreactivity in coastal waters after large, continental discharge events. In recent studies of both temperate and boreal watersheds, investigators have shown that relative biolability increases with hydrologic events (Roberts et al. 2007, Holmes et al. 2008, Mann et al. 2012, Wilson et al. 2013). Thus, the proportion of reactive DOM also may increase under likely global climate-change scenarios that spike increases in river discharge. Arctic watersheds may be especially vulnerable to rapid increases in labile DOM export as the result of melting permafrost (Holmes et al. 2008, Mann et al. 2012). Studies of river DOM geochemistry (Spencer et al. 2013), microbial ecology (Mann et al. 2014), and CO_2 efflux (Butman and Raymond 2011) are essential to understand the fate of terrestrial DOM export.

Opportunities at the frontier of freshwater science

Understanding global C cycling will require advances in knowledge of how terrestrial and marine environments are linked by continental drainage basins. Recognition is growing that freshwater DOM-cycling processes may be as important as terrestrial and open-ocean processes, but great uncertainty remains about how increases in the intensity of event-driven discharge in headwater streams regulates the export (and composition and reactivity) of DOM to downstream freshwater and estuarine ecosystems. Long-term, high-frequency DOM and discharge data sets can be used strategically to evaluate such changes quantitatively. Hydrologic events serve as "hot moments" for loss of DOM, DOM-bound nutrients, and DOM-associated pollutants (McClain et al. 2003). However, the factors affecting these processes remain poorly understood. Temporal scaling of DOM export is an underexploited, frontier research area throughout the environmental sciences, and probably will yield major advances in our understanding of terrestrial, freshwater, and marine ecosystems at all spatial scales. Furthermore, global climate change will influence the characteristics of regional hydrologic events and precipitation patterns throughout the planet, thereby altering watershed biota, biogeochemistry, and hydrology in highly variable ways (Grimm et al. 2013). Terrestrial DOM export and accompanying transformations in the continents' fluvial networks and freshwater ecosystems must be examined across spatial and temporal scales and viewed as an integral and highly dynamic component of the global C cycle.

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