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Quantity and composition of stream dissolved organic matter in the watershed of Conesus Lake, New York

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ABSTRACT

Dissolved organic matter (DOM) is a complex mixture of soluble organic compounds that plays important roles in stream ecosystem function. We examined temporal and spatial variation in stream DOM characteristics in the small watersheds draining into Conesus Lake, New York, USA. While all watersheds were impacted by human activity, our study sites spanned multiple land uses, with distinct differences in the proportion of agriculture and natural land cover. Concentrations of dissolved organic carbon and inorganic and organic nitrogen and phosphorus were measured seasonally, with a more detailed analysis during the growing season. DOM composition was assessed with a suite of optical indices and multidimensional fluorescence with parallel factor analysis. Seasonal shifts in the composition and quantity of DOM, characterized by increased protein-like fluorescence in the growing season and maximum DOC concentrations in the fall, were consistent with abiotic seasonal controls and the seasonal influx of allochthonous organic matter to all streams. However, agriculturally dominated streams had higher inorganic nutrients, along with less-humified, less-molecularly complex, and more protein-like fluorescent DOM than those with less agriculture, suggesting that nutrients may be stimulating greater in-stream DOM production. Stream order also played a strong role, with more similarity in the DOM pools in second order streams, consistent with high in-stream processing of both allochthonous and autochthonous DOM. We conclude that agriculture is an important driver of stream water nutrients and the quantity and composition of DOM, in conjunction with abiotic seasonal drivers and in-stream processing time.

Introduction

Human land use alters the biogeochemical cycling of C, N, and P in headwater stream systems. Groundwater, streams, rivers, and lakes typically have increased inorganic nutrient and dissolved organic matter (DOM) concentrations in catchments with heavy agricultural land use leading to impairment of water quality (Carpenter et al., 1998; Mattsson et al., 2009; USEPA, 2013; Williams et al., 2010). The dynamics of inorganic nutrients in stream ecosystems have been well studied, but much less is known about the role of DOM in the observed declines in water quality (Graeber et al., 2012). DOM, a complex mixture of organic compounds from both allochthonous and autochthonous sources, plays important chemical, biological, and physical roles in aquatic ecosystems (Sinsabaugh and Findlay, 2003). As such, measures of the quantity and composition of DOM are increasingly recognized as significant water quality parameters (Stedmon et al., 2003), and studies of the spatial and temporal dynamics of DOM in streams provide valuable information and insight into the effects of anthropogenic modification of stream catchments on stream ecosystems and their receiving waters (Fellman et al., 2010).

In temperate streams, a large proportion of DOM may be supplied allochthonously, with both quantity and composition reflecting terrestrial sources (e.g. Cory et al., 2011; Fellman et al., 2010; Williams et al., 2010). Lignin and tannin derivatives, the degraded structural components of plants, accumulate in the organic horizon of the soil and are transported to aquatic ecosystems through advective transport in surface and ground waters (Aitkenhead-Peterson et al., 2003; Kalbitz et al., 2000). This flux is mediated by a variety of factors such as soil microbial activity, soil composition and pH, land cover/land use, topography, UV light exposure, precipitation, temperature, and nitrogen and sulfur deposition (Pagano et al., 2014; Roulet and Moore, 2006). In general, DOM of terrestrial origin is structurally complex and composed of aromatic, high molecular weight compounds such as humic and fulvic acids (Williams et al., 2010). These compounds are subject to photochemical transformations (Helms et al., 2014) and can be utilized by bacteria to varying extents (Amon and Benner, 1996), so their

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persistence in water can vary in duration depending on varying ecosystem functions. Overall, changes in land use surrounding a stream ecosystem can influence the quantity and composition of stream DOM through alterations in terrestrial loading and by influencing DOM processing rates and in situ production (Williams et al., 2010).

Where light and nutrient availability are high, autochthonous DOM production may be substantial in streams (e.g. Lutz et al., 2012; Miller et al., 2009; Royer and David, 2005). DOM produced in situ by microbes, algae, and macrophytes is released into the environment by predatory grazing, “sloppy feeding,” cell death and senescence, cell lysing, excretion, and extracellular release from active cells (e.g. Bertilsson and Jones, 2003; Bratbak et al., 1994; Fuhrman, 1992; Gergel et al., 1999; Tyler et al., 2003). This DOM consists mainly of colorless, low-molecular-weight, chemically labile compounds that may quickly stimulate microbial growth (e.g. Guillemette and del Giorgio, 2011; Persson, 1997; Vanni and Layne, 1997). Because of this rapid cycling, autochthonous DOM constitutes an important component of the standing DOM pool in natural waters (Gergel et al., 1999). In streams with high C, N, and P availability, heterotrophic metabolism may enhance autochthonous DOM production (Forsstrom et al., 2013) leading to downstream eutrophication as these nutrients are later released by microbial decomposition (Mattsson et al., 2005). Additionally, predicted warmer temperatures and increased precipitation associated with climate change may further enhance nutrient and DOM exports from watersheds (Carpenter et al., 1998; Pagano et al., 2014; Porcal et al., 2009), which, when combined with changes in land use, can have a negative impact on the quality of surface waters.

While the importance of DOM to streams and receiving waters is recognized, our understanding of land use influence on DOM composition is less thorough because characterization of individual constituents of the DOM pool remains challenging. Spectroscopic analyses, such as fluorescence excitation–emission matrix (EEM) spectroscopy combined with advanced chemometric techniques that exploit the optical properties of DOM can provide information about DOM source and ecological reactivity (Cory et al., 2011; Pagano et al., 2012). The use of EEM–PARAFAC techniques to characterize DOM in both pristine and anthropogenically modified systems has the capacity to greatly enhance our understanding of land use influence on the quality of DOM in stream ecosystems (e.g. Fellman et al., 2010; Matson et al., 1997; McKnight et al., 2001; Pagano et al., 2012; Williams et al., 2010; Wilson and Xenopoulos, 2009).

The Finger Lakes are a series of eleven linear, glacially carved lakes in Upstate New York State, USA. The unique topography of these lakes, with their multiple small watersheds with differing land use characteristics (from forested to agricultural to developed), makes them ideal locations for the study of spatial and temporal differences in DOM quantity and composition if we assume that the quantity and quality of DOM will differ between neighboring small-catchments with contrasting land use (Glendell and Brazier, 2014). Conesus Lake, part of the Lake Ontario drainage basin, is the western-most of the 11 Finger Lakes and is arguably the most studied lake in the region. This scrutiny comes, in part, because watershed and shoreline development combined with intensification of agriculture have resulted in a decline in water quality (Makarewicz, 2009; Moran and Woods, 2009; NYSDEC, 2008). In spite of improvements in the watershed and experimental implementation of agricultural best management practices, recovery of the lake has been slow and monitoring continues (Makarewicz et al., 2007; Makarewicz, 2009; Makarewicz et al., 2012; CLWC, 2013). While the relationship between inorganic nutrient loading and water quality in the Finger Lakes is fairly well understood (Makarewicz, 2009), little is known about dissolved organic matter (DOM) inputs, even though DOM contains significant amounts of C, N, and P (Mattsson et al., 2005).. We assessed seasonal variation in DOM in a series of Conesus Lake streams that vary in proportion of agricultural land use and stream morphology (stream-order and slope) to determine if these factors are significant predictors of watershed DOM quantity and quality.

Methods

Site description

The humid climate of the Genesee Valley and western Finger Lakes region of New York is characterized by warm, dry summers and cold, often snowy winters (Makarewicz, 2009). The annual mean daily temperature for the region is 8.4 °C with the coldest mean maximum daily temperatures recorded in February (~0 °C) and the warmest mean maximum daily temperatures recorded in July (~22 °C; SOCL, 2001). Average yearly precipitation is approximately 80.5 cm (Makarewicz, 2009); however, in the spring of 2011 during our sampling the region experienced some of the highest rainfall totals in at least 11 years (CLWC, 2013). For example, the 30 year average precipitation amounts for April and May are 7.5 cm and 8.3 cm, respectively, but in April and May of 2011 the region received 14.7 cm and 12.2 cm, respectively (Hemlock Station, NOAA, 2015). Conesus Lake is located about 40 km south of Rochester, New York, in a broad glacial valley with gently sloping hills in the northern outlet and southern inlet areas, and steeper slopes flanking the eastern and western sides of the lake. The lake has one of the smallest watersheds (167.13 km^2) and is among the shallowest of the Finger Lakes (mean depth 11.6 m). The watershed elevation ranges from 249 m to 549.9 m (Forest et al., 1978). In the southern third of the watershed, steep slopes exceeding 45% flank the lake, restricting agricultural areas to the flatter, more productive northern reach (Makarewicz, 2009). In general, the soils in the watershed are derived from glacially reworked shale and sandstone bedrock and consist predominantly of alfisols and inceptisols (Table 1). The more fertile alfisols soils are concentrated in the north of the basin (Bloomfield, 1978), where the majority of the agricultural activity is also located.

Geospatial analyses

A network of 18 streams and several smaller tributaries surround the lake, and its topology creates well-delineated small watersheds (Forest et al., 1978; SOCL, 2001). We selected 12 of these streams for our study and conducted subwatershed delineation using IDRISI version 15 (Clark Labs, 2006) using 7.5-min digital elevation models (DEMs) for Livingston County, NY and a subwatershed area threshold value of 5000 m^2 (0.5 ha). A flow accumulation model was used with the IDRISI-generated watershed layer to verify stream location and to reclassify small subwatersheds that contributed to a larger stream drainage area. The reclassified image was then imported into ArcMap 10 (ESRI, 2011) for subwatershed land use/land cover (LULC) analysis, soils analysis, and map construction. A 2006 LULC raster image was obtained for Conesus Lake watershed from the National Land Cover Database (NLCD). For this study, the main 15 LULC categories of the 2006 NLCD classification system were reduced into five LULC categories: Agriculture (Pasture/Hay and Cultivated Crops), Forest (Deciduous, Evergreen, and Mixed), Developed (Open, Low, Medium, and High), Wetland (Woody and Emergent Herbaceous), and Other (Open Water, Barren Land, Shrub/Scrub, and Grassland/Herbaceous). As of 2006, the largest proportion of land use within the watershed (~42%) was agricultural, primarily field crops, dairy farming and livestock operations, with the northwestern quadrant of the catchment containing the most active agriculture operations. Other major LULC in the watershed include forests (~24%), developed areas (~7.5%), and wetlands (~2.5%). Land use areas for each subwatershed were determined using the raster calculator in ArcMap 10 (ESRI, 2011).

To determine the effect of agricultural land use on the composition of DOM in the Conesus Lake watershed, we used a categorical approach similar to the Conesus Lake Watershed Project (Makarewicz, 2009). In this study, agricultural streams (AG) were defined as streams with >70% agricultural land use within their catchment, and all other streams were classified as reference streams (REF; Table 1). Catchments