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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

The watershed of Conesus Lake, New York is drained by more than 18 unique streams and several smaller tributaries and has multiple land uses, varying from highly agricultural to primarily wooded, making the lake an ideal study site for analysis of the effects of land use on various water quality parameters. Previous water quality and watershed-health studies at Conesus Lake have focused on the delivery of inorganic nutrients to the lake. We know much less, however, about the effects of watershed land use on the quantity and composition of dissolved organic matter (DOM) exported to the lake. We sought to determine how stream DOM quantity and composition varied with space and time within the watershed during 2011. The concentrations of dissolved organic carbon and inorganic and organic nitrogen and phosphorus were measured seasonally in 7 streams, with a more detailed analysis of water chemistry in 12 streams during the growing season. The composition of DOM entering Conesus Lake was assessed with a suite of optical indices and with fluorescence excitation-emission matrices (EEMs) with parallel factor analysis (PARAFAC), a chemometric technique for the decomposition of characteristic fluorescence peaks. A 4-component PARAFAC model showed one allochthonous, humic-like component (C1), one semi-labile component with allochthonous and/or autochthonous origin (C2), and two autochthonous, protein-like components (C3 & C4). We showed seasonality in the composition and quantity of DOM that is consistent with abiotic seasonal controls and principle components analyses (PCA) suggest that agriculturally-dominated streams are associated with increased nitrate and phosphate, a greater proportion of protein-like PARAFAC components (C3 & C4), and that the DOM tends to be less humified. These results imply that a) seasonal controls on DOM govern the abundance of protein-like DOM and can alter the quantity of bulk DOM, b) agricultural land use may augment autochthonous production in a stream, particularly in the spring and summer, thus creating a more labile pool of DOM that is exported to the lake, and c) stream order can alter DOM quantity and composition, possibly through instream processing and variations in light availability.

Introduction

Stream ecosystems occur at the confluence of land and water and the chemistry of stream waters, particularly the inorganic nutrients and the quantity and chemical composition of dissolved organic matter (DOM), reflects the biogeochemical processes occurring on land (Findlay & Sinsabaugh, 2003). In headwater stream systems, human land-use alters the biogeochemical cycling of C, N and P, and in catchments with heavy agricultural land-use, ground water, streams, rivers and lakes have shown increased inorganic nutrient and DOM concentrations (Carpenter, et al., 1998; Williams, et al., 2010). Indeed, results of the most recent National Water Quality Inventory implicate nutrient inputs from agricultural soils to be the top source of non-point source pollution, responsible for the impairment of nearly 60% of surveyed US rivers and streams (U.S. EPA, 2013). Waters with excess C, N, and P are often impaired by eutrophication and altered water temperature and clarity (Carpenter, et al., 1998; Findlay, et al., 2001). While the dynamics of inorganic nutrients in stream ecosystems have been well-studied, much less is known about the role of DOM, both allochthonous and autochthonous, in the observed declines in water quality (Graeber, et al., 2012).

DOM, a complex mixture of organic compounds from both allochthonous and autochthonous sources, is ubiquitous in freshwater systems where it plays an important chemical, biological, and physical role (Findlay & Sinsabaugh, 2003). 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 in relation to catchment land use and seasonal changes can provide valuable information and insight into the effect(s) of anthropogenic modification of stream catchments on water chemistry (Fellman et al., 2010). Additionally, with impending changes to the global climate, warmer temperatures and increased precipitation may result in increased inorganic nutrient and DOM exports to temperate lakes and their downstream networks (Carpenter, et al., 1998). High C, N, and P availability combined with warmer temperatures have been shown to augment DOM processing rates by bacteria and increase heterotrophic activity in aquatic ecosystems, which can have implications for water quality under future climate conditions (Forsström, et al., 2013).

In temperate streams, the majority of DOM is supplied from allochthonous sources and the quantity and composition of the material reflects the terrestrial plant sources (e.g. Cory et al.,

2011; Fellman et al., 2010; Williams, et al., 2010). Cellulose, lignin, and tannins, the former 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). The flux of DOM from a watershed is mediated by a variety of factors such as soil microbial activity, soil composition, land cover/land use, topography, UV light exposure, precipitation, temperature, and nitrate and sulfate deposition (Roulet & Moore, 2006). In general, DOM originating from the terrestrial landscape is structurally complex and composed of aromatic, high molecular weight compounds such as humic and fulvic acids (Williams, et al., 2010). Due to their complexity, allochthonous DOM compounds are generally recalcitrant in the environment and have limited bioavailability to the microbial community in freshwater systems (Wetzel R. G., 2003). In forested streams where shade limits autochthonous DOM production, microbes do rely on the nutrient subsidy provided by allochthonous DOM, but because of the recalcitrance of allochthonous DOM, many streams in pristine forested areas are largely oligotrophic (Lutz, et al., 2012).

Autochthonous sources of DOM in streams are more important in streams with high light availability (e.g. Royer & David, 2005; Miller, et al., 2009; Lutz, et al., 2012). DOM is produced in-situ by microbes, algae and macrophytes and released into the environment by several different mechanisms, predatory grazing, cell death and senescence, cell lysing, and extracellular release from active cells (e.g. Gergel, et al., 1999; Bertilsson & Jones, 2003). The release of DOM from living cells occurs both actively, through exudation, and passively across cell membranes (e.g. Bertilsson & Jones, 2003; Tyler & McGlathery, 2003). Predatory grazing releases DOM and particulate organic matter, primarily through excretion and "sloppy feeding" by heterotrophic organisms (Bertilsson & Jones, 2003). Cellular lysing and senescence releases internally produced DOM, where all constituents of the cell are released to the surroundings (e.g. Fuhrman, 1992; Bratbak, et al., 1994). Autochthonous DOM consists mainly of colorless, low-molecular-weight, chemically labile compounds that may quickly stimulate microbial growth (e.g. Persson, 1997; Vanni & Layne, 1997; Guillemette and del Giorgio, 2011). Because of this rapid cycling, autochthonous DOM often constitutes a small proportion of the standing DOM pool in natural waters (Gergel, et al., 1999). The microbial metabolism of DOM in a stream ecosystem is an important process that releases nutrients back into the water column for transport

downstream, with obvious implications for the eutrophication of downstream systems (Mattsson, et al. 2005).

Spectroscopic analyses, such as fluorescence excitation-emission matrix (EEM) spectroscopy, that exploit the optical properties of DOM provide information about the source and ecological reactivity (Cory, et al., 2011). The humic/fulvic materials in DOM possess fluorophoric components with relatively strong quantum yields, making fluorescence spectroscopy a sensitive characterization tool (Pagano, et al. 2012). A suite of fluorescence indices have been developed in a variety of studies and are used to extract ecologically significant information about the composition of DOM. The fluorescence index (FI) FI is commonly used to differentiate between microbial and terrestrial sources of DOM (Wilson & Xenopoulos, 2009), where high values of FI (~1.8) indicate a greater contribution of microbially derived DOM (i.e. bacteria and algae) and low values (~1.2) indicate a terrestrial source from plants or soil (Fellman, *et al.*, 2010). The humification index (HIX) represents the humic substance content or extent of humification of DOM where higher values (>10) indicate an increasing degree of humification (Fellman, et al., 2009). HIX values around 1-2 are associated with non-humified plant materials (Williams, *et al.*, 2010). The β:α ratio is used to determine the contribution of recently produced DOM, β, and its more decomposed forms, α. β:α values > 1 indicate that the DOM is of autochthonous origin and values < 0.6 are from DOM with an allochthonous origin (Williams, *et al.*, 2010).

Fluorescence spectroscopy, however, cannot be used for quantification because we currently lack a suitable reference material (Nollet, 2007). The complex makeup of DOM, and the varying photo-physical phenomena (such as inner filtering and energy transfer) that can occur within its molecular complexity, make interpretation of resultant fluorescence spectra challenging (Pagano, et al., 2012). But, when combined with advanced chemometric techniques, multidimensional fluorescence can sometimes overcome data interpretation barriers. The chemometric technique, parallel factor analysis (PARAFAC), has provided a significant advancement in the interpretation of EEMs because it enables the mathematical separation of chemically independent, yet spectrally overlapping fluorescence components (e.g. Stedmon et al., 2003; Fellman, et al., 2010; Murphy, et al., 2011). Pagano et al. (2012) have shown the ability to use PARAFAC to resolve humic and fulvic acid standards into components that can be identified as phenolic-in-nature, protein-like, and lignified material. The successful use of EEM-

PARAFAC techniques to characterize DOM in both pristine and anthropogenically modified systems has greatly enhanced our understanding of the influence of land use on the quality of DOM in stream ecosystems (e.g. Matson, et al., 1997; McKnight, et al., 2001; Wilson and Xenopoulos, 2008; Williams, et al., 2010; Pagano, et al., 2012).

The Finger Lakes region in New York State is composed of eleven linear, glacially-carved lakes that are oriented on a north-south axis. The lakes are unique in that their watersheds drain into lakes with relatively small surface area to perimeter ratios. Much of the region is used for agriculture, recreation and tourism and it hosts a variety of natural resources, including fresh water, fish, wildlife habitat, wetlands, and forests, making preservation of the lakes essential for the region from both environmental and economic standpoints (Moran & Woods, 2009). Some major environmental management issues challenging the viability of the Finger Lakes region include diminishing water quality, alterations to aquatic habitat, abundant invasive species, and changes in watershed hydrology (Moran & Woods, 2009).

Conesus Lake, part of the Lake Ontario drainage basin, is the western-most of the 11 Finger Lakes and serves as a drinking water source for about 22% of Livingston County, NY, or about 20,000 residents (NYSDEC, 2006). Eighteen unique, first and second-order streams and several smaller tributaries (rivulets) drain the lake's rural/agricultural watershed (Forest, et al., 1978). In recent decades, increased shoreline and upland residential development and the intensification of agricultural practices have resulted in a general decline in near-shore water quality, diminishing the ability to support its multiple uses, particularly its use as a drinking water source (Makarewicz, 2009; Moran & Woods, 2009). In general, water quality declines have been characterized by increased inorganic nitrogen and phosphorus loadings from streams, abundant near-shore macrophyte growth, and frequent open water algal blooms (Makarewicz, 2009). From 2002 to 2007, the lake was the focus of a USDA-funded study, the Conesus Lake Watershed Project (CLWP), which included the implementation of agricultural best management practices (BMPs) to mitigate declining water quality (Makarewicz J. C., et al., 2009). Initially the implementation of these BMPs showed limited improvements to water quality parameters, but after continued monitoring efforts, some recent results suggest that the lake may now be returning from a eutrophic to a mesotrophic state (Makarewicz, et al., 2012). However, nutrient-induced near-shore algal blooms persist and in the last three years watershed management resources have, subsequently, been allocated for the real-time monitoring of algal blooms on

Conesus Lake (CLWC, 2012). In addition, monitoring of inorganic nutrient concentrations and annual nutrient loadings from select streams continues (Makarewicz, et al., 2012).

At Conesus Lake (and the entire Finger Lakes region), much less is known about the quantity and composition of dissolved organic matter (DOM) delivered to the lake, despite the fact the DOM contains significant amounts of carbon, nitrogen and phosphorus (Mattsson, et al., 2005). The Conesus Lake watershed has a topography that lends itself to a study of differences in DOM quantity and composition according to sampling season, land use, and stream order. The objectives of our study, therefore, were to assess seasonal variation in DOM and determine if agricultural land use and stream morphology (stream order and slope) are significant predictors of watershed DOM quantity and quality. To the best of our knowledge, this study will provide the first measures of stream DOM concentrations and the first use of multidimensional fluorescence spectroscopy with PARAFAC, to describe the composition of DOM in the Finger Lakes Region. Further, because of the predicted changes in watershed exports under a changing climate, this provides baseline values for DOM concentration and composition with which to compare future changes and offer a more comprehensive understanding of the regional effects of climate change.

Methods

Site Description

Conesus Lake is located about 25 miles 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. It is the western-most of 11 Finger Lakes in New York State and part of the Genesee River drainage basin, which ultimately flows into Lake Ontario. Conesus Lake has one of the smallest watersheds (16,713 ha) and it is among the shallowest of the Finger Lakes, with an average depth of 11.6 m. In the southern third of the watershed, steep slopes exceeding 45% flank the lake so the most active agricultural areas are concentrated in the flatter, more productive northern portions of the watershed (Makarewicz, 2009). The elevation in the watershed ranges from 249 m to 549.9 m (Forest et al., 1978). A network of 18 streams and several smaller tributaries surround the lake, and its topology creates well-delineated small watersheds, referred to hereafter as *subwatersheds* (Forest et al., 1978; SOCL, 2002).

The Genesee Valley and western Finger Lakes region of New York has a humid climate, 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, 2002). Average yearly precipitation is approximately 80.5 cm (Makarewicz, 2009), however in the spring of 2011 the region experienced some of the highest rainfall totals in at least 11 years (CLWC 2012), with 10.85 cm and 11.39 cm recorded at the Avon, NY metrological station (USC00300343) for April and May, respectively.

In general, the soils in the watershed are derived from glacially reworked shale and sandstone bedrock and they tend to be the most fertile in the north due to the influence of limestone materials transported by glaciers (Bloomfield, 1978). Throughout the watershed, the soils are diverse and vary in terms of drainage and erosion potential, so watershed land management decisions are often made on the field scale (Makarewicz, 2009, Noll *et al.*, 2009). In general the soil orders found in the watershed consist of predominantly alfisols and inceptisols, though a small proportion of histosols soils are located in the North Gully and Wilkin's Creek subwatersheds (see supplementary Table S1).

Geospatial Analyses

Subwatershed delineation for the Conesus Lake catchment area was performed in IDRISI version 15 (Clark Labs, 2006) using 7.5-min digital elevation models (DEMs) for Livingston Country, 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, 2010) 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). The main LULC types defined by the NLCD classification system in 2006 included 15 categories: Open Water, Developed Open Space, Developed Low Intensity, Developed Medium Intensity, Developed High Intensity, Barren Land, Deciduous Forest, Evergreen Forest, Mixed Forest, Shrub/Scrub, Grassland/Herbaceous, Pasture/Hay, Cultivated Crops, Woody Wetlands, and Emergent Herbaceous Wetlands. For this study, the 15-category NLCD classification

system was reduced into 5 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). Land use areas for each subwatershed were determined using the raster calculator in ArcGIS 10.1. In 2002, there were 78 parcels of field crops, 15 parcels of dairy farming and 7 parcels of livestock operations in the watershed, according to the Livingston County Planning Department (SOCL, 2002). Other major land covers and land uses in the watershed include forests (~24 %), developed areas (~7.5 %), and wetlands (~2.5 %). As of 2006, the largest proportion of land use within the watershed was agricultural (~42 % of watershed) with the northwestern quadrant of the catchment containing the most active agriculture operations.

In order to best determine the effect of agricultural land use on the composition of DOM in the Conesus Lake watershed, subwatersheds were categorized by subwatershed type. AG streams were defined as streams with > 70 % agricultural land use within their catchment. All other streams were classified as reference streams (REF), having < 70 % agricultural land use. Forested land uses were not always the dominant land use in the catchments classified as REF, as shrub/scrub and lakeshore developed area also contributed (Table 1). Many of the shrub/scrub areas in the Conesus Lake watershed are old fields, plots of land in their early successional state having been formerly used for agricultural purposes. This categorical approach is similar to that of the CLWP, where agricultural streams were compared to reference streams based on land use statistics to evaluate the effectiveness of agricultural BMPs (Makarewicz, et al. 2009).

Sampling Methods

We collected 225 grab samples from 12 independent streams, all tributaries to Conesus Lake (Fig. 1). We examined the watershed land use characteristics for each stream and performed spectrophotometric and chemical analyses on all samples. Triplicate grab samples of ~0.5 L were collected at or near the discharge point from each stream into the lake using sterile Whirlpak sample bags during baseline conditions. Samples were stored in coolers on ice (0-4 °C) during transport to the laboratory where they were subsequently filtered under pressure through 0.45 µm Whatman nylon membranes within 4 hours of collection and stored in the dark at -80 °C pending chemical analysis. All samples were analyzed within 1 year of collection and

underwent a single freeze-thaw cycle to minimize potential alterations to the DOM contained in the sample (Fellman, et al., 2008).

To survey seasonal DOM variation, we sampled about quarterly during 2011, once in each season and all data collected from these samples made up our *seasonal dataset*. Triplicate grab samples were collected in the winter (January 28, 2011), spring (May 20, 2011), summer (August 4, 2011) and fall (October 20, 2011) from 7 streams: Graywood, Sand Point, Long Point, Cottonwood, Southwest, South McMillan, and North McMillan. Five of these streams had catchments dominated (> 70 %) in agricultural land use and two streams were reference streams (Table 1). A large manure operation is located upstream of the Cottonwood sampling point and Graywood, which has a small catchment area, is dominated by one dairy farm. S. McMillan and N. McMillan streams were classified as REF streams because they have catchments that are predominantly forested, shrub/scrub (other), and developed (Table 1). Both of these streams have less than 30 % agricultural land use in their catchments, with operations mostly localized in higher elevations with well-established riparian vegetation.

To assess differences in DOM according to land use (*subwatershed type)* and stream order, we sampled 7 AG streams (Hanna's Creek, Graywood, Sand Point, Long Point, Cottonwood, Southwest, and Densmore) and 5 REF streams (North McMillan, South McMillan, North Gully, South Gully, and Wilkin's Creek) during the 2011 growing season. The 12 streams were sampled on June 21, 2011, July 6, 2011, August 11, 2011, and September 21, 2011. All data collected from these samples made up the *growing season dataset*.

Analytical Methods

Dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrite and nitrate (*hereafter referred to as NO_3^- or nitrate*), ammonium (NH_4^+), total dissolved phosphorous (TDP), and phosphate (PO_4^{3-}) were measured for each sample. TDN (Lachat method: 31-107-04-3-A), NO_3^- (Lachat method: 31-107-04-1-C), TDP (Lachat method: 31-115-01-3-D), and PO_4^{3-} (Lachat method: 31-115-01-1-J) were each quantified using a Lachat QuikChem 8500 analyzer. NH_4^+ was determined using the colorimetric assay described by Solorzano (1969). DOC analysis was performed on a PC-controlled Shimadzu TOC-V analyzer using the platinum-catalyzed oxidation method. DON concentrations were calculated as the difference between TDN and the sum of

nitrate-nitrite and ammonium concentrations (DON=TDN - [NO_2^- + NO_3^- + NH_4^+]). DOP was calculated as the difference between TDP and PO_4^{3-} (TOP=TDP – PO_4^{3-}).

Spectroscopic Methods

UV-visible absorbance spectra were recorded for each filtered sample between 200 – 600 nm at intervals of 1 nm on a baseline corrected Perkin Elmer Lambda 650 Double-Beam UV-Vis/NIR spectrophotometer in 10 mm pathlength quartz cuvettes with ultrapure water as the reference blank. Fluorescence EEMs were measured with a Varian Cary Eclipse Fluorimeter at room temperature in 10 mm quartz cuvettes (Chen & Kenny, 2007). Fluorescence intensity was measured across excitation wavelengths 240 nm to 550 nm at 5 nm increments and emission wavelengths from 295 nm to 550 nm at 1 nm increments. Raw EEMs were corrected for Rayleigh and Raman scatter and inner-filter effects, respectively (Pagano, et al., 2012). Rayleigh and Raman scatter from an ultrapure water sample was used to remove regions of scatter in the sample EEMs using a MATLAB program from Hall *et al.* (2005). Inner filter effects were compensated for prior to analysis by diluting samples that had absorbance values greater than 1.0, usually occurring below 254 nm, to ≥ 1.0 with ultrapure water. Inner filter effects were additionally removed using an in-house MATLAB program that followed the inner filter effect compensation model described by MacDonald *et al.* (1997). The EEMs from diluted samples were multiplied by the appropriate dilution factor in MATLAB after removing scatter and correcting for inner filter effects, prior to PARAFAC analysis.

To extract ecologically relevant insight from the fluorescence data, corrected EEMs from each sample were used to calculate the fluorescence index (FI), the humification index (HIX) and the β:α ratio. FI was calculated as the ratio of fluorescence intensities for emission wavelengths of 470 nm and 520 nm recorded at an excitation wavelength of 370 nm (Cory & McKnight, 2005). The humification index (HIX) was calculated as the area under the EM spectra from 435-480 nm divided by the sum of peak areas between emission wavelength of 300 – 345 nm and 435 – 480 nm as measured at an excitation wavelength of 254 nm (Zsolnay, et al., 1999). The β:α ratio was determined as the ratio of fluorescence intensity at an emission wavelength of 380 nm (β region) divided by the maximum intensity observed between emission wavelengths 420 and 435 nm (α region) at an excitation of 310 nm (Fellman, et al., 2009, Williams, *et al.*, 2010).

Parallel Factor Analysis

EEMs from all samples (n = 225) were combined into a three-way array and PARAFAC was used to reduce EEM matrix data into discrete components according to the tutorial from Stedmon and Bro (2008) using MATLAB 7.12.0 (The Mathworks Inc., 2011) with the PLS_Toolbox 7.0 (Eigenvector Research, Inc., 2012). The resulting PARAFAC model was validated using model fit analysis, the core consistency diagnostic, residuals analysis, split-half analysis, and visual validation (Andersen & Bro, 2003). We expressed PARAFAC component loading scores as the percent contribution of each component to the overall DOM fluorescence in each sample, consistent with the approach used in other studies (e.g. Kraus, et al., 2010; Graeber, et al., 2012).

Data Analysis

Prior to statistical analysis, the distributions of all variables were visually examined for normality. Most variables showed significant skew to the right, with occasional, though infrequent extreme measures. Data were transformed to meet conditions of normality and to dampen the effect of extreme values. We used logarithmic and square root transformations, which can be an appropriate treatment for variables with right-skew (Quinn & Keough, 2002). Variables that were logarithmically transformed included: DOC, DON, NO_3^-, PO_4^{3-}, NH_4^+, HIX, FI, % C1, % C2, % C3, and % C4. DOP was square-root transformed. β:α did not require transformation.

We performed separate principle components analyses (PCA) with varimax factor rotation on the seasonal and growing season datasets, respectively. Variables included in the two PCAs were: DOC, DON, DOP, NO_3^-, ammonium, phosphate, HIX, FI, β:α, and the percent contribution of each of the four PARAFAC components. Rotated principle components were considered significant when their eigenvalues were ≥ 1 and variables loading on each factor were considered significant when their rotated factor loadings were ≥ 0.60.

We tested the general effect of sampling date (season) and subwatershed type in the seasonal dataset using a two-way ANOVA with Tukey Kramer post hoc analysis on all variables used in this study and all PCA component loading scores. Similarly, a two-way ANOVA with Tukey Kramer post hoc analysis was used to examine the effect of agricultural land use and

stream order and determine if significant differences exist. All data analyses were performed using JMP 10 (SAS Institute Inc., 2012).

Results

Seasonal Bulk DOM Results

In terms of bulk DOM concentrations for the seasonal dataset, DOC concentrations ranged from 0.79 to 13.55 mg L^{-1} C. Significantly lower mean DOC concentrations across all streams (Fig. 2a) were observed in the winter, followed by spring, summer, and a fall maximum (Table 2). DOC concentrations in AG streams were significantly higher than REF streams across all seasons (Table 2; Fig. 2a). Concentrations of DON ranged from 0.03 to 9.88 mg L^{-1} N and made up an average of 38.9 ± 2.8 % of TDN recorded across all sampling dates. Mean DON concentrations (Fig. 2b) were significantly higher in the winter and spring and decreased in the summer to a fall minimum. This was especially pronounce in the AG streams compared to REF streams (Fig. 2b). DOP concentrations ranged from 1.2 to 415.0 µg L^{-1} P and made up an average of 64.2 ± 3.1 % of the TDP measured during all collection dates. Mean DOP concentrations (Fig. 2c) were the highest in the spring, followed by winter and fall. The lowest mean DOP concentrations were recorded in the summer (*for seasonal means by stream see Supplemental Table S-2*). AG streams had significantly higher DOM concentrations compared to REF streams, particularly with respect to DOC and DON. DOP was higher during spring, summer and fall, but these differences were not significant (Fig. 2a-c; Table 2)

Mean molar DOM C:N ratios were lowest in the spring and winter (Fig. 3 and Table S-3), increasing through summer and fall. DOM C:N produced a significant interaction term in the two-way ANOVA, indicating that the seasonal changes vary by subwatershed type (Table 2). Mean DOM N:P was lowest in the spring, followed fall, then summer, and the highest mean values were recorded for the winter. DOM C:P was highly variable and followed a similar pattern as the mean DOM C:N ratios, where the highest mean values were recorded for summer and fall and the lowest were recorded for winter and spring (Fig. 3). No significant effects or interactions were observed for DOM C:P (Table 2).

Seasonal Inorganic Nutrient Results

NO_3^- concentrations ranged from 0.04 to 5.40 mg L^{-1} N for the seasonal dataset (Table S-1). Lower mean NO_3^- concentrations (Fig. 2d) occurred in the spring and higher concentrations

were observed in our fall samples, but these differences were not significant (Table 2). NO_3^- produced a significant effect from subwatershed type, where AG streams had higher NO_3^- concentrations compared to REF streams (Fig. 2d; Table 2). Mean seasonal PO_4^{3-} concentrations (range =1.9 to 1085.0 µg L^{-1} P) followed a similar pattern to the DOC (Fig. 2e) with significantly lower values in winter (Table S-1) and the highest mean PO_4^{3-} in fall. AG streams had significantly higher PO_4^{3-} in the seasonal dataset (Table 2). NH_4^+ concentrations were generally low and most samples were recorded at or below the limit of quantification for the method, calculated to be 3.5 µg L^{-1}. The highest mean NH_4^+ concentrations (Fig. 2f) occurred in the fall and the lowest in the spring (Table S-2).

Growing Season Bulk DOM Results

During the 2011 growing season, DOC concentrations ranged from 1.91 to 7.44 mg L^{-1} C and the mean (± SE) DOC concentrations across all streams during this period was 3.82 ± 0.10 mg L^{-1} C (Table S4). Significantly higher mean DOC concentrations for the growing season were observed in the second-order reference stream, South McMillan (Table S4), while the lowest was found in the first-order reference stream, South Gully (Table S4). First-order Ag streams showed the highest combined mean DOC concentrations and first-order REF streams had the lowest mean DOC concentrations (Fig. 4a). In the two-way ANOVA (Table 3), DOC produced a significant interaction effect from subwatershed type and stream order. DON concentrations ranged from 0.01 to 2.56 mg L^{-1} N, with a mean DON concentration across all streams of 0.53 ± 0.05 mg L^{-1} N. In general, first and second-order AG streams showed higher mean DON concentrations than first and second-order REF streams (Fig. 4b). Interestingly, Graywood and Cottonwood streams, both first-order AG streams with dairy operations in their subwatersheds, showed the highest mean DON concentrations (1.18 ± 0.13 mg L^{-1} N and 1.11 ± 0.24 mg L^{-1} N, respectively), while the lowest mean DON concentrations were recorded in North and South Gully streams, both first-order REF streams (0.19 ± 0.01 mg L^{-1} N and 0.18 ± 0.01 mg L^{-1} N, respectively). DON also produced a significant interaction term between subwatershed type and streams order (Table 3). DOP ranged from 0.7 to 274.7 µg L^{-1} P during the 2011 growing season, with an overall average DOP concentration of 61.1 ± 4.7 µg L^{-1} P across all streams. The highest mean concentration for DOP was recorded in the second-order reference stream, North McMillan (92.3 ± 23.5 µg L^{-1} P), while the lowest mean DOP concentration was

observed in Densmore (32.1 ± 7.2 µg L^{-1} P), a second-order AG stream. DOP concentrations were highest in second-order REF streams, followed by first-order AG streams, second-order AG streams, and the lowest DOP concentrations were recorded in the first-order REF streams (Fig. 4c). The results of a two-way ANOVA did not indicate that differences with respect to subwatershed type or stream order were significant. The mean DOM molar ratios for C:N, N:P, and C:P during this time were 23.8 ± 7.0, 46.8 ± 8.5, and 34.2 ± 2.9, respectively (Fig. 5; *see Table S-6 for individual stream means*).

Growing Season Inorganic Nutrient Results

NO_3^- concentrations in the growing season subset ranged from 0.01 to 4.27 mg L^{-1} N and the mean (± SE) NO_3^- concentration across all streams was found to be 0.60 ± 0.05 mg L^{-1} N (Table S-4). The highest mean NO_3^- concentrations were recorded in three AG streams, Long Point, Cottonwood, and Southwest (Table S-4). The REF stream North McMillan and the AG stream, Hanna's Creek, both second-order streams, showed the mean lowest NO_3^- concentrations during the growing season (Table S-4). Collectively, first and second-order AG streams had significantly higher mean NO_3^- concentrations compared to the first and second-order REF streams we sampled (Fig. 4d), but the effect of stream order did not show significance. PO_4^{3-} concentrations ranged from 1.6 to 167.3 µg L^{-1} P, with a mean PO_4^{3-} concentration across all streams of 31.8 ± 2.7 µg L^{-1} P. The highest mean PO_4^{3-} concentrations were recorded in the first-order AG streams Graywood and Cottonwood (Table S-4), while the lowest mean PO_4^{3-} concentration was observed in the second-order reference stream, North McMillan (8.2 ± 1.6 µg L^{-1} P). Mean phosphate concentrations tended to be higher in the first and second-order AG streams compared to first and second-order REF streams (Fig. 4e), however the significant interaction term indicates a more complex interplay between stream order and land use (Table 3). NH_4^+ concentrations during the 2011 growing season showed a lower range than for the seasonal dataset, with values often below our limit of quantification of 3.5 µg L^{-1}. Nonetheless, the mean NH_4^+ concentration across all streams during this period was found to be 2.3 ± 0.2 µg L^{-1} N, with the highest mean concentration found in the second-order REF stream, North McMillan (4.5 ± 1.1 µg L^{-1} N), and the lowest recorded in the first-order AG stream Cottonwood (> 0.5 µg L^{-1} N; Fig. 5f).

Seasonal DOM Fluorescence Indices

For the seasonal subset, HIX ranged from 0.46 to 15.25, values that span the gradient from non-humified DOM to more humified types (Table S4). The highest mean (± SE) seasonal value of HIX was recorded in the spring, followed by winter, summer and fall (Fig. 6a). FI ranged from 0.97 to 1.72, the highest mean FI was observed in the summer and fall, then winter, and lowest occurred during spring (1.19 ± 0.02; Fig. 6b). The β:α ratio ranged from 0.61 to 0.95, indicating DOM that was composed of a mixture of terrestrial and microbial sources. Mean values did not differ greatly across sampling dates, but the highest mean β:α was recorded in the winter, followed by summer, fall and spring (Fig. 6c). HIX and β:α produced a significant effect from subwatershed type and stream order, while FI showed a significant effect between subwatershed type only (Table 2).

Growing Season DOM Fluorescence Indices

During the 2011 growing season, HIX values ranged from 0.03 to 15.25 in the 12 streams sampled (Table S7). The highest mean (± SE) value for HIX was recorded in the second-order REF stream, South McMillan (9.06 ± 1.19), while the lowest mean was recorded in North McMillan (3.88 ± 0.36), also a second-order REF stream. First and second-order REF streams both had higher mean HIX values during the growing season compare to first and second-order AG streams (Fig. 7a). Similarly, mean values for FI were found to be higher in first and second-order AG streams compared to the reference streams (Fig. 7b). Mean β:α did not differ significantly between AG and REF streams (Fig. 7c; Table 3).

PARAFAC Modeling Results

PARAFAC results indicated that a 4-component model explained 99.4 % of the variance in the dataset with a core consistency of 88 % (Table 4). Excitation-emission loading spectra for each of the four PARAFAC components were visually inspected for similarity to organic fluorophores and these spectra compared well to those from a split-half validation analysis (Fig. 8). Further, visual examination of the corrected EEMs, the modeled EEMs, and the PARAFAC residual EEMs for each sample showed residual EEMs with little to no remaining fluorescence signal (*see examples provided with supplemental material, Figs. S1-3)*. Component

characteristics, source assignment, and examples from the literature are listed in Table 5. In the 4-component model generated in this study, PARAFAC component 1 (C1) had characteristics similar to the reduced-quinone component, SQ1, identified by Cory and McKnight (2005), which has been associated with compounds resulting from lignin degradation. Similarly, C1 had features corresponding to the ubiquitous freshwater humic-like component associated with terrestrially-derived organic matter (e.g. Pagano, et al., 2012; Stedmon and Markager, 2005; Williams, et al., 2010). Component 2 (C2) was blue-shifted relative to C1, indicating DOM with a reduced aromatic carbon content. Components similar to C2 have been identified in freshwater streams and are generally considered to be more bioavailable than C1, though the source of this material is largely unknown (Lutz, et al., 2012). Component 3 (C3) and component 4 (C4) both had spectral characteristics resembling protein-like DOM fluorescence (Cory, et al., 2011). Specifically, C3 closely resembled a tryptophan-like component, while C4 had characteristics similar to tyrosine-like components (Cory and McKnight, 2005; Pagano, et al., 2012; Stedmon and Markager, 2005). The combined loadings of C1 and C2 in the PARAFAC model explained 87.7 % of the variance, indicating that the bulk of optically-active DOM in our samples consists of terrestrially-derived, humic-like DOM (C1) and the semi-labile component C2 whose source is unknown. Collectively, C3 and C4 explained 11.7 % of the variation in our EEMs, indicating a lesser contribution from protein-like fluorescence in the overall fluorescent DOM pool.

Seasonal Contributions of PARAFAC Components

For the seasonal dataset, we observed changes in the relative contribution of each of the four PARAFAC components to the fluorescent DOM pool according to sampling date. The mean (± SE) contribution from C1 was significantly higher during the spring collection date (55.7 ± 1.9 %), followed by winter (49.6 ± 1.7 %), then fall (45.6 ± 2.4 %). Mean values for % C1 were lowest during the summer collection date (42.5 ± 3.3 %; Fig. 6d; Table 2). For C2, the mean values were highest in the winter (37.0 ± 0.6 %), followed by summer (34.3 ± 2.1 %), spring (34.2 ± 0.7 %), then fall (32.2 ± 0.8 %; Fig. 6e), but these differences were not significant (Table 2). The contribution to the fluorescent DOM pool from C3 was significantly higher in the fall (14.8 ± 1.6 %) and summer (14.7 ± 3.0 %) and lowest in the winter (7.4 ± 0.7 %) and spring (6.8 ± 1.0 %; Fig. 6f). Similar to C3, the contribution from C4 was also highest in the summer (8.5 ± 1.1 %) and fall (7.5 ± 0.8 %) and lowest in the spring (3.3 ± 0.4 %) and winter (6.0 ±

0.5 %; Fig. 6g), but the interaction term was significant, indicating that seasonal changes in C4 vary with subwatershed type (Table 2). Individual means for each stream are shown with the supplemental material (Table S-4).

Growing Season Contributions of PARAFAC Components

During the growing season, the mean contribution from C1 was greater than 50 % in all streams, with significantly higher mean (± SE) values recorded for first and second-order REF streams (1^{st}-order REF: 56.6 ± 1.3 %; 2^{nd}-order REF: 53.2 ± 1.2 %; Table 3). First and second-order AG streams showed lower mean contributions from C1 compared to the REF streams (1^{st}-order AG: 51.0 ± 1.8 %; 2^{nd}-order AG: 50.7 ± 1.5 %), nonetheless, C1 still made up the majority of the fluorescent DOM pool in these streams (Fig. 7d). Differences in %C1 with respect to subwatershed type were significant, while the differences with respect to stream order were not (Table 3). The mean contribution of C2 was highest in second-order AG streams and lowest in first-order AG streams (1^{st}-order AG: 34.6 ± 1.0 %; 2^{nd}-order AG: 36.2 ± 0.7 %), while mean values of C2 for first and second-order REF streams fell between the values recorded for the AG streams (1^{st}-order REF: 34.9 ± 0.4 %; 2^{nd}-order REF: 35.9 ± 0.7 %; Fig. 7e), but these differences were not significant (Table 3). Mean values for C3 were highest in the first and second-order AG streams (1^{st}-order AG: 9.0 ± 1.3 %; 2^{nd}-order AG: 8.1 ± 1.3 %) compared to first and second-order REF streams (1^{st}-order REF: 5.0 ± 0.9 %; 2^{nd}-order REF: 6.8 ± 0.5 %; Fig. 7f). Similarly, the mean contribution from C4 was also highest in first and second-order AG streams (1^{st}-order AG: 5.5 ± 0.6 %; 2^{nd}-order AG: 5.0 ± 0.5 %) compared to first and second-order REF streams (1^{st}-order REF: 3.5 ± 0.4 %; 2^{nd}-order REF: 4.1 ± 0.4 %; Fig. 7g). Both %C3 and %C4 showed a significant effect from subwatershed type, but the effect of stream order was not found to be significant (Table 3). Individual means for each stream are shown with the supplemental material (Table S-7).

Seasonal PCA Results

Principle components analysis with factor rotation produced 4 significant components (eigenvalues > 1), collectively explaining 75.8 % of the variance in the seasonal dataset (Table 6). All variables included in the PCA for the seasonal dataset loaded on the first four components

with the exception of ammonium. Principle component 1 (PC-1) explained 33.7 % of the variance and was characterized by positive loadings from nitrate-nitrite, β:α, and the protein-like PARAFAC components, C3 and C4. Additionally, PC-1 was associated with strong negative loadings from HIX and C1. Mean PC-1 loading scores showed significant differences between collection dates (Fig. 9), where negative PC-1 scores in the spring indicated lower nitrate-nitrite concentrations, a lower β:α ratio, and a decreased protein-like fluorescence. Winter samples showed a lower mean PC-1 score compared to summer and fall, but these differences were not significant (Figs. 9 & 10).

PC-2 explained 14.6 % of the variance in the seasonal dataset and was associated with positive loadings from DOC and phosphate concentrations (Table 6). Mean PC-2 loading scores showed a significant effect between sampling dates (Table 3) with significant differences between the mean scores for the winter samples when compared to those from the fall collection date (Figs. 9 & 10). Streams showed significantly lower mean PC-2 scores in the winter samples, indicating lower DOC and phosphate concentrations. The opposite was true for the fall samples, which were characterized by higher DOC and phosphate concentrations. Spring and summer mean PC-2 scores were significantly lower than fall and significantly higher than winter, but did not differ significantly from each other (Fig. 9).

PC-3 showed positive loadings from DON and DOP concentrations and it explained 14.2 % of the variance. Mean factor scores showed significant differences between sampling dates (Table 4) with the highest mean PC score recorded for the spring. Winter showed a moderate mean PC-3 score, followed by the lowest mean scores in the summer and fall (Fig. 9).

PC-4 explained an additional 10.5 % of the variance and was characterized by positive loadings for % C2, FI, and β:α. A significant effect from collection date was also observed for PC-4 (Table 4). The highest mean PC-4 loading score was recorded for the winter samples and mean PC-4 scores were lowest in the fall. Spring showed negative mean component scores that were higher than winter, but not significantly different. Summer mean loading scores were positive and lower than the fall, though this difference was also not significant (Fig. 9).

Growing season PCA results

PCA results from the growing season subset showed that PC-1 explained 29.0 % of the variance in the dataset and was characterized strong positive loadings from the protein-like

PARAFAC components, C3 and C4, while HIX and C1 both loaded strongly negative (Table 7). PC-2 explained 14.8 % of the variance and showed strong positive loadings for the inorganic nutrients, nitrate-nitrite and phosphate. PC-3 explained 11.8 % of the variance and was associated with a strong positive loading from C2 and a positive loading from the β:α ratio. PC-4 explained 11.8 % of the variance and was characterized positive loadings for DOM concentration variables, DOC, DON, and DOP. Ammonium and FI did not load strongly on any of the four significant principle components.

ANOVA results (Table 3) show that for PC-1, there was significantly higher protein-like fluorescence (% C3 and % C4) in agricultural subwatersheds compared to reference streams, but this difference was not significant between first and second-order streams (Fig. 11). The significant interaction term for PC-2 indicates that subwatershed type and stream order both have an effect on nitrate-nitrite and phosphate concentrations (Fig. 11). First-order agricultural subwatersheds showed significantly higher nitrate-nitrite and phosphate concentrations compared to first order reference streams and all second order streams. PC-3 did not produce significant effects from subwatershed type or stream order and their interaction was also not significant (Fig. 11). PC-4 showed a significant interaction between subwatershed type and stream order. A Tukey-Kramer test revealed that first-order reference streams had significantly lower DOM concentrations compared to first-order agricultural and second order reference streams. Second-order agricultural streams showed a higher mean value for factor 4 compared to the first-order Ag streams, but this difference was not significant. PCA score plots of PC-1 and PC-2, as well as PC-2 and PC-4 for AG and REF streams show a clear separation in ordinate space (Fig. 12) and illustrate increased variability in analyte concentrations and DOM composition for agricultural streams.

Discussion

Our study of the temporal and spatial variation in DOM and inorganic nutrients in the Conesus Lake watershed is the first known study of its kind in the Finger Lakes Region and suggests significant variation in DOM and inorganic nutrient concentrations and DOM quality driven by seasonality, stream order and catchment land use. We observed DOM concentrations comparable to those previously reported in the literature, although direct comparison was limited by differences in water collection and analysis methods, inclusion of flow-weighted

concentrations, varied ecoregions, and the limited number of DOM studies in temperate streams. In this study, multidimensional fluorescence with PARAFAC proved to be a valuable tool to gain insight into DOM composition. By exploiting the fluorescence properties of the DOM in the Conesus streams, we revealed that DOM in the streams was predominantly allochthonous (between 50-60%) in origin with varying contributions to the fluorescent pool from autochthonous DOM seasonally, notably during growing season months. Additionally, we observed differences in the quantity and composition of DOM according to agricultural land use within a subwatershed. Finally, we noticed differences between streams of different order, noting that first-order agricultural streams were the most erratic in terms of the range of DOM and inorganic nutrient concentrations recorded.

The concentrations of DOC we observed in this study were comparable to the ranges reported for other stream studies, where concentrations were reported to range from about 0.5 – 50 mg L^{-1} C (Mullholland, 2003). Other studies have reported larger ranges of DOC concentration than those we recorded in the Conesus Lake watershed. As examples, samples from 31 small streams in the US produced a range of annual DOC means of 0.7 - 30.6 mg L^{-1} C and in the southern Province of Quebec, a Canadian study of 42 streams produced a DOC concentration range of 3.5-40 mg L^{-1} C based on 8-month mean values (Eckhardt & Moore, 1990). An additional Canadian study reported a range of 1.7 to 24.1 mg L^{-1} C from samples of 32 streams over 2 years in southern Quebec (Wilson & Xenopoulous, 2008). While the range in DOC concentrations was small in this study compared to others, we did not sample streams that contained many wetland areas, which have been shown to contribute to higher DOC concentrations in stream water (e.g. Mullholland, 2003; Williams, et al., 2010; Cory, et al., 2011). In the Conesus Lake Inlet, water passes through a wetland area of about 4.5 km^2 where we consistently recorded DOC concentrations ~ two times higher than those found in streams flanking the lake, during baseline conditions (Bida, *unpublished data*).

Seasonal DOM variation

The results of this study suggest significant seasonal changes in both bulk DOM quantity and DOM chemical composition (Table 2). Seasonal changes in DOC concentrations reflected a gradual increase from a winter minimum to a fall maximum. Hydrologic flowpaths across the landscape influence inputs of DOM to streams (Mullholland, et al., 1990) and flushing of organic

soils would be minimized during the winter as the ground in this region is often frozen up to one meter below ground, which could account for the winter minimum in DOC that we observed in both the AG streams and the REF streams (Fig 2a). Other studies also report peak DOC inputs in the fall for forested US streams, with DOC concentrations often 1-3 times higher than during other times (*See review by* Mullholland, 2003). However, in a two-year, 32 stream study in southern-Ontario, Canada, monthly sampling showed that the summer months consistently produced the highest DOC concentrations and DOC tended to decrease through the following spring in a cyclical pattern (Wilson & Xenopoulous, 2008).

While DON concentrations in the REF streams remained fairly constant, with a slight maximum in the spring and a minimum in the winter, AG streams demonstrated a fairly consistent decrease from a winter maximum to a fall minimum (Fig. 2b). Seasonal minimums in DON have been reported during the fall and snowmelt periods in forested Massachusetts streams (Wilson, et al, 2013), which is similar to the trends we observed in our REF streams, but contrasts with our findings of relatively high winter DON in the AG streams we sampled.

DOP concentrations in both AG and REF streams reached a maximum in the spring and showed fairly consistent levels in the other seasons. In the summer and fall DOP concentrations in the AG streams were higher than in the REF streams, suggesting REF streams may be exporting more DOP than AG streams.

The DOM C:N ratio showed an increasing pattern from a winter and spring low (< 30) to a fall maximum (> 40; Fig. 3). The increasing DOM C:N ratio as the growing season progressed indicates an increased contribution from higher-order plants, as high DOM C:N ratios (10-1,000) are indicative of terrestrial plants (Kortelainen, et al., 2006), and DOM C:N ratios near 6.6:1 indicate algal derived OM (Redfield, et al., 1963). Additionally, in the winter, spring and fall, the generally higher DOM C:N ratios in the REF streams compared to AG streams, also suggests a contribution from terrestrial plants as the REF streams have less disturbed riparian areas that contribute terrestrial plant material to the stream, particularly during leaf-fall. High concentrations of high C:N DOC suggests that much of the additional DOC may come from a gradual buildup of terrestrial organic material in soils throughout the season, coupled with a flushing of this material in the fall.

Seasonal changes in DOM composition were also apparent as determined through the fluorescence properties of DOM in our study. The most pronounced seasonal differences

appeared in HIX and the PARAFAC components, while FI and β:α showed minimal seasonal changes. HIX was highest in the winter and spring and decreased into the summer and fall in both AG and REF streams, but the REF streams had higher HIX mean values than AG streams in all seasons. Humic-like component C1 decreased in relative abundance in the summer and fall compared to its higher values in the winter and spring. This was coupled with an increase in the contribution of protein-like fluorescence from components C3 and C4 in the summer and fall months.

A shift in DOM composition from more humic-like in the winter to more protein-like during the growing seasons was also reported for streams draining agricultural catchments in Illinois, USA, where allochthonous DOM was found to dominate the stream pool in late winter and early-summer, while autochthonous DOM from algal blooms dominated in the late-summer and autumn (Royer & David, 2005). It is apparent in our data that there is a shift to more autochthonous DOM production in the growing season months, much of which is likely governed by light availability, temperature and nitrate availability. High light and nitrate availability, combined with warmer temperatures results in an increase in soil microbial activity (Sinsabaugh & Findlay, 2003) and the subsequent accumulation of bacterial biomass would result in the increased leaching of more decomposed, protein-like DOM moieties as the growing season progressed and the metabolism of decomposition peaked (Tank, et al., 2010). Further, in situ DOM production peaks during growing season months and can contribute to increased protein-like fluorescence (Royer & David, 2005).

It was expected that nitrate and phosphate concentrations during the growing season months would decrease in our streams as these inorganic nutrients were assimilated by both terrestrial and aquatic plants and microbes (Graeber, et al., 2012). In our study, however, we observed peak nitrate and phosphate concentrations in the fall, which may be an effect of the seasonal dormancy of plants, but may also suggest excess fertilizer, likely applied during the early and late summer months, was probably flushed during the fall collection date. The consistently high nitrate and phosphate in the AG streams relative to the REF streams, as previously observed by Makarewicz et al. (2009), suggests that the agricultural BMPs implemented throughout the course of the CLWP to control for excess nutrient losses from agricultural soils via these streams have yet to bring inorganic nutrient levels in line with REF streams.

PCA results suggest that there was a positive relationship between protein-like fluorescence and the concentration of nitrate in the seasonal dataset (PC-1, Table 6), a relationship that has been described in several other studies (e.g. Williams, et al., 2010; Lutz, et al., 2012). DOC and phosphate appeared to be positively related in the PCA and mean PC-2 scores for each season corroborate the observed winter minima and fall maxima in the concentrations of these analytes (Fig. 2a & 2e). DOC and phosphate can both be bound to soil particles to some extent, which may explain their apparent coupling in this portion of our study (*See review by:* Kalbitz, 2000). Additionally, seasonal changes are known to alter hydrologic flowpaths across the landscape and in headwater stream channels this can result in increased soil erosion, which may free additional DOC and phosphate for transport downstream, especially during seasons with increased soil moisture (Wilson & Xenopoulous, 2008).

In our seasonal dataset we examined the concentrations and composition of DOM from 5 AG streams that were both first and second-order, while the 2 REF streams included in the dataset were both second-order and had the largest catchment areas of any streams in the watershed, limiting to some extent our ability to compare across streams. Additionally, many of the AG streams are often ephemeral and "flashy" in their delivery of analytes to the downstream sampling locations in this study. This could account for the large swings in seasonal DOM and inorganic nutrient concentrations observed in the first-order AG streams. A similar effect was reported for German agricultural streams that showed a greater seasonal variation in DOC concentrations than stream with forests or wetlands in their catchments (Graeber, et al., 2012).

Graywood Gully for example, contains a small, heavily modified (i.e. tile drains, roads, dairy farming, etc.) watershed, which has resulted in increased runoff from the built portions of the watershed that have modified flowpaths, including contributions from outside the delineated subwatershed (Noll & Magee, 2009). The watershed is extended by including runoff from roads, road ditches and tile drains to which roof gutter systems of residential and agricultural structures often connect (Noll & Magee, 2009). Reach-level studies into DOM quantity and composition at Conesus Lake are needed to better understand the baseline concentrations and composition of DOM and the seasonal controls governing DOM dynamics.

Land use and stream morphological controls on the quantity and composition of DOM

Agricultural land use causes a disturbance to stream systems that can affect the quantity and composition of DOM. The most obvious disturbance is the removal of trees, allowing greater light exposure to soils and streams that can alter DOM composition through direct photodegredation and chemical-reduction of DOM, as well as increased production of autochthonous DOM moieties (Williams, 2010). In conditions where fertilizer is applied, elevated inorganic nutrient levels can stimulate autochthonous DOM production even further. Agricultural land use has been associated with increased suspended soilds in streams draining their catchments (Makarewicz, et al., 2007), particles that can provide a substrate for microbial decomposition of DOM to occur and may contribute to increases in bulk DOM concentrations (Wilson & Xenopoulos, 2009; Williams, 2010).

In our study AG streams had higher concentrations of inorganic nutrients, a greater signature from the semi-labile C2 PARAFAC component, an increased abundance of protein-like PARAFAC components C3 and C4 and higher FI (indicative of more recently produced DOM). In the reference streams, we observed higher PARAFAC scores for C1 and HIX showed higher mean values for the REF streams compared to AG streams. These data indicate that AG streams in the Conesus watershed tend to contain more chemically-reduced forms of DOM compared to more forested watersheds. While there may be a higher contribution to the DOM pool from humic material in REF streams, the humic material is also present in AG streams with apparent contributions from more developed riparian zones or from existing soil DOM.

Bulk DOM measurements during the 2011 growing season indicated that first-order AG streams had higher mean DOM concentrations when compared to first-order REF streams (Fig. 4 a-c). Elevated DOC and DOP concentrations were found in the second-order REF streams, compared to second-order AG streams, and nitrate and phosphate concentrations in AG streams were consistently higher in both first and second-order streams compared to the REF stream (Fig. 4 d-f). High DON and DOP concentrations in Graywood and Cottonwood streams could be a result of instream bacterial and algal uptake of inorganic nutrients and incorporation into organic molecules as these streams have dairy operations in their subwatersheds that have previously been associated with high bacterial counts during summer non-event conditions in the stream (Simon & Makarewicz, 2009). Therefore much of the DON may have been leached from soil-

derived bacterial biomass, which is known to have a higher concentration of inorganic nutrients compared to the surrounding soil.

The growing season PCA showed that PARAFAC component C1 was inversely related to C3 and C4, as shown by the strong loadings (PC-1, Table 7). The PCA also produced a positive relationship between nitrate and phosphate concentrations (PC-2; Table 7) that could be attributed to fertilizer additions containing both inorganic N and P. The fact that β:α and C2 both loaded positively together on PC-3 may be an indication that C2 has a terrestrial source due to the fact that high values of β:α are indicative of terrestrial DOM (Fellman, et al., 2010). DOM concentrations (DOC, DON, and DOP) appeared to be positively related to each other in the PCA (PC-4) during the growing season.

Water residence time is an important stream characteristic to consider in studies of the composition of DOM. In headwater streams, water residence times can be on the order of about 1 – 4 hours, while in second order streams it can be between 4 – 24+ hours (Kalff, 2002). Stream order serves as a general indicator of the time DOM has been exposed to uptake by microbial communities and transformation by other in-stream processes, processes that may be more pronounced in agricultural subwatersheds. In general, second order streams have a lower stream gradient (% slope) than first-order streams and are subject to less erosion (Kalff, 2002). This allows microbial communities to have more stable sediment and riparian environments where they can build more complex communities than in ephemeral, often turbulent first-order streams, which is important in terms of instream nutrient processing (Foreman & Covert, 2003). More developed microbial communities are often better at processing DOM in streams, resulting in changes in its composition and the amounts of DOM exported.

The differences in DOM and inorganic nutrient concentrations we observed between AG and REF streams were more pronounced for first order streams than for second order streams, but this was not repeated for DOM composition. HIX, FI, and β:α showed differences between land use categories that were consistent for first and second-order streams indicating that a similar transformation or source material may be influencing the DOM composition as measured by fluorescence indices. In the PARAFAC analysis, our results suggest that first order REF streams have a lower contribution from the protein-like components (C3 & C4) compared to second-order REF streams, which may be a function of light availability, as second-order streams are often wider and may facilitate breaks in the canopy that could stimulate

autochthonous DOM production. This was not repeated for the AG streams where both first and second-order streams showed similar contributions of protein-like fluorescence.

Conclusions

This study showed spatial and temporal controls on DOM can alter its composition and quantity in streams in the watershed of Conesus Lake. We demonstrated seasonality in the composition and quantity of DOM that is consistent with abiotic seasonal controls (e.g. light and nutrient availability, hydrologic conditions, and temperature). We showed that agricultural land use in the catchment can potentially alter the structural complexity of DOM to more chemically-reduced forms. Additionally we showed differences in the temporal and spatial characteristics of DOM between first and second-order streams, suggesting that stream order should be an important consideration for future studies. Alterations to native DOM in streams can damage aquatic food webs, increase acidity and decrease the ability of the water to protect biota from contaminants. Additionally, the composition of DOM can dictate the bioavailability of the vast amount of nutrients carried down the stream in the DOM, which can have implications for the eutrophication of downstream systems. Since the bioavailability of DOM governs the availability of nutrients, a more complete picture of the effect of spatial and temporal controls on the DOM at Conesus Lake could incorporate biodegradability studies in addition to examining bulk quantity and optically-derived composition. DOM plays a large role in water quality, especially for waters used for drinking, so continued research into DOM in the lake's watershed is needed.

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Tables

Table 1: Select subwatershed characteristics for 12 streams in the Conesus Lake catchment.

Stream Name	Area (ha)	Ave. Slope	Stream Order	Agriculture	Forest	Wetland	Developed	Shrub/ Other
Hanna's Creek	762	2.5%	2	68%	13%	3%	12%	4%
Graywood	81	11.7%	1	73%	14%	1%	8%	2%
Sand Point	265	7.1%	1	79%	13%	2%	4%	2%
Long Point	540	2.0%	2	78%	13%	0%	5%	3%
Cottonwood	89	9.1%	1	76%	18%	0%	3%	4%
Southwest	191	7.1%	1	72%	19%	0%	5%	3%
S. McMillan	2726	4.3%	2	27%	49%	2%	6%	15%
N. McMillan	2034	3.1%	2	27%	51%	1%	7%	13%
S. Gully	295	3.3%	1	56%	37%	0%	4%	2%
N. Gully	696	2.1%	1	48%	32%	1%	8%	10%
Densmore	720	2.0%	2	70%	14%	0%	9%	6%
Wilkin’s Creek	627	1.8%	2	50%	21%	2%	21%	6%

Table 2: Two-way ANOVA results for the seasonal dataset. Significant ($p < 0.05$) seasonal and subwatershed type effects and interactions are shown in bold.

	Season (S)			**Subwatershed Type (T)**			**S X T**		
Inorg. Nutrients									
NO_3^-/NO_2^-	$F_{3,79}$	=	2.08	$F_{1,81}$	=	65.79	$F_{3,79}$	=	2.23
	p	=	0.1094	***p***	**<**	**0.0001**	*p*	=	0.0914
PO_4^{3-}	$F_{3,79}$	=	13.28	$F_{1,81}$	=	50.75	$F_{3,79}$	=	2.42
	p	**<**	**0.0001**	***p***	**<**	**0.0001**	*p*	=	0.0728
NH_4^+	$F_{3,79}$	=	3.32	$F_{1,81}$	=	1.44	$F_{3,79}$	=	2.36
	p	**=**	**0.0242**	*p*	=	0.2346	*p*	=	0.0784
DOM Composition and Optical Properties									
DOC	$F_{3,79}$	=	42.29	$F_{1,81}$	=	16.76	$F_{3,79}$	=	1.69
	p	**<**	**0.0001**	***p***	**=**	**0.0001**	*p*	=	0.1760
DON	$F_{3,79}$	=	3.16	$F_{1,81}$	=	8.55	$F_{3,79}$	=	2.02
	p	**<**	**0.0296**	***p***	**<**	**0.0046**	*p*	=	0.1184
DOP	$F_{3,79}$	=	21.91	$F_{1,81}$	=	2.38	$F_{3,79}$	=	1.40
	p	**<**	**0.0001**	*p*	=	0.1270	*p*	=	0.2501
DOM C:N	$F_{3,79}$	=	28.728	$F_{1,81}$	=	24.877	$F_{3,79}$	=	11.61
	p	**<**	**0.0001**	***p***	**<**	**0.0001**	***p***	**<**	**0.0001**
DOM N:P	$F_{3,79}$	=	4.41	$F_{1,81}$	=	15.60	$F_{3,79}$	=	10.25
	p	**=**	**0.0065**	***p***	**=**	**0.0002**	***p***	**<**	**0.0001**
DOM C:P	$F_{3,79}$	=	2.41	$F_{1,81}$	=	0.66	$F_{3,79}$	=	1.16
	p	=	0.0736	*p*	=	0.4207	*p*	=	0.3301
HIX	$F_{3,79}$	=	5.90	$F_{1,81}$	=	19.04	$F_{3,79}$	=	0.75
	p	**=**	**0.0011**	***p***	**<**	**0.0001**	*p*	=	0.5276
β:α	$F_{3,79}$	=	4.20	$F_{1,81}$	=	9.65	$F_{3,79}$	=	0.81
	p	**=**	**0.0084**	***p***	**=**	**0.0027**	*p*	=	0.4927
FI	$F_{3,79}$	=	3.43	$F_{1,81}$	=	3.44	$F_{3,79}$	=	1.82
	p	**=**	**0.0212**	*p*	=	0.0678	*p*	=	0.1506
% C1	$F_{3,79}$	=	5.00	$F_{1,81}$	=	27.211	$F_{3,79}$	=	0.6682
	p	**=**	**0.0033**	***p***	**<**	**0.0001**	*p*	=	0.5742
% C2	$F_{3,79}$	=	2.23	$F_{1,81}$	=	2.37	$F_{3,79}$	=	0.77
	p	=	0.0920	*p*	=	0.1280	*p*	=	0.5144
% C3	$F_{3,79}$	=	6.61	$F_{1,81}$	=	28.32	$F_{3,79}$	=	2.48
	p	**=**	**0.0005**	***p***	**<**	**0.0001**	*p*	=	0.0678
% C4	$F_{3,79}$	=	9.80	$F_{1,81}$	=	30.03	$F_{3,79}$	=	4.26
	p	**<**	**0.0001**	***p***	**<**	**0.0001**	***p***	**=**	**0.0078**
Seasonal PCA Component Scores									
PC1	$F_{3,79}$	=	5.96	$F_{1,81}$	=	34.22	$F_{3,79}$	=	0.93
	p	**=**	**0.0011**	***p***	**<**	**0.0001**	*p*	=	0.4326
PC2	$F_{3,79}$	=	28.13	$F_{1,81}$	=	23.16	$F_{3,79}$	=	4.77
	p	**<**	**0.0001**	***p***	**<**	**0.0001**	***p***	**=**	**0.0043**
PC3	$F_{3,79}$	=	40.96	$F_{1,81}$	=	40.59	$F_{3,79}$	=	3.85
	p	**<**	**0.0001**	***p***	**<**	**0.0001**	***p***	**=**	**0.0128**
PC4	$F_{3,79}$	=	2.23	$F_{1,81}$	=	3.80	$F_{3,79}$	=	0.74
	p	=	0.0912	*p*	<	0.0551	*p*	=	0.5333

Table 3: Two-way ANOVA results for the growing season dataset. Significant ($p < 0.05$) subwatershed type and stream order effects and interactions are shown in bold.

	Subwatershed Type (T)			**Stream Order (O)**			**T X O**		
Inorg. Nutrients									
NO_3^-	$F_{1,139}$	=	26.12	$F_{1,139}$	=	3.24	$F_{1,139}$	=	1.37
	p	**<**	**0.0001**	*p*	=	0.0741	*p*	=	0.2436
PO_4^{3-}	$F_{1,137}$	=	12.25	$F_{1,137}$	=	15.94	$F_{1,137}$	=	25.08
	p	**=**	**0.0006**	***p***	**<**	**0.0001**	***p***	**<**	**0.0001**
NH_4^+	$F_{1,139}$	=	0.90	$F_{1,139}$	=	16.70	$F_{1,139}$	=	0.83
	p	=	0.3434	***p***	**<**	**0.0001**	*p*	=	0.3645
DOM Composition and Optical Properties									
DOC	$F_{1,139}$	=	16.92	$F_{1,139}$	=	8.45	$F_{1,139}$	=	24.90
	p	**<**	**0.0001**	***p***	**=**	**0.0043**	***p***	**<**	**0.0001**
DON	$F_{1,139}$	=	23.72	$F_{1,139}$	=	1.70	$F_{1,139}$	=	16.83
	p	**<**	**0.0001**	*p*	=	0.1951	***p***	**<**	**0.0001**
DOP	$F_{1,139}$	=	1.27	$F_{1,139}$	=	1.83	$F_{1,139}$	=	3.83
	p	=	0.2610	*p*	=	0.1786	*p*	=	0.0524
DOM C:N	$F_{1,139}$	=	12.28	$F_{1,139}$	=	4.95	$F_{1,139}$	=	6.06
	p	**=**	**0.0006**	***p***	**=**	**0.0277**	***p***	**=**	**0.0151**
DOM N:P	$F_{1,139}$	=	24.47	$F_{1,139}$	=	4.12	$F_{1,139}$	=	3.47
	p	**<**	**0.0001**	***p***	**=**	**0.0444**	*p*	=	0.0646
DOM C:P	$F_{1,139}$	=	3.53	$F_{1,139}$	=	0.15	$F_{1,139}$	=	0.04
	p	=	0.0624	*p*	=	0.6979	*p*	=	0.8445
HIX	$F_{1,139}$	=	8.66	$F_{1,139}$	=	2.31	$F_{1,139}$	=	0.001
	p	**=**	**0.0038**	*p*	=	0.1307	*p*	=	0.9737
β:α	$F_{1,139}$	=	0.02	$F_{1,139}$	=	1.17	$F_{1,139}$	=	0.30
	p	=	0.8773	*p*	=	0.2817	*p*	=	0.5857
FI	$F_{1,139}$	=	7.30	$F_{1,139}$	=	5.63	$F_{1,139}$	=	0.15
	p	**=**	**0.0078**	***p***	**=**	**0.019**	*p*	=	0.6949
% C1	$F_{1,139}$	=	5.99	$F_{1,139}$	=	0.49	$F_{1,139}$	=	0.76
	p	**=**	**0.0156**	*p*	=	0.4863	*p*	=	0.3864
% C2	$F_{1,139}$	=	0.14	$F_{1,139}$	=	2.85	$F_{1,139}$	=	0.47
	p	=	0.7134	*p*	=	0.0936	*p*	=	0.4946
% C3	$F_{1,139}$	=	7.47	$F_{1,139}$	=	3.07	$F_{1,139}$	=	3.84
	p	**=**	**0.0071**	*p*	=	0.0819	*p*	=	0.0521
% C4	$F_{1,139}$	=	6.24	$F_{1,139}$	=	0.07	$F_{1,139}$	=	0.00
	p	**=**	**0.0137**	*p*	=	0.7873	*p*	=	0.9688
Growing Season PCA Component Scores									
PC1	$F_{1,137}$	=	10.11	$F_{1,137}$	=	1.29	$F_{1,137}$	=	0.06
	p	**=**	**0.0018**	*p*	=	0.2576	*p*	=	0.8145
PC2	$F_{1,137}$	=	25.64	$F_{1,137}$	=	31.28	$F_{1,137}$	=	16.55
	p	**<**	**0.0001**	***p***	**<**	**0.0001**	***p***	**=**	**0.0001**
PC3	$F_{1,137}$	=	0.11	$F_{1,137}$	=	0.02	$F_{1,137}$	=	0.81
	p	=	0.7394	*p*	=	0.8932	*p*	=	0.3688
PC4	$F_{1,137}$	=	5.84	$F_{1,137}$	=	1.73	$F_{1,137}$	=	21.68
	p	**=**	**0.0170**	*p*	=	0.1905	***p***	**<**	**0.0001**

Table 4: PARAFAC modeling statistics used to determine the optimal number of components and to assess the validity of the optimal model

No. Components	Iterations	% variance explained	Sum of squared residuals	Core consistency
2	85	98.3	2.124×10^{9}	100 %
3	91	99.2	9.339×10^{8}	96 %
4	87	99.4	7.237×10^{8}	88 %
5	211	99.6	5.118×10^{8}	< 0 %
6	1083	99.6	4.321×10^{8}	< 0 %

Table 5: Summary of four-component PARAFAC model showing two humic-like and two protein-like components. Maximum excitation and emission wavelengths are listed with secondary excitation maxima shown in parentheses.

Component	**Ex. Max (nm)**	**Em. Max (nm)**	**Description**	**DOM Source**	**EEM Region (Coble *et al.* 1990, Coble 1996)**	**Components in other studies**
C1	< 240 (355)	492	Humic-like	Terrestrial	A, C	C2 (Pagano *et al.* 2012) C1 (Stedmon and Markager 2005) C1 (Williams et al. 2010)
C2	< 240 (310)	390	Humic-like	Terrestrial, Microbial, Autochthonous	A, C	C3 (Pagano *et al.* 2012) C2 (Stedmon and Markager 2005) C3 (Williams *et al.* 2010)
C3	280 (350)	336	Tryptophan-like or protein-like	Terrestrial, Microbial, Autochthonous	T	C8 (Cory and McKnight 2005) C7 (Murphy *et al.* 2006) C4 (Stedmon and Markager 2005)
C4	265 (329)	305	Tyrosine-like or protein-like	Terrestrial, Microbial, Autochthonous	B, T	C13 (Cory and McKnight 2005) C4 (Pagano *et al.* 2012) C6 (Stedmon and Markager 2005)

Table 6: PCA results for the seasonal dataset produced 4 rotated components with eigenvalues > 1. The combined variance explained by the components was 75.8 %. Variables with principle component loadings ≥ 0.6 were considered significant and are indicated by bold type.

Variable	**PC-1 (33.7 %)**	**PC-2 (14.6 %)**	**PC-3 (14.2 %)**	**PC-4 (13.3 %)**
DOC	0.01	**0.89**	0.02	0.25
DON	0.13	-0.08	**0.88**	-0.13
DOP	-0.10	0.01	**0.83**	0.12
NO_3^-	**0.77**	0.23	0.16	0.16
NH_4^+	0.22	0.49	-0.23	0.02
PO_4^{3-}	0.26	**0.71**	0.47	0.18
HIX	**-0.87**	-0.06	0.02	-0.14
FI	0.29	0.40	-0.22	**0.59**
β:α	**0.58**	-0.17	0.02	**0.58**
% C1	**-0.89**	-0.22	-0.04	-0.13
% C2	0.15	-0.17	0.11	**0.90**
% C3	**0.93**	0.20	0.03	0.11
% C4	**0.90**	-0.01	-0.08	0.19

Table 7: PCA results for the growing season dataset produced 4 rotated components with eigenvalues > 1. The combined variance explained by each component is shown in parentheses, totaling 67.4 %. Variables with principle component loadings of 0.6 or greater were considered significant and are indicated by bold type.

	PC-1 (29.0 %)	**PC-2 (14.8 %)**	**PC-3 (11.8 %)**	**PC-4 (11.8 %)**
DOC	0.22	0.30	-0.26	**0.54**
DON	-0.06	0.23	-0.02	**0.78**
DOP	0.12	-0.29	0.11	**0.70**
NO_3^-	0.44	**0.67**	-0.17	-0.12
NH_4^+	0.28	-0.51	0.14	-0.12
PO_4^{3-}	-0.01	**0.83**	0.07	0.16
HIX	**-0.77**	0.07	0.14	-0.04
FI	0.38	0.48	0.44	-0.23
β:α	0.54	-0.16	**0.58**	-0.02
% C1	**-0.91**	-0.17	-0.13	-0.07
% C2	-0.17	-0.05	**0.89**	0.01
% C3	**0.90**	0.01	-0.14	0.16
% C4	**0.86**	0.02	0.17	0.01

Figures

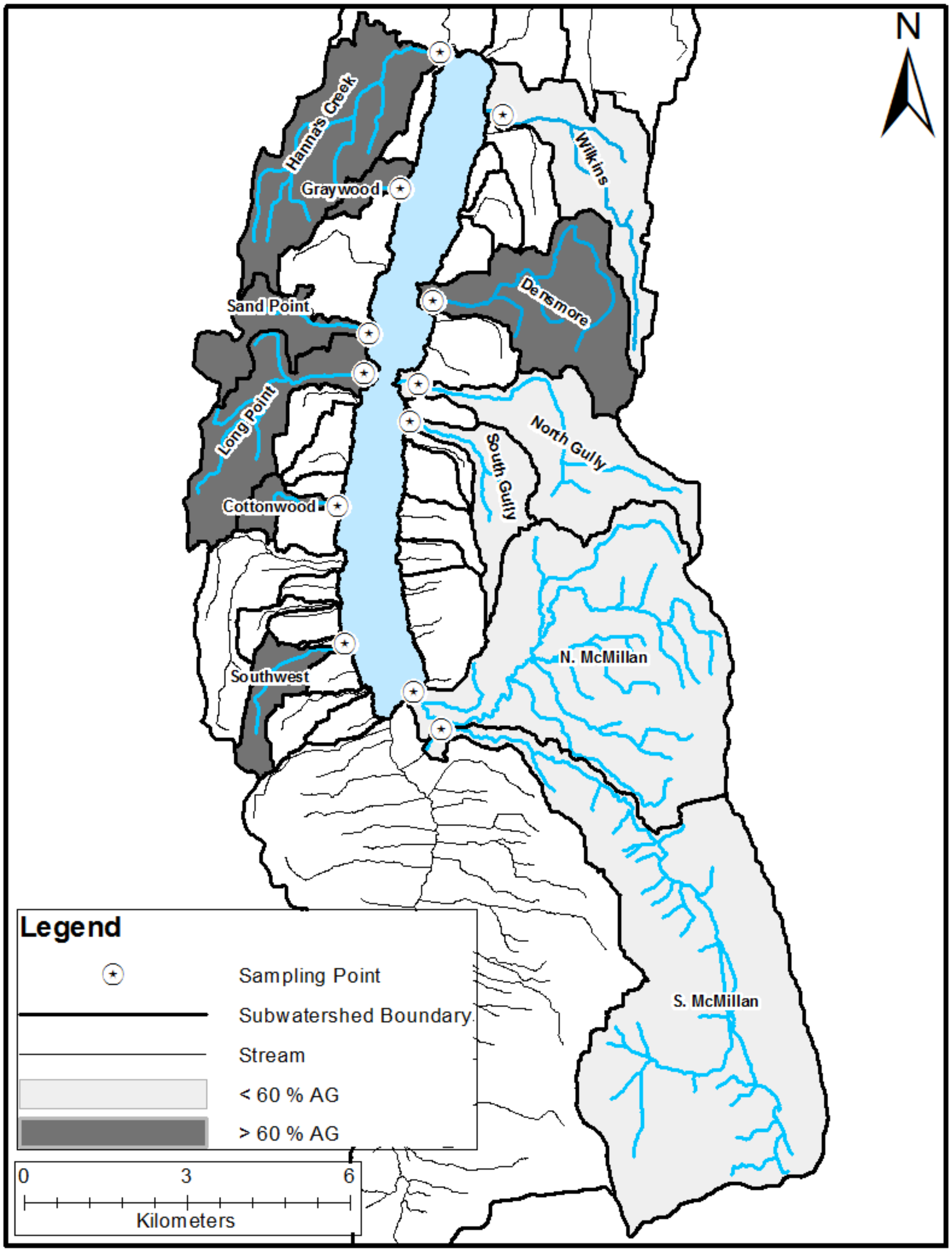

Figure 1: Study-specific subwatershed delineation map for Conesus Lake, NY. Subwatershed boundaries (black lines), subwatershed agricultural land use designation (fill), and sampling points (circles/points) for 14 streams (gray lines) are depicted in the map. The watershed consists of mixed agricultural and rural land uses, including shoreline residential development. The northern and eastern portions of the watershed are predominantly used in agriculture due to the productive soils.

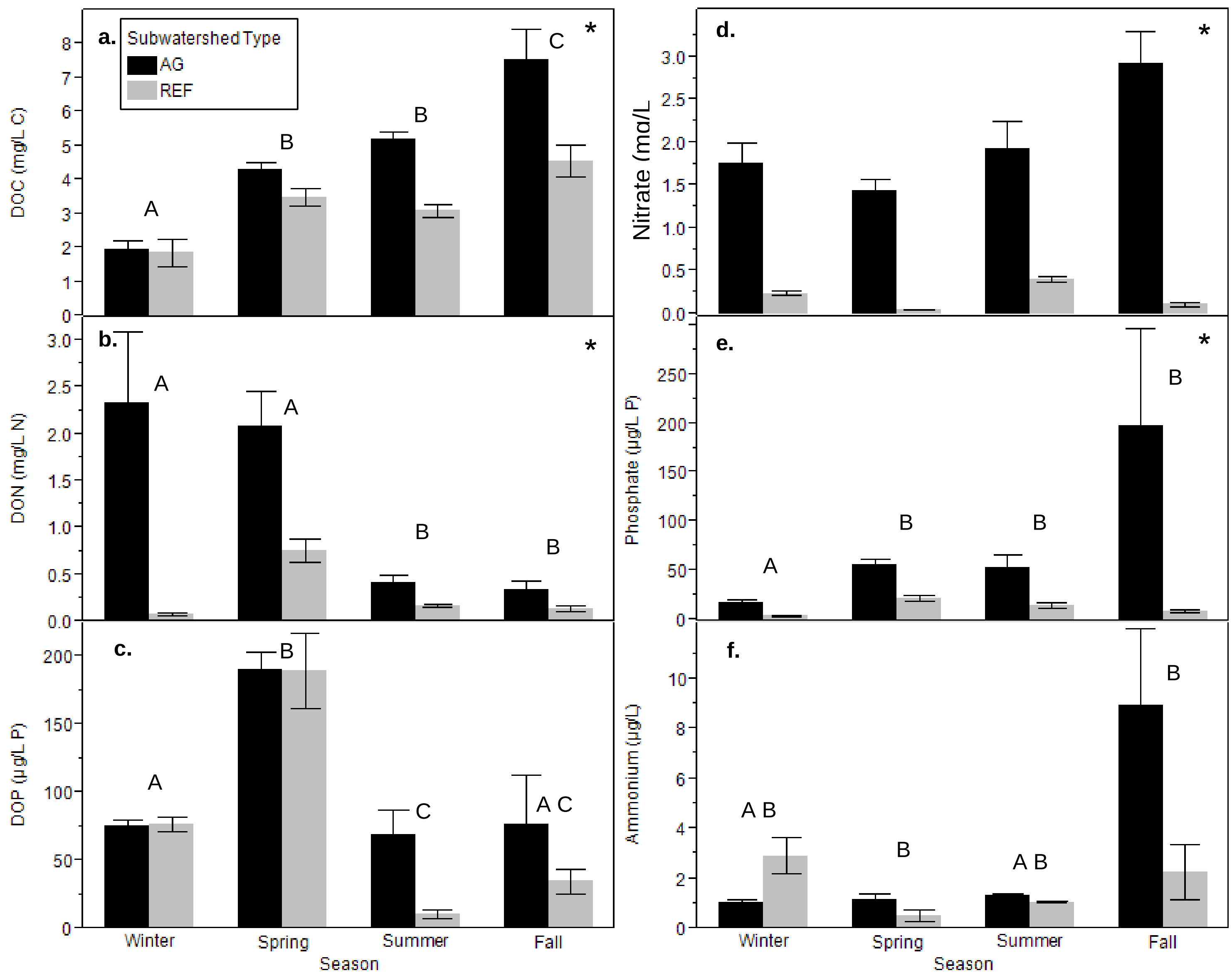

Figure 2 (a-f): Seasonal mean dissolved organic matter (**a.** DOC, **b.** DON, & **c.** DOP) and inorganic nutrient (**d.** NO_3^-, **e.** PO_4^{3-}, & **f.** NH_4^+) concentrations for 7 streams draining into Conesus Lake during 2011 with two-way ANOVA results shown. Error bars show standard error and AG streams are shown with REF streams as difference colors. Different connecting letters (capitalized) indicate a significant ($\alpha = 0.05$) effect from season, an "*" on the right of each panel indicates a significant effect from subwatershed type (AG vs. REF), and S.I. indicates a significant interaction term (Season X Subwatershed Type).

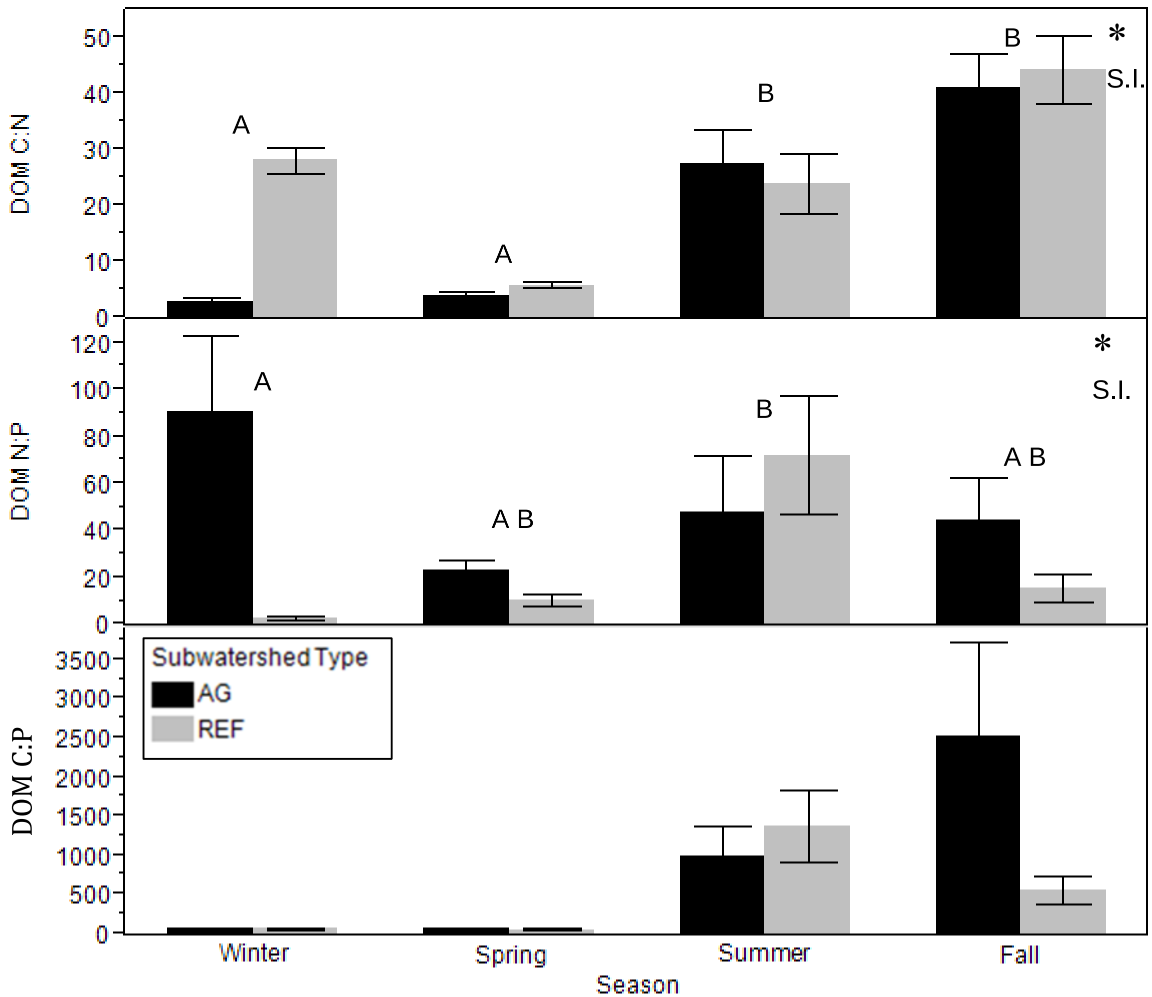

Figure 3: Mean values for DOM C:N, N:P, and C:P ratios for the seasonal dataset with two-way ANOVA results. Error bars show standard error and AG streams are shown with REF streams as difference colors. Different connecting letters (capitalized) indicate a significant ($\alpha = 0.05$) effect from season, an "*" on the right of each panel indicates a significant effect from subwatershed type (AG vs. REF), and S.I. indicates a significant interaction term (Season X Subwatershed Type).

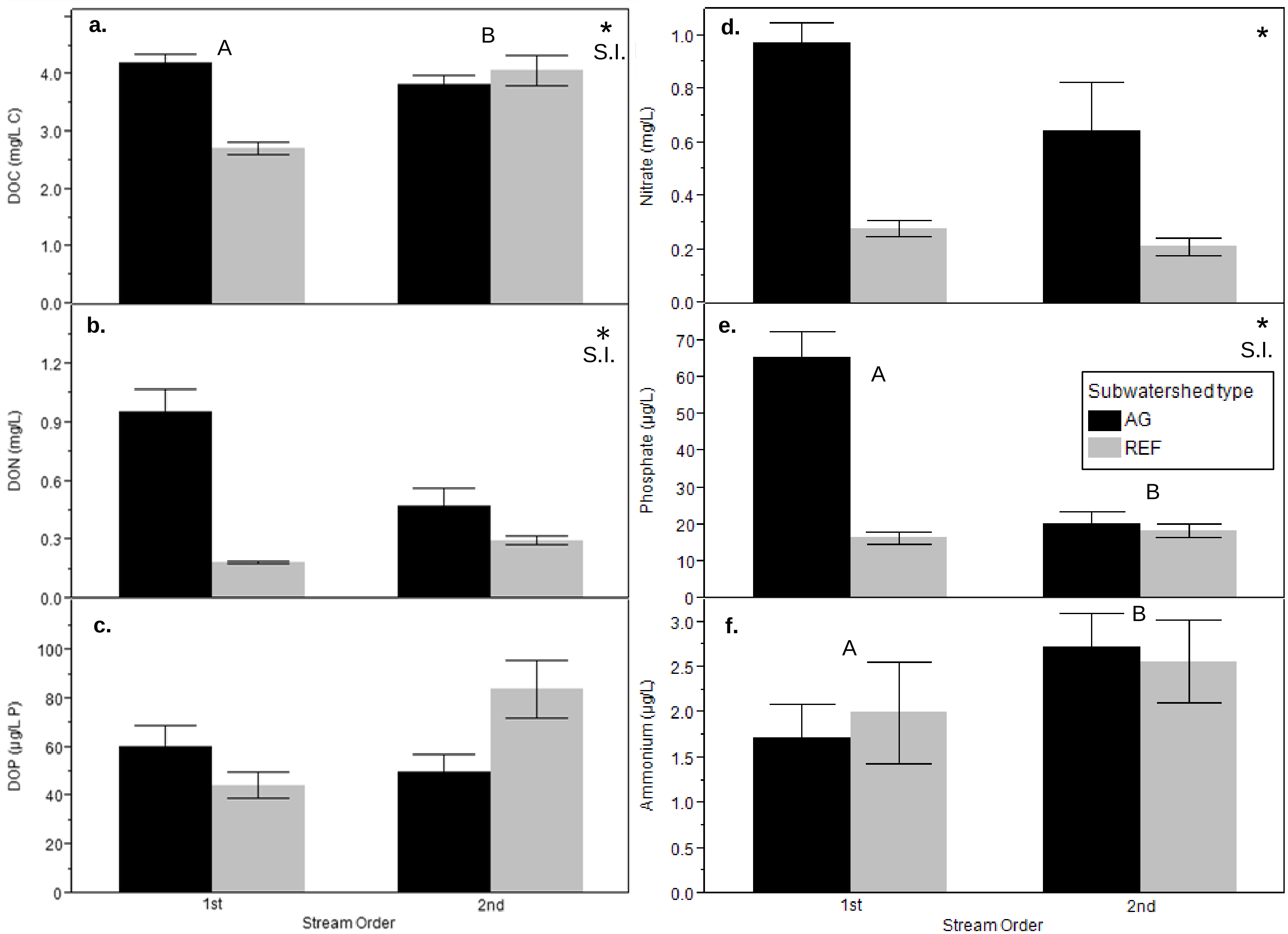

Figure 4 (a-f): 2011 growing season mean dissolved organic matter (**a.** DOC, **b.** DON, & **c.** DOP) and inorganic nutrient (**d.** NO_3^-, **e**. PO_4^{3-}, & **f**. NH_4^+) concentrations for 12 streams at Conesus Lake. Error bars show standard error and AG streams are shown with REF streams as difference colors. Different connecting letters (capitalized) indicate a significant (α = 0.05) effect from stream order, an "*" on the right of each panel indicates a significant effect from subwatershed type, and S.I. indicates a significant interaction term (Subwatershed Type X Stream Order).

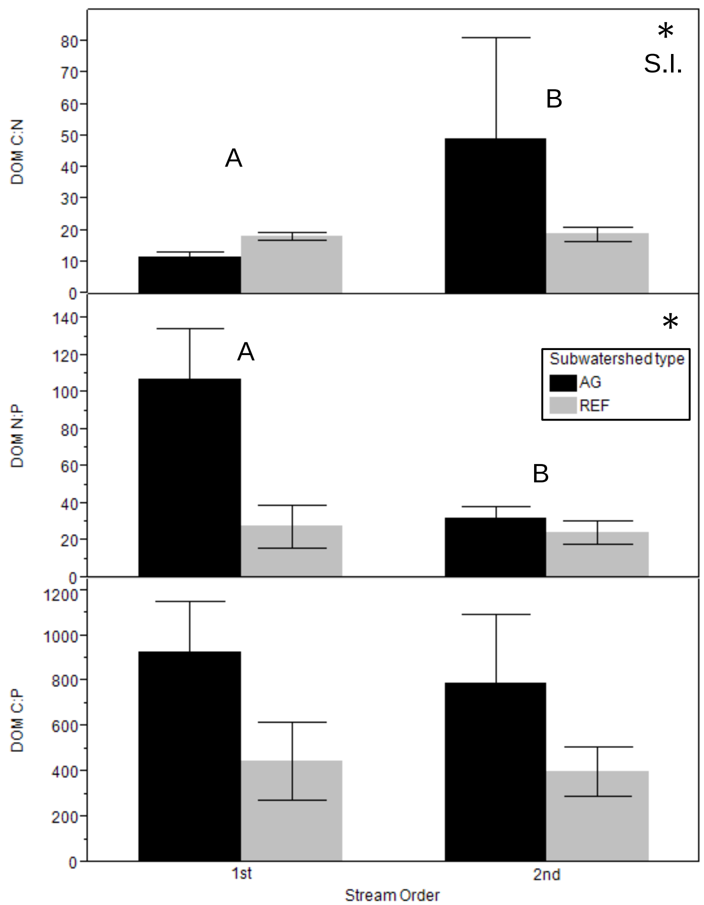

Figure 5: Mean DOM C:N, N:P, and C:P ratios for the growing season dataset with two-way ANOVA statistics. Error bars show standard error and AG streams are shown with REF streams as difference colors. Different connecting letters (capitalized) indicate a significant ($\alpha = 0.05$) effect from stream order, an "*" on the right of each panel indicates a significant effect from subwatershed type, and S.I. indicates a significant interaction term (Subwatershed Type X Stream Order).

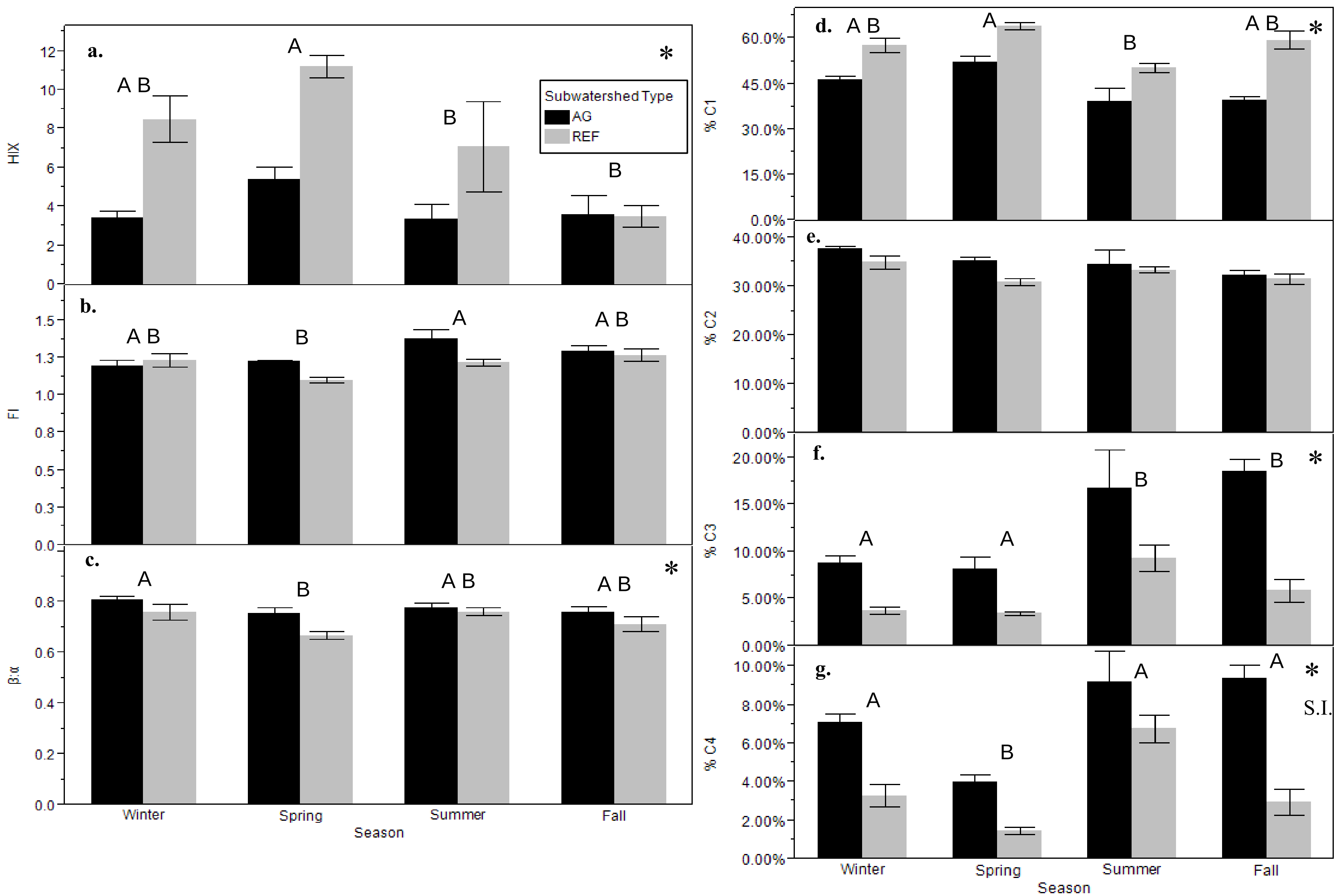

Figure 6 (a-g): Seasonal mean values with standard error (bars) for fluorescence indices (**a.** HIX, **b.** FI, **c.** β:α) and relative abundance of PARAFAC components (**d.** %C1, **e.** %C2, **f.** %C3, **g.** %C4) during 2011. AG streams are shown with REF streams as difference colors. Different connecting letters (capitalized) indicate a significant (α = 0.05) effect from season, an "*" on the right of each panel indicates a significant effect from subwatershed type (AG vs. REF), and S.I. indicates a significant interaction term from a two-way ANOVA (Season X Subwatershed Type).

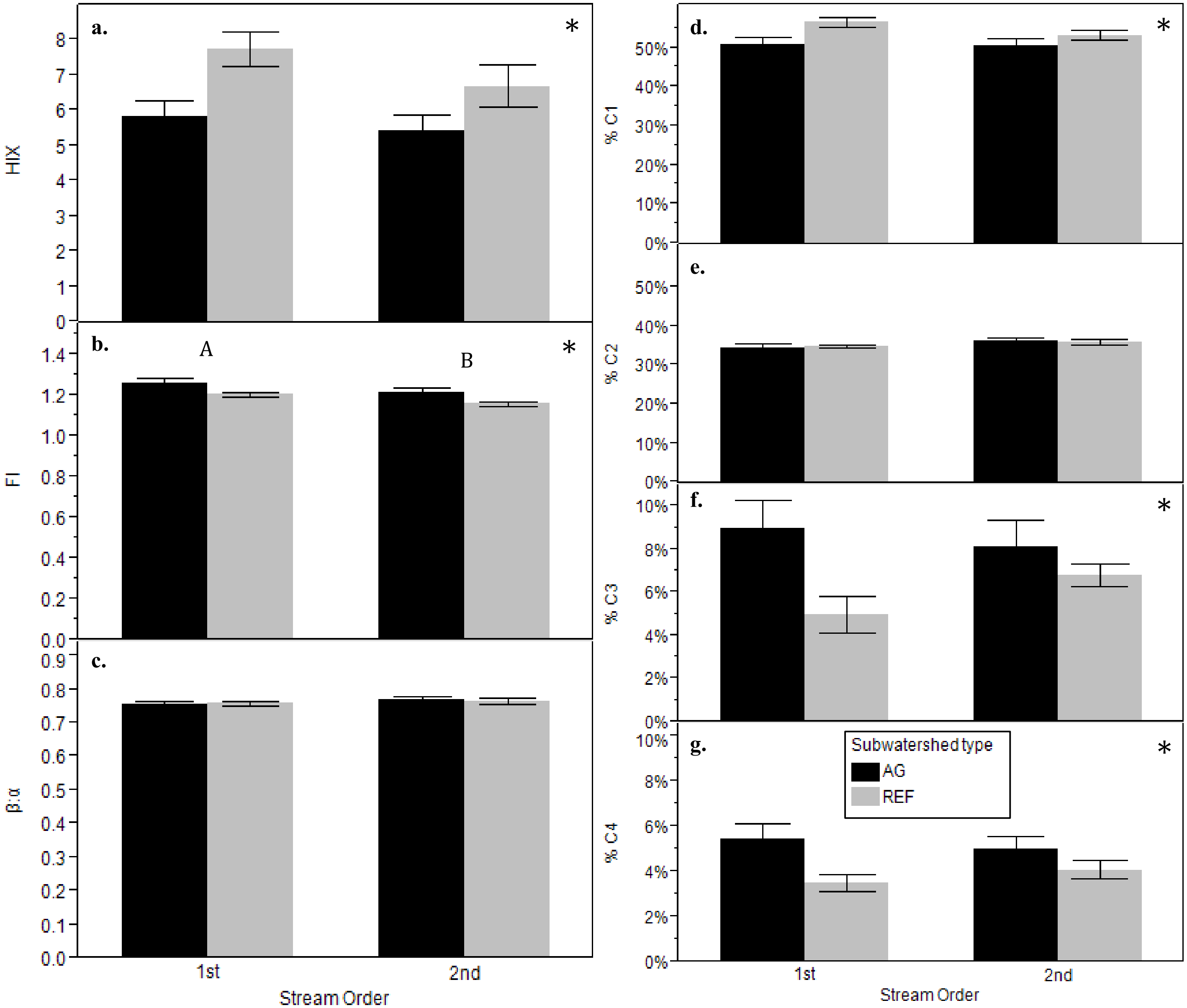

Figure 7 (a-g): 2011 growing season mean values for DOM composition parameters, showing fluorescence indices (**a.** HIX, **b.** FI, **c.** β:α) and relative abundance of PARAFAC components (**d.** %C1, **e.** %C2, **f.** %C3, **g.** %C4) during 2011. Error bars show standard error and AG streams are shown with REF streams as difference colors. Different connecting letters (capitalized) indicate a significant ($\alpha = 0.05$) effect from stream order, an "*" on the right of each panel indicates a significant effect from subwatershed type, and S.I. indicates a significant interaction term (Subwatershed Type X Stream Order).

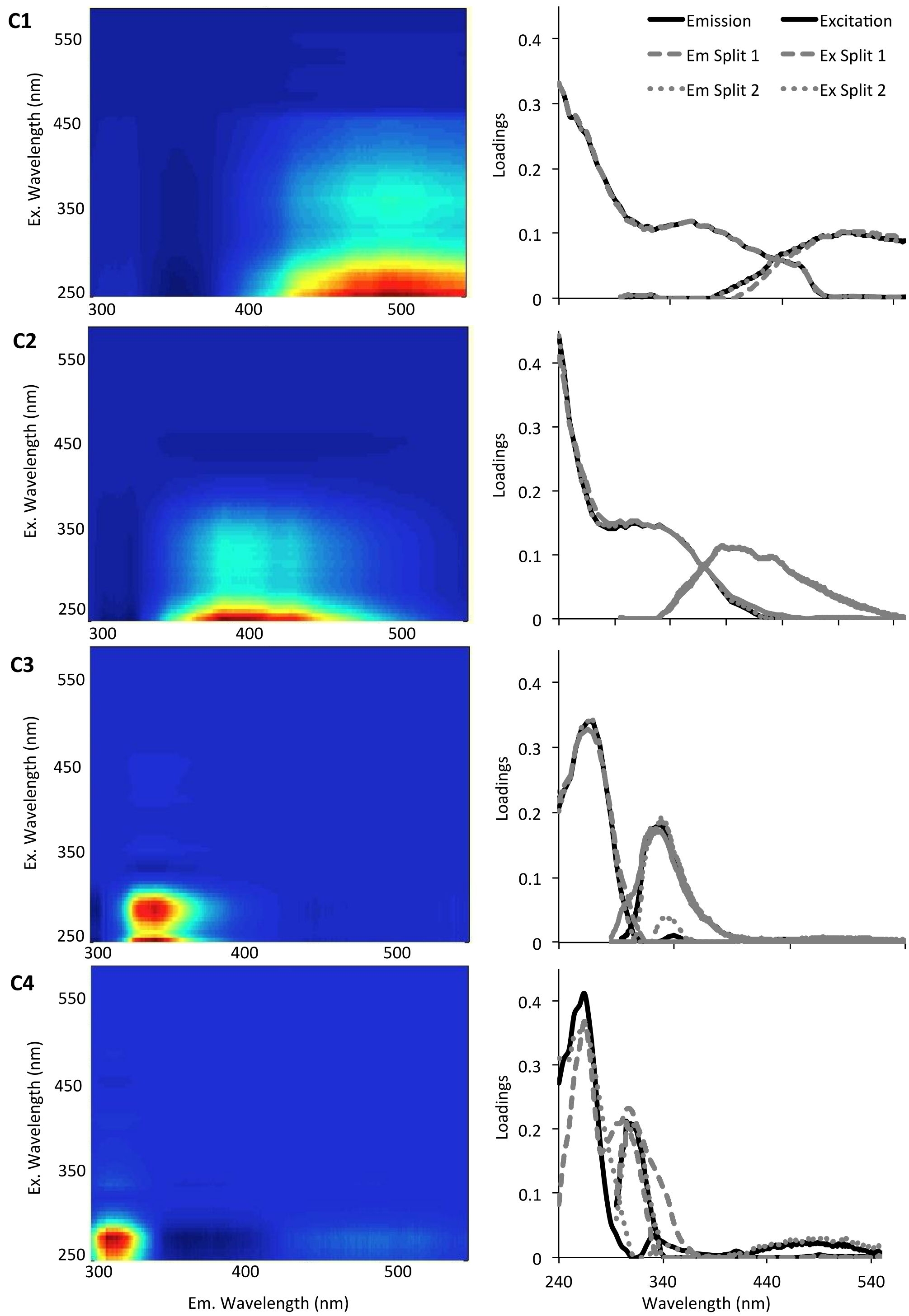

Figure 8: Modeled EEMs (left) and the excitation and emission loading spectra (right, solid lines) for a 4-component PARAFAC model generated from 225 stream samples taken in streams surrounding Conesus Lake, NY during 2010-2011. C1 is associated with humic-like DOM, C2 has associated with microbially-transformed humic-like material, while C3 and C4 are associated with protein-like fluorescence. The gray dashed lines show the similarity of two independent, four-component PARAFAC models generated using two halves (n = 112) of the whole data set

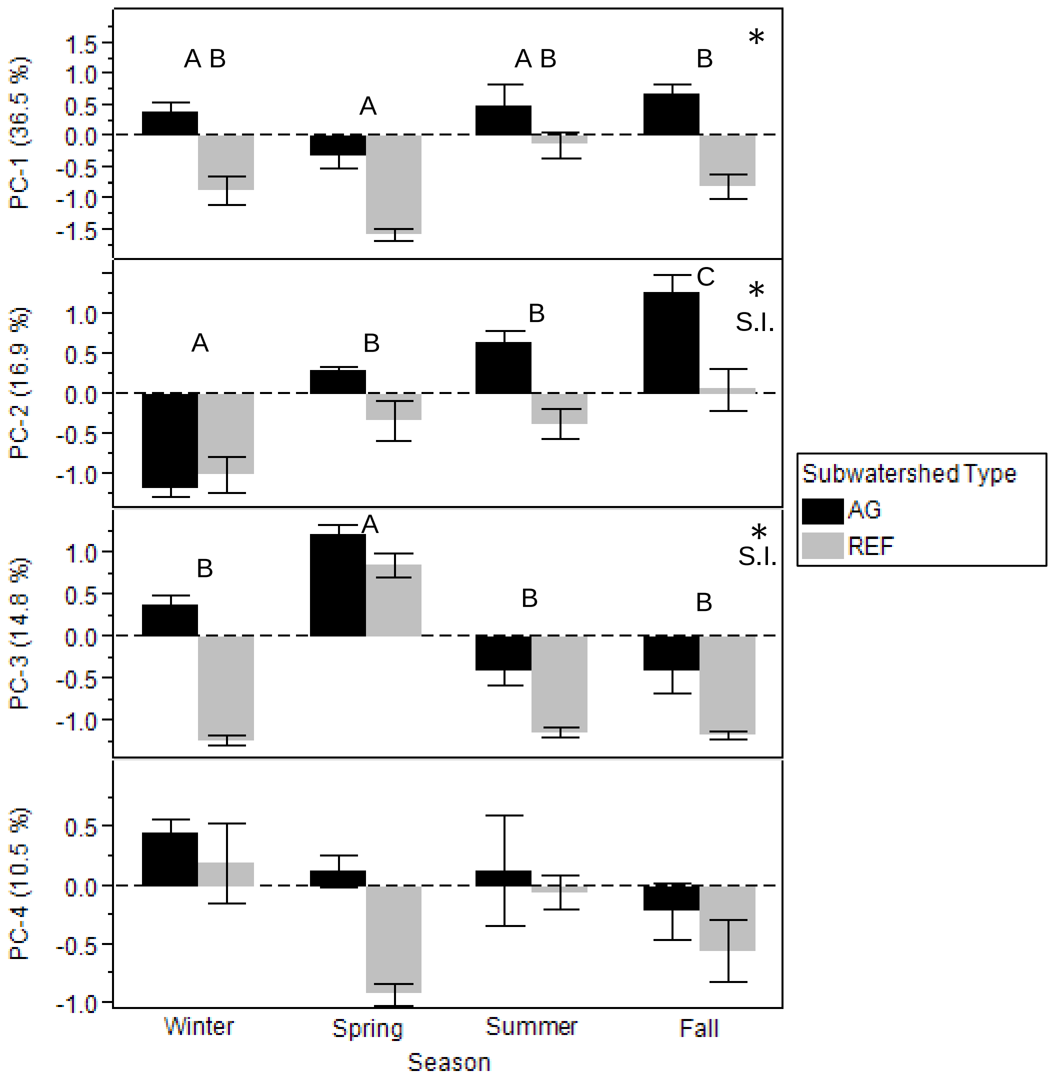

Figure 9: Mean seasonal PCA scores showing standard error (bars). Letters indicate significant differences from a two-way ANOVA with Tukey-Kramer comparison testing, where different letters indicate significant differences between seasons for each PC. An "*" indicates a significant effect from subwatershed type and S.I. indicates a significant interaction term.

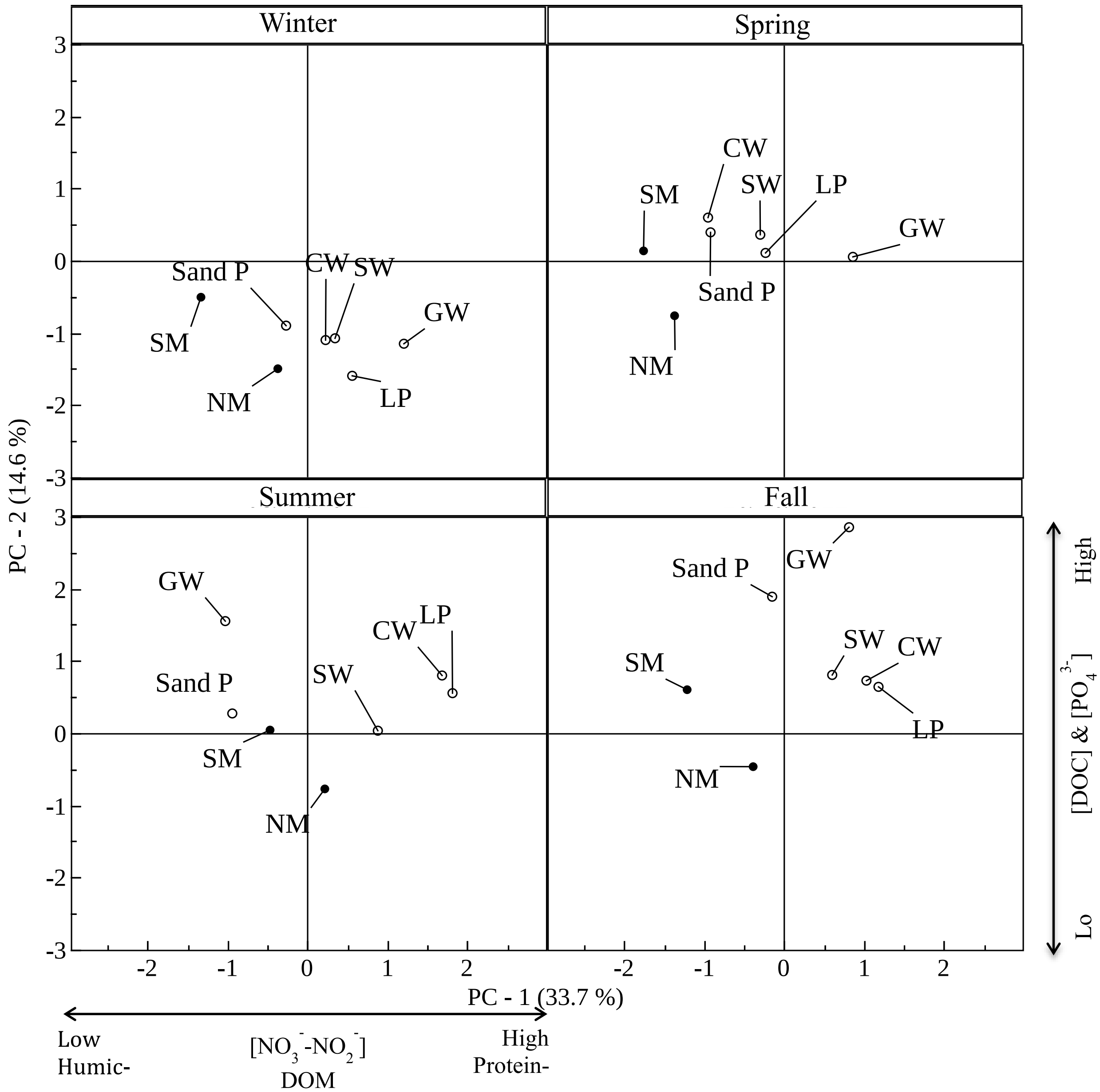

Figure 10: Principle component plots for the seasonal dataset showing PC-1 and PC-2 for each season. Mean factor scores for each stream are shown with open circles indicating AG streams and closed circles indicating REF streams. In general, REF streams appeared to show limited seasonal variability compared to AG streams.

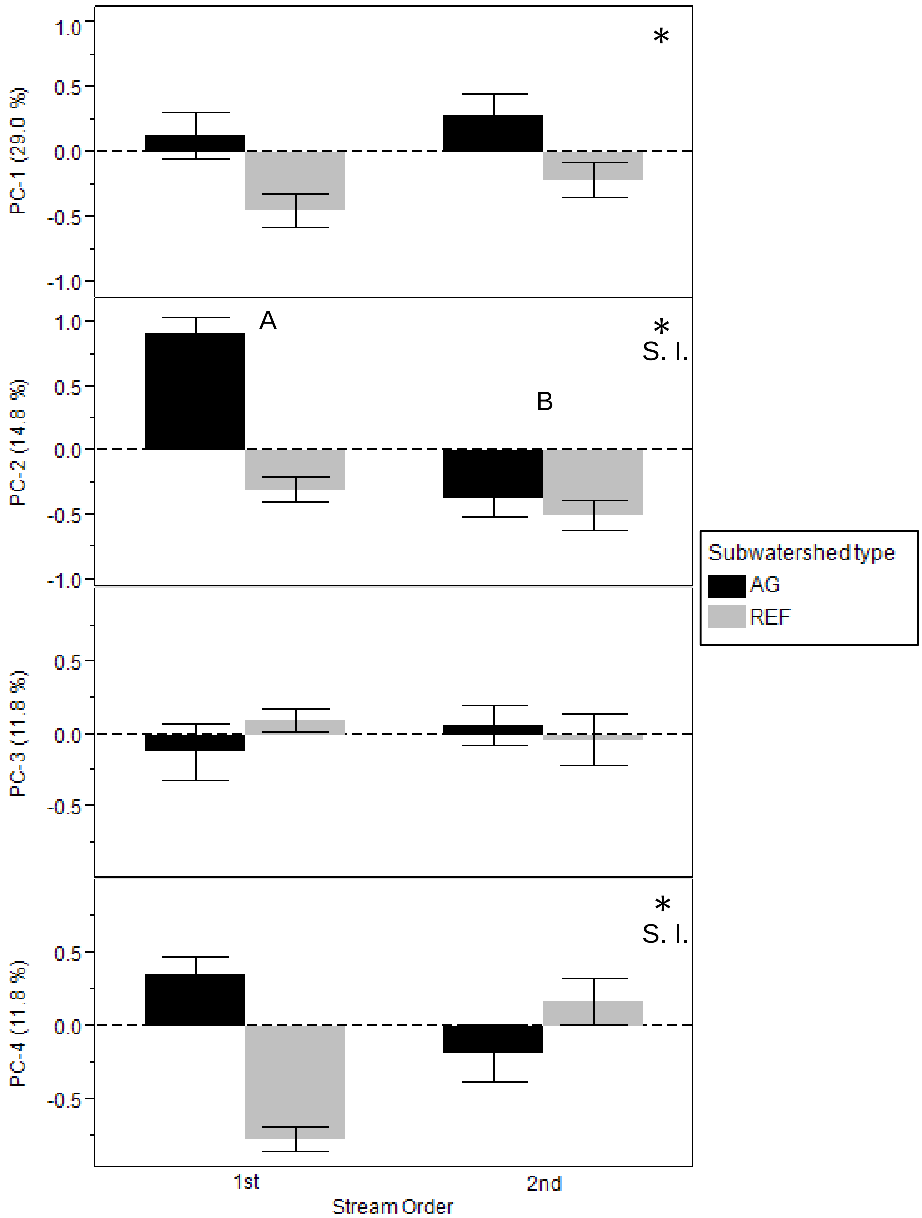

Figure 11: Mean growing season PCA scores showing standard error (bars). For two-way ANOVA results, see Table 3. PC-1 represents a gradient from humic-like fluorescence to protein-like fluorescence where positive values indicate greater protein-like and negative values indicate more humic-like. PC-2 represents inorganic nutrient concentrations where positive values indicate high inorganic nutrient concentrations. Positive values for PC-3 represent a greater contribution from % C2 and increase values for β:α. Positive values for PC-4 indicate higher concentrations of DOM (DOC, DON, DOP).

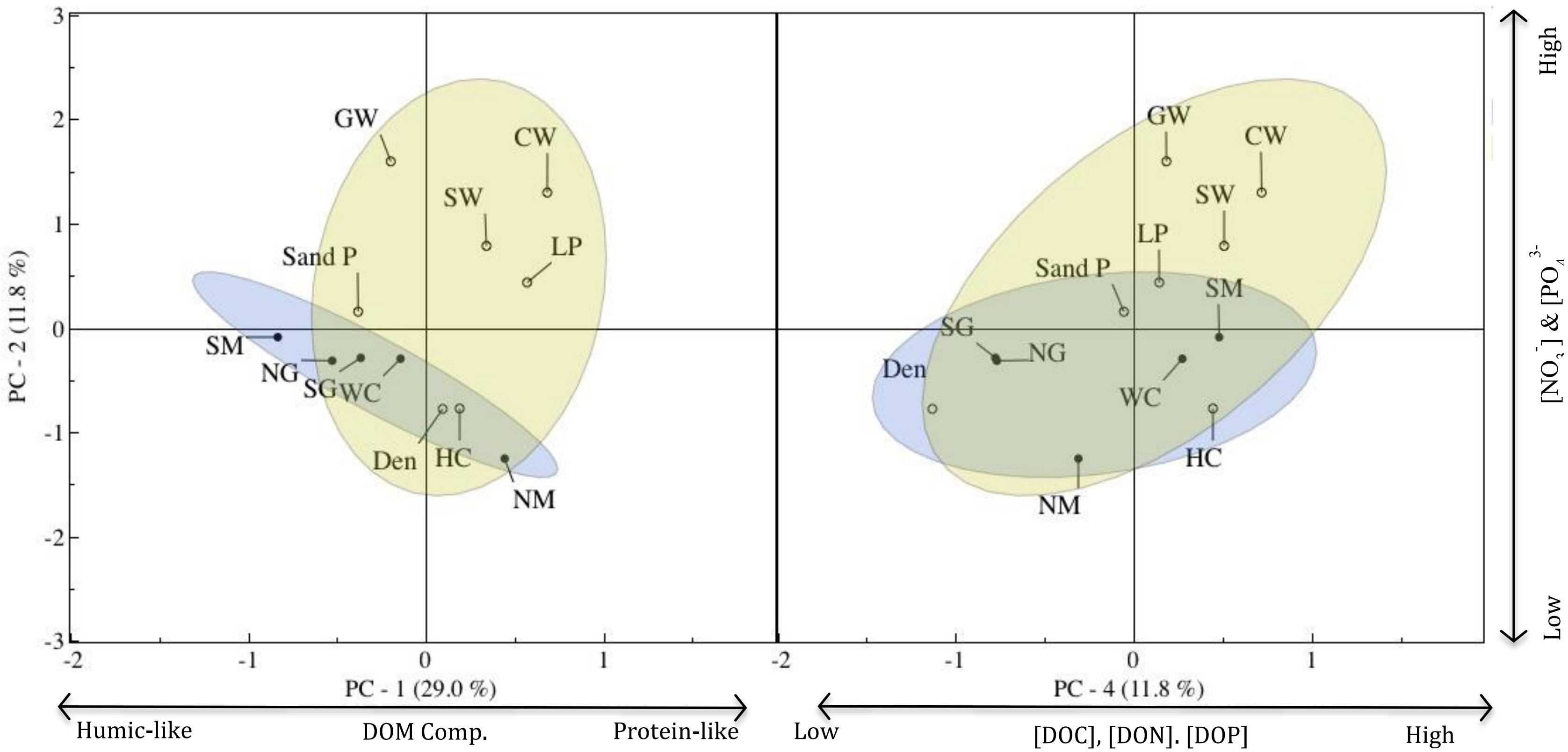

Figure 12: Principle component plots for the growing season dataset showing PC-1 vs. PC-2 and PC-4 vs. PC-2. Mean factor scores for each stream are shown with open circles indicating AG streams and closed circles indicating REF streams. Ellipses are used to show the general distribution of AG and REF stream mean PC scores and cover 90 % of the data for each category.

Appendix

Supplemental Tables

Table S 1: Soil orders for each subwatershed, shown as percent area. Soil types were determined in ArcMap 10 using data from the USDA-NRCS Soil Survey. The category "other" includes steep slopes, gravel pits, and a minimal number of water pixels.

Stream name	Subwatershed area (km^2)	Alfisols (% area)	Histosols (% area)	Inceptisols (% area)	Other (% area)
Hanna's Creek	7.62	84.4	0.0	15.7	0.1
Graywood	0.81	95.3	0.0	4.0	0.6
Sand Point	2.65	78.3	0.0	17.1	4.7
Long Point	5.40	83.8	0.0	7.4	8.7
Cottonwood	0.89	85.6	0.0	4.6	9.7
Southwest	1.91	87.9	0.0	7.2	4.9
S. McMillan	27.26	14.7	0.0	78.6	6.2
N. McMillan	20.34	23.7	0.0	62.2	14.3
S. Gully	2.95	71.8	0.0	20.7	7.7
N. Gully	6.96	68.8	2.8	18.0	10.5
Densmore	7.20	84.5	0.0	11.8	3.7
Wilkin's Creek	6.27	83.7	0.5	11.1	4.7

Table S 2: Seasonal mean (± 1 SE) values for DOM and inorganic nutrient concentrations for stream samples collected on four sampling dates.

Stream Name	N	DOC ($mg\cdot L^{-1}$)	DON ($mg\cdot L^{-1}$)	DOP ($\mu g\cdot L^{-1}$)	NO_3^- ($mg\cdot L^{-1}$)	NH_4^+ ($\mu g\cdot L^{-1}$)	PO_4^{3-} ($\mu g\cdot L^{-1}$)
				Winter (1/28/2011)			
GW	3	1.46 ± 0.10	7.74 ± 1.08	50.7 ± 6.3	3.50 ± 0.11	1.2 ± 0.3	32.6 ± 0.30
Sand P	3	3.11 ± 1.04	0.45 ±0.01	99.0 ± 6.9	0.74 ± 0.01	1.1 ± 0.2	6.8 ± 1.7
LP	3	1.41 ± 0.04	0.89 ± 0.18	82.3 ± 2.9	1.68 ± 0.01	0.8 ± 0.1	7.5 ± 2.4
CW	3	2.33 ± 0.43	1.37 ± 0.53	76.2 ± 7.2	1.50 ± 0.02	0.9 ± 0.4	13.4 ± 2.1
SW	3	1.42 ± 0.09	1.22 ± 0.06	68.5 ± 12.0	1.36 ± 0.04	1.3 ± 0.5	26.6 ± 1.5
SM	3	2.74 ± 0.04	0.12 ± 0.01	69.5 ± 7.4	0.18 ± 0.01	4.5 ± 0.2	2.5 ± 0.4
NM	3	0.97 ± 0.13	0.04 ± 0.01	83.8 ± 7.3	0.30 ± 0.01	1.3 ± 0.4	5.5 ± 0.3
				Spring (5/20/2011)			
GW	3	2.93 ± 0.03	3.48 ± 0.31	233.7 ± 5.6	1.81 ± 0.05	2.8 ± 0.2	77.6 ± 1.3
Sand P	3	4.25 ± 0.03	0.60 ± 0.02	128.1 ± 28.3	0.84 ± 0.02	0.9 ± 0.1	34.7 ± 0.3
LP	3	4.14 ± 0.04	2.03 ± 0.14	187.2 ± 15.8	1.37 ± 0.08	1.1 ± 0.4	25.5 ± 2.0
CW	3	5.10 ± 0.06	1.61 ± 0.28	225.1 ± 19.1	1.18 ± 0.16	0.6 ± 0.1	55.2 ± 0.2
SW	3	5.04 ± 0.11	2.76 ± 1.49	181.7 ± 6.3	2.04 ± 0.03	0.5 ± 0.3	85.4 ± 1.1
SM	3	4.03 ±0.06	1.01 ± 0.07	163.1 ± 26.7	0.05 ± 0.01	0.8 ± 0.4	21.4 ± 2.8
NM	3	2.94 ± 0.12	0.51 ± 0.08	216.4 ± 48.1	0.05 ± 0.01	0.3 ± 0.2	23.9 ± 5.7
				Summer (8/4/2011)			
GW	3	5.55 ± 0.03	0.41 ± 0.01	7.8 ± 3.5	0.71 ± 0.01	1.3 ± 0.1	133.7 ± 12.4
Sand P	3	4.40 ± 0.07	0.15 ± 0.01	26.3 ± 9.0	0.94 ± 0.02	1.2 ± 0.1	17.1 ± 2.4
LP	3	5.31 ± 0.06	0.09 ± 0.01	13.9 ± 5.3	4.14 ± 0.07	1.3 ± 0.1	33.8 ± 5.7
CW	3	6.29 ± 0.19	0.89 ± 0.07	128.2 ± 4.8	1.93 ± 0.07	1.4 ± 0.1	71.6 ± 2.2
SW	3	4.51 ± 0.02	0.56 ± 0.15	168.2 ± 26.2	1.88 ± 0.06	1.5 ± 0.2	11.9 ± 2.0
SM	3	3.55 ± 0.03	0.14 ± 0.03	12.0 ± 5.0	0.46 ± 0.03	1.1 ± 0.1	20.2 ± 3.7
NM	3	2.65 ± 0.04	0.20 ± 0.01	8.8 ± 4.8	0.35 ± 0.01	1.0 ± 0.1	8.7 ± 0.2
				Fall (10/20/2011)			
GW	2	9.05 ± 0.13	1.08 ± 0.17	395.0 ± 20.0	2.38 ± 0.08	34.7 ± 0.5	1075.0 ± 10.0
Sand P	3	13.05 ± 0.30	0.40 ± 0.04	35.7 ± 0.8	1.33 ± 0.03	7.4 ± 0.2	47.2 ± 3.7
LP	3	5.30 ± 0.03	0.24 ± 0.05	43.6 ± 5.7	5.26 ± 0.08	9.3 ± 0.6	28.7 ± 4.4
CW	3	6.31 ± 0.09	0.11 ± 0.01	3.4 ± 2.2	3.09 ± 0.04	0.8 ± 0.1	59.1 ± 0.5
SW	3	4.47 ± 0.02	0.11 ± 0.01	12.5 ± 1.4	2.39 ± 0.03	1.0 ± 0.1	72.5 ± 0.2
SM	3	5.59 ± 0.02	0.20 ± 0.01	16.8 ± 3.2	0.05 ± 0.01	4.0 ± 1.8	11.0 ± 0.5
NM	3	3.51 ± 0.06	0.08 ± 0.01	53.0 ± 9.4	0.18 ± 0.01	0.5 ± 0.1	7.0 ± 0.3

Table S 3: Mean (± 1 SE) seasonal DOM molar ratios C:N, N:P, and C:P, as well as total (inorganic + organic) N:P for each stream.

Stream Name	N	DOM C:N	DOM N:P	DOM C:P	Total N:P
Winter (1/28/2011)					
GW	3	0.2 ± 0.1	336.9 ± 8.2	76.8 ± 11.4	297.5 ± 8.0
Sand P	3	8.0 ± 2.7	10.3 ± 0.8	78.3 ± 22.5	25.1 ± 1.4
LP	3	2.0 ± 0.3	24.2 ± 5.5	44.2 ± 1.5	63.3 ± 4.2
CW	3	2.4 ± 0.7	37.9 ± 12.1	79.2 ± 12.5	69.8 ± 7.3
SW	3	1.4 ± 0.1	42.4 ± 8.9	56.2 ± 8.2	61.8 ± 7.8
SM	3	26.1 ± 1.2	4.0 ± 0.4	104.1 ± 11.0	9.7 ± 1.0
NM	3	30.2 ± 4.6	1.0 ± 0.1	30.4 ± 5.0	8.5 ± 0.7
Spring (5/20/2011)					
GW	3	1.0 ± 0.1	32.9 ± 2.3	32.3 ± 0.5	37.6 ± 1.3
Sand P	3	8.3 ± 0.3	11.1 ± 1.8	93.3 ± 17.5	20.5 ± 3.1
LP	3	2.4 ± 0.2	24.0 ± 0.5	57.8 ± 4.5	35.5 ± 1.6
CW	3	4.0 ± 0.8	16.3 ± 3.8	59.4 ± 5.5	22.3 ± 2.3
SW	3	3.5 ± 1.3	32.9 ± 17.3	71.6 ± 1.4	39.4 ± 11.6
SM	3	4.7 ± 0.4	15.0 ± 4.0	68.2 ± 13.5	13.8 ± 3.5
NM	3	7.1 ± 0.9	5.6 ± 1.4	38.1 ± 7.0	5.5 ± 1.3
Summer (8/4/2011)					
GW	3	15.9 ± 0.3	185.0 ± 87.1	2958.1 ± 1401.6	17.7 ± 1.2
Sand P	3	35.3 ± 2.5	14.4 ± 3.0	524.2 ± 136.7	62.2 ± 12.8
LP	3	67.4 ± 7.0	19.1 ± 6.3	1248.5 ± 353.1	196.5 ± 1.2
CW	3	8.3 ± 0.4	15.3 ± 0.8	126.7 ± 3.5	31.2 ± 0.6
SW	3	11.4 ± 3.9	7.8 ± 2.5	73.2 ± 13.1	31.4 ± 5.1
SM	3	32.6 ± 8.1	62.5 ± 47.4	1481.5 ± 914.1	45.5 ± 10.6
NM	3	15.4 ± 1.1	81.7 ± 28.8	1264.6 ± 454.1	78.8 ± 16.8
Fall (10/20/2011)					
GW	3	10.0 ± 1.7	6.0 ± 0.6	59.3 ± 3.8	5.3 ± 0.1
Sand P	3	39.1 ± 5.0	24.7 ± 2.0	945.4 ± 42.4	46.5 ± 2.1
LP	3	28.5 ± 7.3	12.1 ± 1.3	326.6 ± 50.3	175.0 ± 25.5
CW	3	70.6 ± 6.6	144.7 ± 62.5	949.0 ± 3711.9	113.3 ± 2.9
SW	3	47.6 ± 4.9	20.9 ± 4.7	948.6 ± 107.1	65.3 ± 2.1
SM	3	33.5 ± 1.3	27.9 ± 5.8	921.2 ± 161.8	20.3 ± 3.0
NM	3	55.1 ± 8.5	3.3 ± 0.4	185.6 ± 41.6	9.9 ± 1.5

Table S 4: Mean seasonal values (± 1 SE) for DOM compositional indices and PARAFAC components.

Stream Name	N	HIX	FI	β:α	C1 (%)	C2 (%)	C3 (%)	C4 (%)
				Winter (1/28/2011)				
GW	3	1.67 ± 0.47	1.26 ± 0.16	0.83 ± 0.01	39.4 ± 1.8	37.8 ± 1.0	13.0 ± 0.5	9.8 ± 0.3
Sand P	3	5.18 ± 0.09	1.17 ± 0.04	0.80 ± 0.02	53.8 ± 0.8	35.9 ± 0.6	5.2 ± 0.2	5.0 ± 0.2
LP	3	3.05 ± 0.20	1.19 ± 0.04	0.79 ± 0.04	43.8 ± 0.1	38.6 ± 1.3	9.8 ± 0.5	7.8 ± 0.4
CW	3	3.82 ± 0.16	1.17 ± 0.12	0.83 ± 0.01	49.4 ± 0.4	36.9 ± 0.7	7.5 ± 0.7	6.2 ± 0.5
SW	3	3.52 ± 0.34	1.18 ± 0.05	0.81 ± 0.02	44.8 ± 1.6	39.7 ± 0.3	9.0 ± 1.2	6.5 ± 0.4
SM	3	11.20 ± 0.23	1.14 ± 0.02	0.70 ± 0.01	63.0 ± 0.2	32.2 ± 0.2	2.9 ± 0.1	2.0 ± 0.1
NM	3	5.81 ± 0.22	1.33 ± 0.04	0.83 ± 0.01	52.8 ± 0.3	37.8 ± 0.3	4.7 ± 0.2	4.6 ± 0.2
				Spring (5/20/2011)				
GW	3	1.95 ± 0.68	1.30 ± 0.02	0.89 ± 0.02	38.2 ± 2.2	38.9 ± 0.7	16.7 ± 2.5	6.2 ± 0.8
Sand P	3	7.56 ± 0.04	1.19 ± 0.02	0.69 ± 0.01	59.5 ± 0.1	33.2 ± 0.1	4.4 ± 0.1	2.9 ± 0.2
LP	3	4.49 ± 0.13	1.23 ± 0.01	0.71 ± 0.02	52.9 ± 0.8	34.2 ± 0.4	8.6 ± 0.4	4.4 ± 0.1
CW	3	8.05 ± 0.30	1.20 ± 0.02	0.71 ± 0.01	59.6 ± 0.2	33.3 ± 0.1	4.8 ± 0.1	2.3 ± 0.1
SW	3	5.10 ± 0.19	1.20 ± 0.04	0.78 ± 0.02	51.5 ± 0.5	37.8 ± 0.1	6.4 ± 0.3	4.4 ± 0.2
SM	3	12.30 ± 0.52	1.12 ± 0.04	0.64 ± 0.01	66.4 ± 0.6	29.3 ± 0.4	3.2 ± 0.1	1.2 ± 0.2
NM	3	10.10 ± 0.32	1.09 ± 0.01	0.70 ± 0.01	61.9 ± 0.3	32.5 ± 0.2	3.8 ± 0.2	1.8 ± 0.1
				Summer (8/4/2011)				
GW	3	8.11 ± 1.01	1.55 ± 0.03	0.81 ± 0.01	39.7 ± 2.1	53.1 ± 1.7	3.2 ± 0.3	4.0 ± 0.5
Sand P	3	4.10 ± 0.13	1.12 ± 0.06	0.68 ± 0.01	66.6 ± 2.6	26.9 ± 0.8	5.0 ± 2.5	1.6 ± 0.9
LP	3	1.05 ± 0.27	1.40 ± 0.04	0.80 ± 0.04	27.6 ± 6.3	29.0 ± 3.0	28.7 ± 8.4	14.6 ± 0.9
CW	3	1.52 ± 0.97	1.40 ± 0.19	0.81 ± 0.02	27.4 ± 9.3	27.7 ± 5.1	30.9 ± 11.5	14.1 ± 3.2
SW	3	2.05 ± 0.57	1.42 ± 0.16	0.79 ± 0.06	35.4 ± 4.9	36.8 ± 4.4	16.1 ± 5.2	11.7 ± 2.3
SM	3	10.90 ± 3.43	1.22 ± 0.02	0.74 ± 0.02	52.3 ± 0.9	33.8 ± 0.6	8.3 ± 0.5	5.6 ± 0.4
NM	3	3.24 ± 0.85	1.23 ± 0.04	0.78 ± 0.02	48.6 ± 2.6	33.1 ± 1.2	10.3 ± 2.8	8.0 ± 1.0
				Fall (10/20/2011)				
GW	2	1.49 ± 0.11	1.38 ± 0.01	0.80 ± 0.01	35.6 ± 1.2	31.8 ± 0.2	24.8 ± 0.2	7.8 ± 1.2
Sand P	3	10.50 ± 0.95	1.27 ± 0.08	0.77 ± 0.06	47.3 ± 2.7	30.5 ± 0.3	14.8 ± 2.0	7.4 ± 0.5
LP	3	1.51 ± 0.01	1.16 ± 0.01	0.74 ± 0.01	39.5 ± 0.2	30.2 ± 0.1	19.3 ± 0.1	11.1 ± 0.1
CW	3	1.79 ± 0.53	1.35 ± 0.16	0.83 ± 0.06	35.9 ± 1.3	33.8 ± 4.5	21.1 ± 2.9	9.2 ± 2.4
SW	3	1.90 ± 0.15	1.33 ± 0.05	0.67 ± 0.03	38.3 ± 1.3	35.6 ± 0.5	15.1 ± 1.9	11.0 ± 0.3
SM	3	2.42 ± 0.31	1.22 ± 0.01	0.65 ± 0.01	65.7 ± 0.6	29.4 ± 0.1	3.5 ± 0.3	1.5 ± 0.2
NM	3	4.60 ± 0.40	1.32 ± 0.08	0.78 ± 0.01	53.4 ± 1.1	33.9 ± 0.1	8.3 ± 0.9	4.4 ± 0.2

Table S 5: Mean (± 1 SE) DOM and inorganic nutrient concentrations for four sampling dates during the 2011 growing season.

Stream Name	N	DOC ($mg \cdot L^{-1}$)	DON ($mg \cdot L^{-1}$)	DOP ($\mu g \cdot L^{-1}$)	NO_3^- ($mg \cdot L^{-1}$)	NH_4^+ ($\mu g \cdot L^{-1}$)	PO_4^{3-} ($\mu g \cdot L^{-1}$)
HC	12	4.70 ± 0.11	0.41 ± 0.02	42.2 ± 10.3	0.11 ± 0.02	2.8 ± 0.5	12.8 ± 1.6
GW	9	3.83 ± 0.43	1.18 ± 0.33	33.7 ± 13.6	0.80 ± 0.05	0.6 ± 0.2	107.0 ± 21.5
Sand P	12	3.62 ± 0.16	0.75 ± 0.20	60.7 ± 22.2	0.72 ± 0.09	3.7 ± 0.8	38.7 ± 8.4
LP	12	4.05 ± 0.27	0.80 ± 0.25	76.5 ± 14.8	1.47 ± 0.47	1.6 ± 0.3	38.6 ± 7.6
CW	12	5.18 ± 0.33	1.11 ± 0.24	55.3 ± 14.2	1.17 ± 0.17	0.3 ± 0.2	67.8 ± 9.1
SW	12	4.10 ± 0.20	0.85 ± 0.19	84.7 ± 17.3	1.15 ± 0.18	2.1 ± 0.9	59.6 ± 12.9
SM	12	5.35 ± 0.58	0.39 ± 0.05	68.4 ± 21.1	0.23 ± 0.05	0.7 ± 0.3	18.1 ± 2.2
NM	12	3.19 ± 0.20	0.26 ± 0.02	92.3 ± 23.5	0.11 ± 0.04	4.5 ± 1.1	8.2 ± 1.6
SG	12	2.49 ± 0.15	0.18 ± 0.01	53.1 ± 6.2	0.34 ± 0.05	2.3 ± 1.0	16.8 ± 1.9
NG	12	2.94 ± 0.15	0.19 ± 0.01	35.8 ± 8.4	0.22 ± 0.04	1.7 ± 0.5	16.2 ± 2.7
Den	12	2.73 ± 0.05	0.21 ± 0.03	32.1 ± 7.2	0.35 ± 0.05	3.7 ± 0.9	9.0 ± 1.1
WC	12	3.69 ± 0.13	0.25 ± 0.02	91.5 ± 17.3	0.29 ± 0.06	2.5 ± 0.4	29.1 ± 2.8

Table S 6: Mean (± 1 SE) DOM C:N, N:P, and C:P molar ratios as well as total N:P during the 2011 growing season

Stream Name	N	DOM C:N	DOM N:P	DOM C:P	Total N:P
HC	12	13.5 ± 0.3	39.7 ± 7.9	536.6 ± 112.0	31.6 ± 5.2
GW	9	7.5 ± 2.2	216.5 ± 84.8	1713.8 ± 670.7	34.3 ± 7.4
Sand P	12	15.0 ± 4.1	61.0 ± 17.5	709.1 ± 291.9	50.0 ± 10.3
LP	12	23.3 ± 8.0	22.0 ± 4.6	393.0 ± 167.1	69.5 ± 22.7
CW	12	10.6 ± 2.6	138.2 ± 74.7	1254.0 ± 561.7	45.7 ± 6.0
SW	12	11.9 ± 3.0	40.5 ± 15.4	231.2 ± 82.2	34.6 ± 5.2
SM	12	19.1 ± 3.1	37.2 ± 14.4	628.0 ± 257.3	26.2 ± 5.5
NM	12	14.8 ± 0.4	26.0 ± 11.6	396.3 ± 181.0	25.1 ± 10.1
SG	12	17.7 ± 1.8	8.5 ± 1.2	148.0 ± 25.4	19.2 ± 2.9
NG	12	18.5 ± 1.5	47.2 ± 22.2	745.7 ± 332.5	21.8 ± 3.0
Den	12	110.7 ± 95.8	34.4 ± 17.2	1447.0 ± 881.5	62.9 ± 21.6
WC	12	22.6 ± 5.8	10.5 ± 2.4	182.4 ± 47.3	10.6 ± 0.9

Table S 7: Mean (± 1 SE) values for DOM compositional indices and PARAFAC components for the 2011 growing season.

Stream Name	N	HIX	FI	β:α	C1 (%)	C2 (%)	C3 (%)	C4 (%)
HC	12	4.90 ± 0.25	1.14 ± 0.04	0.78 ± 0.01	49.8 ± 1.8	37.4 ± 1.5	8.2 ± 0.3	4.6 ± 0.3
GW	9	6.58 ± 0.77	1.37 ± 0.05	0.79 ± 0.01	47.3 ± 2.4	43.1 ± 2.5	5.0 ± 0.8	4.6 ± 0.5
Sand P	12	7.32 ± 0.68	1.18 ± 0.02	0.71 ± 0.01	60.3 ± 1.6	30.4 ± 0.7	6.1 ± 1.0	3.2 ± 0.5
LP	12	5.23 ± 0.89	1.26 ± 0.03	0.76 ± 0.02	48.9 ± 4.2	33.2 ± 1.1	11.4 ± 3.5	6.5 ± 1.5
CW	12	4.48 ± 1.02	1.23 ± 0.05	0.77 ± 0.02	45.9 ± 4.5	31.5 ± 1.3	14.9 ± 4.0	7.8 ± 1.8
SW	12	5.15 ± 0.81	1.27 ± 0.05	0.77 ± 0.02	49.4 ± 3.0	35.4 ± 1.0	9.0 ± 1.8	6.1 ± 1.3
SM	12	9.06 ± 1.19	1.12 ± 0.02	0.70 ± 0.01	60.4 ± 1.5	32.2 ± 0.5	4.9 ± 0.6	2.5 ± 0.6
NM	12	3.88 ± 0.36	1.15 ± 0.03	0.80 ± 0.02	49.6 ± 1.2	34.9 ± 0.5	9.0 ± 0.9	6.5 ± 0.5
SG	12	7.54 ± 0.81	1.21 ± 0.02	0.77 ± 0.01	55.7 ± 2.4	34.8 ± 0.3	5.7 ± 1.7	3.8 ± 0.7
NG	12	7.94 ± 0.56	1.20 ± 0.01	0.75 ± 0.01	57.5 ± 1.2	35.0 ± 0.8	4.2 ± 0.4	3.2 ± 0.2
Den	12	6.11 ± 1.13	1.24 ± 0.02	0.78 ± 0.01	53.4 ± 1.0	37.9 ± 0.3	4.7 ± 0.5	4.0 ± 0.4
WC	12	7.13 ± 0.77	1.19 ± 0.02	0.80 ± 0.01	49.6 ± 1.9	40.7 ± 0.8	6.5 ± 0.8	3.2 ± 0.4

Supplemental Figures

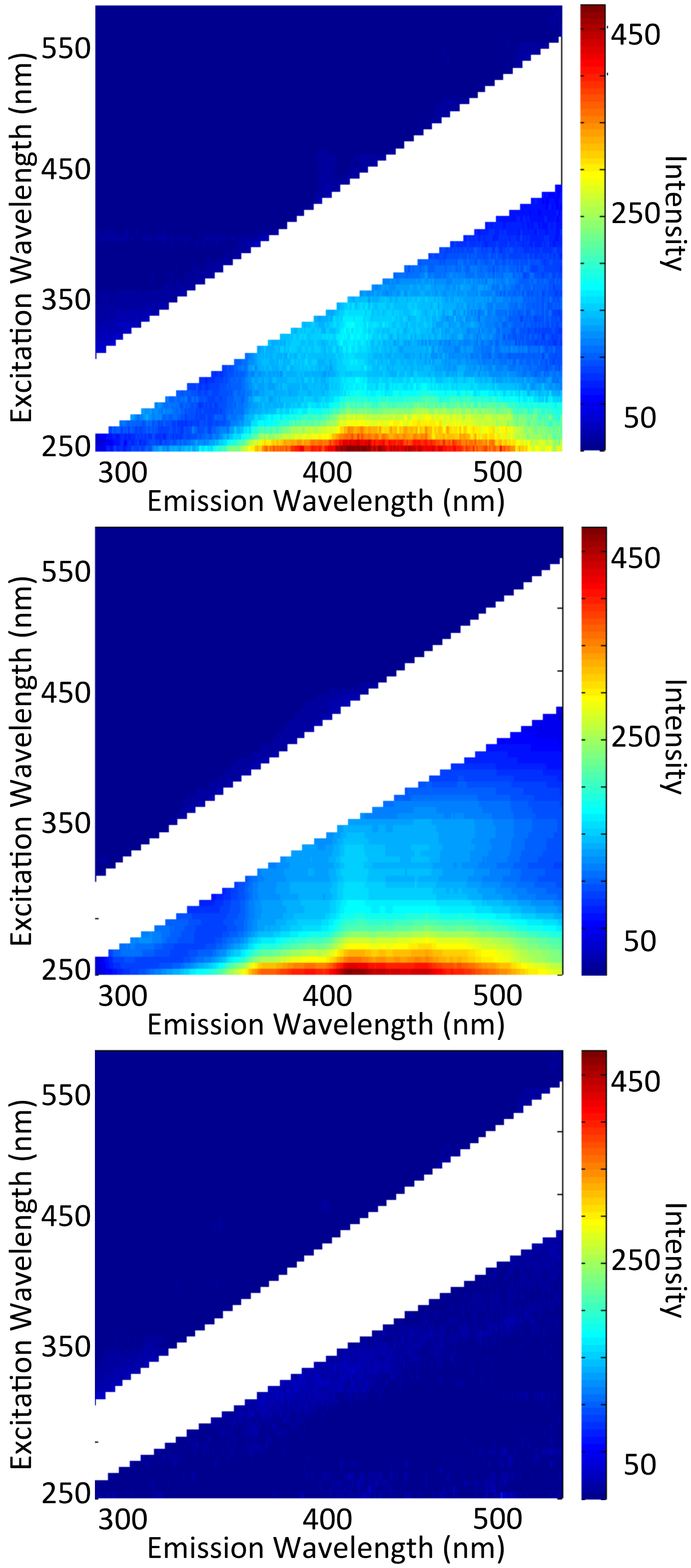

Figure S1: EEMs from Cottonwood stream (sampled on 01/28/2011) showing a corrected EEM (top), a PARAFAC modeled EEM (middle) and a PARAFAC residual EEM (bottom). The fluorescence intensity is shown in relative fluorescence units.

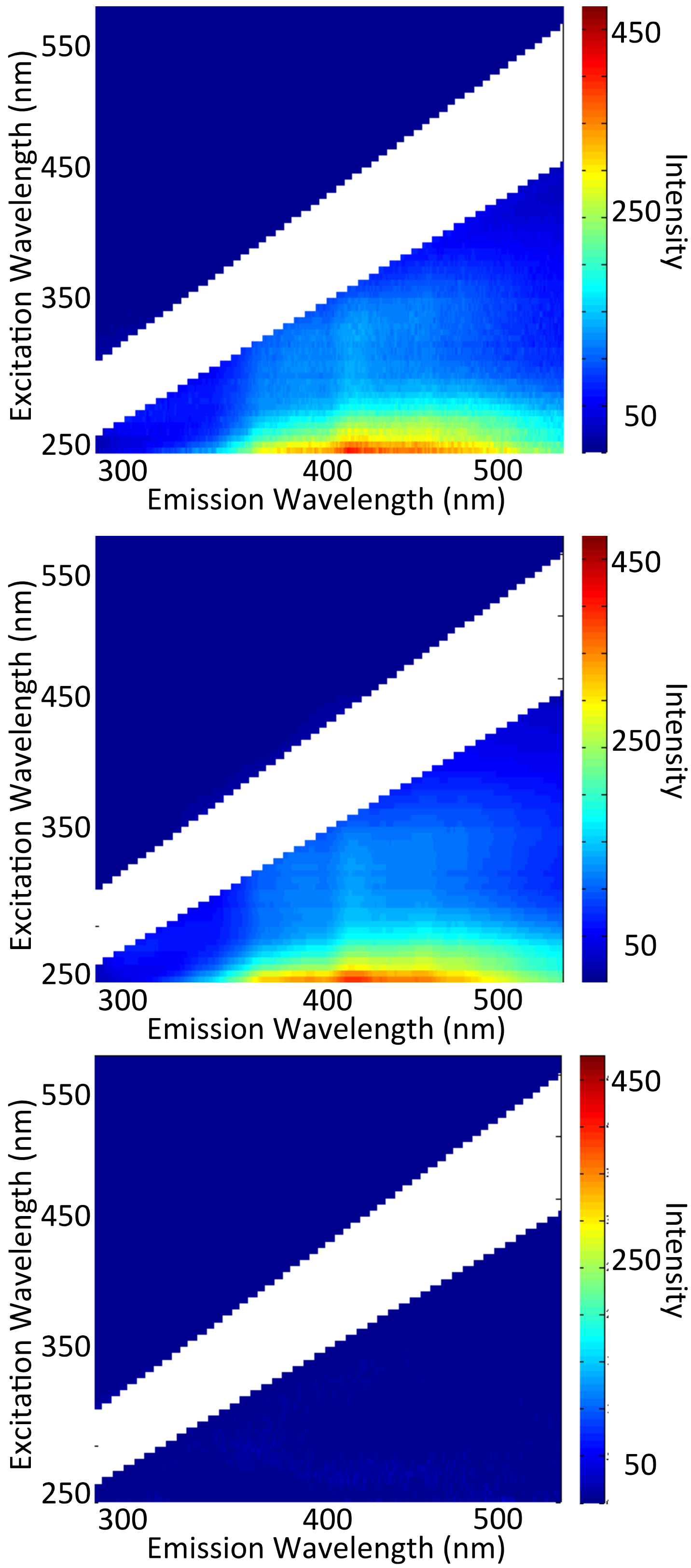

Figure S2: EEMs from Densmore stream (sampled on 09/21/2011) showing a corrected EEM (top), a PARAFAC modeled EEM (middle) and a PARAFAC residual EEM (bottom). The fluorescence intensity is shown in relative fluorescence units.

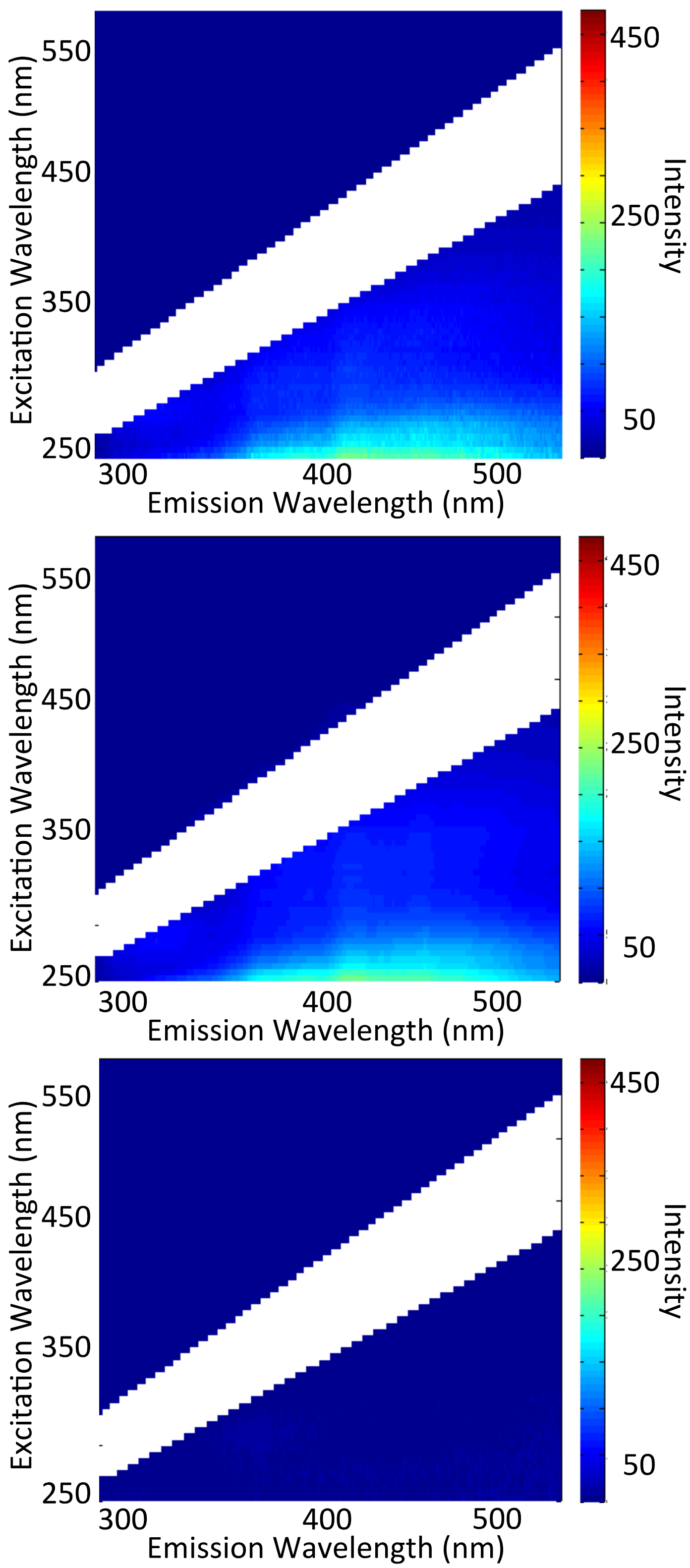

Figure S3: EEMs from North McMillan stream (sampled on 06/21/2011) showing a corrected EEM (top), a PARAFAC modeled EEM (middle) and a PARAFAC residual EEM (bottom). The fluorescence intensity is shown in relative fluorescence units