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Biogeochemical cycling of restored and unrestored wetlands of Lake Ontario

By

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TABLE OF CONTENTS

CHAPTER 1: Nitrogen and phosphorus processing in restored and unrestored coastal wetlands of Lake Ontario

CHAPTER 2: Drivers of dissolved organic matter composition across Lake Ontario coastal wetlands and their tributaries

ABSTRACT

Wetlands provide many ecosystem services, including carbon burial and nutrient pollution remediation from excessive anthropogenic inputs. In response to loss and degradation of Laurentian Great Lake coastal wetlands, restoration efforts along the southern shore of Lake Ontario in recent years aimed to improve habitat quality and biodiversity. It is currently unclear if these restorations impacted biogeochemical processes of key nutrients such as nitrogen (N), phosphorus (P), and carbon. To determine if restoration improved nutrient retention from terrestrial inputs and what factors drive dissolved organic matter (DOM) composition, I analyzed water chemistry, watershed land use, and hydrological connectivity of four restored and four unrestored wetlands over the growing season of 2017 under storm and base flows. All wetlands showed nutrient retention abilities with lower N and P concentrations than their tributaries, but unrestored wetlands had significantly higher nutrient loading and reduction. DOM composition was not significantly affected by restoration, but restored wetlands contained higher concentrations of DOM. N was best removed in the spring, and P was best removed in the fall, with some variation across flow condition. DOM concentration was higher during storm flow and DOM character increased in microbial-like components from spring to fall. DOM, N, and P concentrations correlated positively with agricultural land use across wetlands. The control of watershed-scale land use on downstream water quality coupled with unusually wet conditions of 2017 when these wetlands were sampled may explain why small-scale recent habitat restoration did play a more significant role in N, P, and DOM dynamics. Studying biogeochemistry in wetlands under finer spatial and temporal resolutions over longer time periods may contribute information for future restorative efforts and management practices imposed on Great Lakes coastal wetlands to preserve their health and value.

LIST OF TABLES

CHAPTER 1

CHAPTER 2

LIST OF FIGURES

CHAPTER 1

CHAPTER 2

LIST OF APPENDICES

GENERAL INTRODUCTION

Wetlands link terrestrial and aquatic environments at the land-water interface and provide many ecosystem services, including filtration and improvement of water quality, moderation of floodwater flows, and extensive biodiversity support. Globally, more than half of natural wetlands have been lost in the past 200 years through water-source diversion or land use conversion for agriculture or otherwise developed for human uses, and those that remain are commonly degraded (Dugan, 1993; Mitsch and Gosselink, 2000; Zedler and Kercher, 2005). Invasive species and excessive nutrient loading from the landscape reduce habitat quality for fish and wildlife and dampen ecosystem services and functions of wetlands (Morrice et al., 2004). In US freshwater systems, approximately 40% of fish, 70% of mussel, 50% of crayfish, 40% of stonefly, and 40% of amphibian species have gone or may soon go extinct, in part to water quality issues from nutrient loading. (US EPA, 2009). To combat these concerns of degraded habitat and species loss, wetland restoration has commonly aimed to reduce invasive species, improve habitat quality and suitability for native vegetation, fish, and wildlife, and increase hydrological connectivity (Wilcox and Whillans, 1999; Mitch and Wang, 2000).

Coastal wetlands function as biogeochemical reactors, with high rates of productivity and the ability to buffer downstream habitats from terrestrial nutrient inputs from the watershed, through transformation, removal, and storage (Mitsch and Reeder, 1991; Heath, 1992; Mitsch and Wang, 2000; Saunders and Kalff, 2001; Fisher and Acreman, 2004). In wetlands, nutrient removal is often considered a function of several important factors: nutrient loading, hydrologic residence time, geomorphic type, landscape position, watershed land use, and soil and biotic composition (Howard-Williams, 1985; Whigham et al., 1988; Reddy et al., 1999; Mitsch and Gosselink, 2000). The ability of wetlands to remove nutrients can be observed through close examination of storage compartments and by following input-output nutrient concentrations (i.e., a black box approach), such as this study, which treats the whole wetland as a storage compartment (Johnston, 1991).

Nitrogen (N) and phosphorus (P) in aquatic systems commonly originates from terrestrial sources of effluents from municipal and industrial wastewater, fertilizer application to croplands, and concentrated livestock waste. N and P are transported through surface runoff and interact with sediment and vegetation along the flow path. Nutrient enrichment increases primary production to excessive levels, leading to overgrowth of algae, hypoxic conditions, potentially noxious cyanobacterial algal blooms, and increased water treatment costs (Carpenter et al., 1998; Correll, 1998). Terrestrial-sourced nutrient pollution associated with agricultural land use has also been linked to macrophyte community structure changes (composition and density) and reduced fish and invertebrate abundance in Great Lakes coastal wetlands (Schock et al., 2014; Alvarez et al., 2017). As human activities continue to alter nutrient cycles, the ability to predict the impact of increased nutrient loading to freshwater systems is becoming more important (Saunders and Kalff, 2001).

N is removed through denitrification, biotic uptake form bacteria, algae, and macrophytes, and adsorbed to sediments, while P is retained by chemical precipitation in the water column, biotic assimilation, and sediment adsorption (Richardson, 1985; Saunders and Kalff, 2001). Although N retention can vary widely (11-94%), wetlands typically retain twice the amount of delivered N per unit area as lakes, averaging 64% retention of input (Saunders and Kalff, 2001; Morrice et al., 2004) and P retention is typically high in wetlands— between 40 and 90% (Reddy et al., 1999; Mitsch and Gosselink, 2007). Retention capacity of P in wetlands is generally regulated by vegetation, plankton, detrital accumulation, soil physio-chemical properties (e.g., pH, redox state, organic matter, and extractable elemental composition), P loading, and hydrologic fluctuations (Richardson, 1985; Reddy and DuLaune, 2008). Unlike N, P tends to accumulate in wetlands because there is no significant gaseous removal mechanism and occluded P in particulate materials is buried in sediment for long-term storage. The linkage wetlands serve between terrestrial and aquatic environments, coupled by natural nutrient retention properties provide a potential to use wetlands as a measure of control on excessive anthropogenic nutrient input.

N and P have long been the main macronutrients studied for biogeochemistry since all biota depend on them for cellular processes, but more recently dissolved organic matter (DOM) has been considered as a major biogeochemical mediator in aquatic-terrestrial linked systems. There is a management focus on N and P with the potential use of wetlands as a tool to reduce nutrient loading to eutrophic bodies. However, DOM research often focuses on describing composition to understand the roles DOM plays in ecosystem functions and the implications of human activities on those roles. This thesis contains two chapters, separated by the management focus on

N and P and the descriptive focus on DOM.

The bulk of aquatic DOM pools commonly originates externally from the terrestrial environment as products of decomposing organisms, plant exudates and leachates, and soil microbial biomass. Internally produced DOM from photosynthetic fixation by algae, bacteria, and macrophytes is also released to the surrounding water via subsequent exudation by in-system metabolism of biota (i.e., predatory grazing, cell death, extracellular release). Chemical structure and reactivity of DOM is often defined by source. Terrestrial-derived materials tend to be larger, more complex-aromatic structures (cyclic, stable, planar molecules with many resonance bonds) with greater amounts of humic substances (e.g., lignins, tannins, melanins) than DOM produced internally, which often reflects microbial and protein-like properties of freshly produced, simpler, and smaller compounds with lower molecular weight (e.g., amino acids and sugars). The bioavailability and extent to which DOM is metabolized depends largely on biochemical composition of the carbon pool, nutrient loading, and ambient environmental conditions (Amon and Benner, 1996; Kalbitz et al., 2003; Fellman et al., 2008). Once in the aquatic system, DOM can be altered by various pathways beyond primary production and microbial breakdown, such as sorption to particles and photodegradation. DOM plays an important role in aquatic ecosystem biogeochemistry as it can modulate the fate of other materials and processes by affecting light penetration into the water column, buffer pH change, fuel trophic webs as a carbon and N food source, and act as a medium for the transfer of trace metals and contaminants (Keil and Kirchman, 1991; Wetzel, 1992; Driscoll et al., 1995; Morris et al., 1995;

Palmer et al., 2005; Yamashita et al., 2010).

Most wetland soils tend to accumulate organic matter and serve as a carbon sink through build-up of particulate organic matter (POM) as production rates through carbon fixation often exceed rates of decomposition in anaerobic conditions of flooded soils (Reddy et al., 2000). Concentrations of DOM are high in wetlands due to leaching and decomposition of POM into DOM, which is usually rich in humic-like and structurally complex properties (Biers et al., 2007; Eimers et al., 2008; Graeber et al., 2012). Where wetlands have been lost to agriculture, it can be expected that DOM will be metabolized at faster fates from increased nutrient loading and microbial activity, which can change productivity rates and trophic interactions. In addition to wetland loss, the wetlands that remain are often in poor, eutrophic conditions (Zedler and Kercher, 2005; Trebitz et al., 2007; Morrice et al., 2008). The quality of DOM found in streams draining urban and agricultural watersheds can have different properties of biodegradability than DOM in less human developed areas as an observed shift from terrestrial humic substances in forest-dominated watersheds to more synthetic smaller molecular compounds in human-impacted watersheds (Fellman et al., 2008; Williams et al., 2010; Petrone et al., 2011; Graeber et al., 2012). Reorganized flow paths that connect land and water may change the magnitude, timing, and quality of DOM released, whereas the ecological impact of these changes are not yet well understood (Stanley et al., 2012).

In addition to land use changes, various external controls on nutrient and DOM dynamics have been observed through changes in hydrology, season, and even vegetation. Seasonal change in soil moisture and temperature can influence the release and retention of nutrients and affect the production of vegetation and DOM (Spieles and Mitsch, 1999; Fink and Mistch, 2004; Morrice et al., 2004; Hernandez and Mitsch, 2007; Eimers et al., 2008). Increased hydrologic flows as a result of spring snow melt or heavy precipitation events can increase nutrient and DOM concentrations with greater landscape flushing and downstream delivery (Hinton et al., 1997; Bernal et al., 2002; Bullock and Acreman, 2003). Although external controls on nutrient dynamics have been established, the impacts of internal physical modifications such as wetland restoration on nutrient concentrations, transport, and composition are less understood. Various wetland management practices have attempted to reduce eutrophication and improve habitat quality and ecosystem services through reduction of point and non-point sources of pollution, protection and construction of riparian buffer zones, revegetation of native floral species, and more recently, active habitat modification (Wilcox and Whillans, 1999; Wilcox et al., 2017). The targets of many recent restorations commonly involve increasing native vegetation richness and diversity, reestablishing migratory and resident bird nesting and habitat, and access to fish spawning and nursery, but water quality enhancement and detrital export are rarely used to assess restoration success (Mitsch and Wang, 2000). Restoration efforts conducted at the sites assessed in this study involved the excavation of dense *Typha* (cattail) mats to create channels and potholes, along with native vegetation planting and invasive vegetation cutting and herbicide control, which may have contributed to changes in water flow and biogeochemical cycling.

Unlike extensively studied flow-regulated constructed wetlands used for wastewater treatment, much less is known about the nutrient removal capabilities and DOM composition of natural and restored wetlands receiving unregulated inflows throughout the growing season (Jordan et al., 2003). Information surrounding wetland the influence of restoration on biogeochemical cycles is lacking and this study aims to fill gaps in knowledge on nutrient retention of N and P as well as DOM characteristics of water in restored wetlands. My research applies established patterns observed in stream and wetland nutrient cycling of coastal freshwater systems, coupled with the potential for wetland restoration to influence such cycles, in order to gain a better functional understanding of relationships between wetlands and surrounding landscapes. I studied water chemistry in restored and unrestored wetlands and compared known internal and external drivers of biogeochemistry throughout the growing season of 2017 under storm and base flow regimes to meet objectives.

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CHAPTER 1: Nitrogen and phosphorus processing in restored and unrestored coastal wetlands of Lake Ontario

INTRODUCTION

An estimated 75% of Laurentian Great Lakes wetland areas have been lost through drainage and land use conversion for agricultural or urban development since pre-European settlement in the densely-populated basin, with almost 100% loss in some cases (Whillans, 1982). The wetlands that remain are often considered degraded from hydrologic alterations, high nutrient loading leading to eutrophication, erosion/sedimentation, and invasive species (Zedler and Kercher, 2005). Moreover, water-level regulation in the Great Lakes within the past 60 years has exacerbated poor wetland conditions by contributing to the invasion and establishment of dense monocultures of hybrid cattail (*Typha* x *glauca*), resulting in changes to function, habitat quality, and connectivity of water in coastal wetlands (Wilcox et al., 2008). Despite their often poor conditions, coastal wetlands of the Great Lakes hold disproportionately large value relative to the small area they occupy by providing fundamental ecosystem services (e.g., biodiversity support, nursey habitat, flood abatement, and protection of downstream ecosystems by buffering them from terrestrial nutrient inputs; Sierzen et al., 2012, Uzarski et al., 2017).

As a response to widespread loss and degradation, coastal wetlands are being restored to improve species diversity and habitat quality for fish, amphibians, and birds. Restoration is often accomplished by removing invasive species, reintroduction of native species, and increasing hydrologic connectivity (Wilcox and Whillans, 1999, Zedler and Kercher, 2005; Wilcox et al., 2017). Restoration efforts, however, have generally not considered opportunities for water quality improvement as a primary goal in addition to habitat benefits in the face of eutrophication in many watersheds (Mitsch and Wang, 2000; Ardon et al., 2010). There are many complex external processes known to influence nutrient loads and dynamics (i.e., hydrology, land use, climate, etc.), but it is currently uncertain if internal modifications such as wetland restoration can significantly influence nutrient dynamics.

Coastal wetland ecosystems facilitate biogeochemical cycles that drive high rates of ecosystem productivity and energy movement through the rest of the trophic structure. They also serve as sinks and remineralizers for excess nutrients and organic matter, which are gassed out or retained in temporary to long-term storage compartments in soils, vegetation, biotic litter, and the water column (Howard-Williams, 1985, Johnston, 1991; Jansson et al., 1994; Reddy et al., 1999; Kreiger, 2003; Hey et al., 2012). High external loads of nitrogen (N) and phosphorus (P), from catchments dominated by intensive agricultural and urban lands, alter ecosystem function and reduce a wetlands ability to process nutrients by contributing to excessive autotrophic productivity, hypoxic conditions, poor habitat quality, and species diversity loss and population size reductions (Carpenter et al., 1998; Morrice et al., 2008; Schock et al., 2014).

Seasonal and episodic weather fluctuations influence nutrient cycling rates in both riparian and wetland habitats among wet and dry hydrologic flow regimes (Spieles and Mitsch, 1999; Fink and Mitsch, 2004; Morrice et al., 2004). Water residence time is an important control on retention of nutrients such that longer times and drier conditions of base stream flow improve retention abilities from landscape inputs, while storm events decrease water residence time and compromise a wetland’s ability to process nutrients (Howard-Williams, 1985; Johnston, 1991; Bullock and Acreman, 2003; Fink and Mitsch, 2004; Sierzen et al., 2012).

Seasonal changes lead to variation in temperature, metabolic activity, evapotranspiration, vegetative productivity, and ultimately the rate at which nutrients are processed. In spring, flow and basin wetness is relatively high into the Great Lakes from snow melt. Peak vegetative productivity and high temperatures of the summer season lead to increased nutrient utilization, evapotranspiration, and longer water residence times. During the fall season, vegetation senesces and releases nutrients back to the water column. N reduction is greater in wetter conditions with low oxygen levels of waterlogged soils (spring), while P reduction is greater in drier conditions (summer and fall) due to greater redox potentials and sediment P binding (Haycock et al., 1997). While much is known about nutrient patterns in natural and degraded systems, little is known about the effects on nutrient processes after wetland restoration and manipulation. Methods of active habitat modification restoration, such as those used in these study sites, where channels and potholes were excavated in the wetland vegetative complex may increase hydrologic connectivity in these systems to interact with seasonal and episodic controls to the point at which it affects nutrient retention processes (Wilcox et al., 2008; Salk et al., 2018).

A long history of human-caused degradation in Great Lakes wetlands has urged restoration techniques to mitigate erosion, restore diverted hydrology, suppress invasive species, reduce eutrophication, and other issues (Wilcox and Whillans, 1999). Several studies have broadly explored the impacts of wetland restoration and construction on nutrient cycles (Kovacic et al., 2000; Jordan et al., 2003; Hoffman et al., 2011); yet, most conclude that more restorations need to aim at water quality improvement (Mitsch and Wang, 2000). A lack of sufficient post-restoration monitoring over long enough time-scales with clear restorative target goals, and measurable success criteria related to nutrient pollution and hydrologic dynamics urges the need for more research to be conducted (Kusler and Kentula, 2012). I was interested in studying if the excavation of channels and potholes through *Typha*-invaded wetlands contributes to water quality improvement by enhancing nutrient removal processes and nutrient buffering capacity from landscape inputs to downstream ecosystems.

Given the strong controls landscape composition, nutrient loading, and hydrological patterns have on nutrient retention in these systems (Fisher and Acreman, 2004; Trebitz et al., 2007), it is unlikely to see profound changes due to recent, small scale, down-stream restoration efforts. Delays in biogeochemical responses after restoration raise question to the adequate amount of time to expect results and the difficulty to identify appropriate scale and intensity of methods complicate restoration goals and management practices (Kusler and Kentula, 2012; Moreno-Mateos et al., 2015). Further, most Great Lakes coastal wetlands do not occupy a large enough portion of their landscape to significantly control external nutrient pollution, even if restored (Wang and Mitsch, 1998).

Based on previous research and my knowledge of the system, I hypothesized: 1) there would be no statistically significant difference in nutrient removal between restored and unrestored wetlands, 2) nutrient removal in wetlands would be lower under storm flow conditions regardless of restoration, and 3) nutrient removal in both restored and unrestored wetlands would be high in the summer season during peak productivity. To test these hypotheses, changes in concentration of N and P were monitored as water flowed into and out of four restored and four unrestored wetlands ten times over the growing season from April to October 2017, capturing both base and storm flow events.

This study investigated if coastal riverine wetland restoration within and around the Rochester Embayment affected wetland nutrient buffering capacity from the land to Lake Ontario. Since 2014, U.S. Fish and Wildlife Service, U.S. Environmental Protection Agency, Ducks Unlimited, and the U.S. Army Corps of Engineers have conducted several habitat restorations of varying methods and intensities on four coastal wetlands via construction of channels and potholes, hybrid cattail cutting, herbicide application, and native vegetation planting (Appendix A.1). These wetlands were selected for restoration based on public appeal and failure to meet ecological health targets. The main foci for a majority of these restorations were to improve vegetation species diversity, native vegetation reestablishment, and wildlife habitat. This study determined if these types of wetland restoration projects provide additional benefits to Lake Ontario by enhancing wetland nutrient removal capacity.

METHODS

Study Sites and Sampling Design

Four restored (Braddock Bay, Long Pond, Buck Pond, and Yanty Creek) and four unrestored (Sandy Creek, Brush Creek, East Creek, and Round Pond) coastal wetlands with riverine inputs within 25 km of the Lake Ontario Rochester Embayment Area of Concern (New York, USA) were sampled for water chemistry (Figure 1). Sampling was broken up seasonally into spring, summer, and fall, defined by spring and fall equinoxes and summer solstice. At each wetland, water samples were collected from the main stream input, and within the main flow path of the vegetative wetland complex, but upstream of lake influence. All samples were collected on a single day for each sampling event. Storm flow was defined as rain events that produced ≥ 1.5 cm of rain in a 24-hour period within 48 hours prior to sampling. A longitudinal black box sampling approach was used to determine how nutrient dynamics change along a stream-to-lake flow path. Each black box was a somewhat artificial boundary set up around the wetlands where the processes associated with retention of material and changes occurring in that space were unknown, but they allow the influence of the wetland on nutrient cycles to be determined from the overall change in nutrient concentration from input to output.

At each sampling point, two bottles were filled with water collected just below the surface for laboratory analyses. The following parameters were used to measure water quality: turbidity, soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), total phosphorus (TP), total nitrogen (TN), total dissolved nitrogen (TDN), and nitrite plus nitrate (NO_2/NO_3). For dissolved nutrients, water was filtered on-site using a 0.45 µm polycarbonate membrane filter and syringe system. Each filter was rinsed with 30 ml of DI water and 10 ml of sample prior to collecting sample filtrate. 125 mL bottles for turbidity and total nutrients were filled with whole water. Prior to filling, each bottle was sample-rinsed with whole or filtered water. In addition, water temperature (°C), specific conductance (µS/cm), pH, and chlorophyll fluorescence (µg/L) were taken at approximately 20 to 30 cm depth from water surface with a Hydrolab DS5 multi-probe sonde calibrated the day before use. All samples were stored on ice in the dark for transport back to the lab and analyzed within 36 hours of collection (turbidity) or stored frozen (nutrients) until analysis within two months of collection.

Daily rainfall totals (mm) for the duration of the study were used from standard rain gauges at the Rochester International Airport weather station (https://wunderground.com/calendar/us/ny/rochester), which was within 25 km of all sites. These data were used as an indicator of water transfer and flow through each catchment as a way to describe basin wetness over the suggested seven days prior to sampling via the antecedent precipitation index (API) described in McDonnel et al. (1991):

$$API_x = \sum_{i=1}^{x} \left(\frac{P_i}{i}\right)$$

where x is the number of days of rain considered and P is the total gross precipitation on the ith day beforehand.

Each stream's watershed was delineated, and basin characteristics were generated with the United States Geological Survey (USGS) StreamStats tool version 4.0 (Ries et al., 2004; http://streamstats.usgs.gov/). GIS ArcMap version 10.4 was used in tandem with 2011 edition Northeast National Land Cover Database files provided by USGS to produce percent land use classifications for each stream watershed. These data were used to compare watersheds among streams in reference to size, land use, and watershed-to-wetland area ratio. Partial categories of land use were consolidated into general categories as such: development (high, medium, and low intensities), forest (deciduous, evergreen, mixed, scrub/scrub, and herbaceous), agriculture (hay/pasture and row crop). Wetland land cover area was calculated by manually drawing a polygon over emergent marsh in an imagery base map of the study sites and converting the area of 30 m by 30 m cells into km^2. Categories of open water and barren land in these watersheds were omitted from analyses since percent cover in either category for any watershed did not exceed 1.2% and were considered to have insignificant contribution to the composition of the landscape relative to this study's focus.

Laboratory Analyses

All analytical procedures were done in the Limnology Laboratory of SUNY—the College at Brockport. Turbidity samples were allowed to warm to room temperature and measured as nephelometric intensity of light scatter in reference to standards 0.02 and 1000 nephelometric turbidity unit (NTU) using a turbidimeter with a detection limit of < 0.4 NTU (Method 180.1, EPA 1993).

Samples collected for P analyses (SRP, TDP, and TP) were analyzed as phosphate following the molybdate colorimetric assay method (Murphy and Riley, 1962; SM 4500-P-F, APHA 1992). TDP and TP samples were autoclave-digested (121.5°C for 30 minutes) in the presence of 1% persulfate and measured within 28 days of digestion. P analyses were run using a Technicon Auto Analyzer II (EPA, 1993). The instrument and method detection limit was 2 µg-P/L for SRP, TDP, and TP.

Samples collected for N analysis were analyzed as nitrite according to semi-automated colorimetric methods using Technicon Auto Analyzer II (EPA, 1993). TDN and TN samples were autoclave-digested (121.5°C for 30 minutes) in the presence of persulfate and sodium hydroxide and, prior to analysis, pH-adjusted using borate buffer. Digested TN and digested TDN and NO_2/NO_3 samples were passed through a copper-cadmium reduction column to reduce nitrate to nitrite and measured colorimetrically using a Technicon Auto Analyzer II (SM 4500-P-J, APHA 1992). This instrument and method detection limit was 0.010 mg-N/L for TN, TDN, and NO_2/NO_3.

Statistical Analyses

Means, standard error, and ranges for seasonal stream and wetland nutrient concentrations and water chemistry parameters across samples were calculated using Microsoft Excel. Measurements for pH were converted to hydrogen ion concentration before taking means and ranges, then converted back to pH for reporting. The absolute difference in site concentrations of N and P were calculated such that nutrient removal could be observed as water flows longitudinally through the wetland ([output]-[input]). A “removal efficiency” was calculated for TN and TP only as [((input-output/input) x 100)]. For both absolute differences and removal efficiency, negative values indicate nutrient removal and positive values indicate production. A percent difference standardization (removal efficiency) was not used on other species of nutrients in order to avoid biases of raw data that may report values as zero or fluctuate positive and negative between inputs and outputs of a stream-wetland path. In which case, a percent difference in dissolved fractions of the total nutrient pool would not be proportional to the previous value or adequately convey full removal with division by zero and a goal of nutrient removal as a negative percent change in concentration. Suggesting elemental nutrient transformation is beyond the scope of this study. Entries for events containing missing data for certain parameters were included to preserve cases for those parameters where data were available. Values that measured below set detection limits were replaced with the detection limit itself and considered for analysis.

Data were evaluated for normality using IBM SPSS version 24 Shapiro-Wilk and Kolomogrov-Smirnov tests. A normal distribution was not observed even after attempts to standardize these data to place equal weight on all variables or correct for negative values with a constant of the minimum value for each variable. Therefore, these data remained untransformed, and a resampling approach was taken to create a test distribution for parametric tests. To help assess anthropogenic influence on the system, percent of watersheds covered in agriculture was correlated with nutrient concentrations using Spearman’s Rank correlations at significance threshold of p <

0.05 in SPSS.

Finally, unrestricted full factorial permutation analyses of variance (ANOVA) were run using Manly (2007) approach in R version 3.5.0 using the RStudio (2015) interface to generate an F-statistic distribution from 9999 permutations of the original data (Howell, 2009; http://www.uvm.edu/~dhowell/StatPages/Permutation%20Anova/PermTestsAnova; Appendix B.1). ANOVA of this sort is permitted on non-parametric data because the resampled F distribution and generated probability factor was compared to the F-statistic of the original data instead of a theoretical F distribution for the model's main effects and interactions. ANOVA was run separately on data from stream concentrations and data representing the difference in concentration and removal efficiency from stream to wetland sites of each system to determine if restored and unrestored wetland sites differed significantly ($p < 0.05$) in water chemistry, watershed land use, and nutrient reduction capacity between seasons and flow conditions. A three-way ANOVA was run on stream concentrations (restoration, season, and flow) excluding summer concentrations and two-way ANOVAs were run on stream-to-wetland differences after separating the full dataset into storm and base flow subsets to analyze independently. These methods were used because storm flow was not captured during the summer and would unbalance the models and cause a misrepresentation of the factor of season if kept altogether. Therefore, the three-way ANOVA run on stream concentrations (factors of restoration, season, and flow) was necessary to evaluate interactions between all factors but only included seasonal comparisons between spring and fall. The two-way ANOVA on stream-to-wetland difference data under base flow contained spring, summer, and fall levels to the seasonal factor but the two-way ANOVA on difference data under storm flow only contained spring and fall levels to the seasonal factor. In addition, two-way ANOVA was run with API differed by season and flow. This information was used to determine how well the low and high flow sampling design captured wet and dry conditions across the sampling period.

RESULTS

Comparing Water Chemistry in Restored and Unrestored Wetlands

Restored and unrestored wetlands had similar mean water chemistry properties throughout the duration of the study (Table 1; Appendix C.1). Mean and range water temperature over the course of the study for both wetland groups was 16.3 (7.9 to 24.8) ºC, and seasonal mean water temperatures for both were highest in summer, as expected. Neutral pH was typical, with mean and range slightly higher for unrestored wetlands at 7.4 (6.3 to 8.4) compared to restored wetlands at 7.2 (6.1 to 8.2). Mean and range of dissolved oxygen as percent saturation measured 74.9% (1.2 to 155.3%) in unrestored wetlands and 72.7% (2.5 to 141.3%) in restored wetlands. Mean specific conductance for both wetland groups was comparable (599 and 569 µS/cm); however, greater variation was observed in unrestored wetlands with a maximum at 1667 µS/cm compared to a maximum of 940 µS/cm in restored wetlands. Additionally, maximum chlorophyll a (288.8 µg/L) was again higher in unrestored wetlands despite comparable means of 34.0 and 34.2 µg/L for unrestored and restored wetlands, respectively. Lastly, mean turbidity was similar in restored wetlands at 19.5 NTU (2.7 to 156 NTU) and unrestored wetlands at 19.8 NTU (2.3 to 116.0 NTU).

Mean concentrations of all species of N and P were generally lower in the outflowing wetland water than in inflowing stream water for a single site, indicating net nutrient removal over flow path, but nutrient concentrations were usually higher in unrestored systems than restored. Over the duration of the study, TN ranged from 0.44 to 7.37 mg/L, with a mean concentration of 1.74 mg/L in unrestored wetlands and 0.57 to 5.43 mg/L with a mean of 1.31 mg/L in restored wetlands. TP ranged from 6 to 892 µg/L in unrestored wetlands, with a mean concentration of 176 µg/L and 19 µg/L to 591 µg/L in restored wetlands, with a mean concentration of 131 µg/L. TDN, TDP, NO_2/NO_3, and SRP followed similar patterns as their total nutrient counterparts with higher concentrations in unrestored wetlands compared to restored wetlands. Outliers were present in all variables, but most could not be removed because they were within expected values for disturbed wetlands and streams and the nature of the experimental design tested under storm and base flow events, and cycling rates of N and P were naturally extremely variable over short spatial and temporal resolutions. As such, minimum and maximum concentrations of TN (0.57 to 5.43 mg-N/L) and TP (19 to 591 µg-P/L) for restored wetlands were all observed in Yanty Creek.

Watershed Land Use Land Cover

Total watershed areas for these catchments were relatively small, ranging from 8.5 to 196.6 km^2, with a mean of 50.8 km^2, all of which had less than 8.0% wetland cover (Table 2). Although total watershed size and watershed area:wetland area ratios between sites were somewhat variable, no significant difference ($F_{1,7} < 3.00$, $p > 0.05$; Appendix D.1) was observed when grouped by restored and unrestored wetlands. Land-use-land-cover within each watershed was also variable, but all catchments contained urban development, forests, agriculture, and wetlands. No significant differences in percent land cover categories between restored and unrestored wetlands were observed, except for percent forested cover ($F_{1,7} = 13.8$, $p = 0.001$; Appendix D.1), which was significantly higher in restored wetland watersheds. Urban developed and agricultural cover (as a sum of hay/pasture and cultivated crop covers) were inversely related such that catchments with the most urban development in Round and Buck Ponds at 77.7% and 42.0% respectively, contain the lowest agricultural cover at 8.7% and 21.4% (Table 2).

Sites with repeatedly high N and P concentrations (above 2.0 mg-N/L TN and 300 µg-P/L TP), such as Brush and East Creeks, contained the highest percent cover of watershed in agriculture at 79.5% and 88.7%, respectively. Across streams, mean N and P concentrations per site were significantly positively correlated with agriculture (Figure 2). Within the N species, TN and TDN had a stronger association with agriculture (both $r = 0.74$, $p = 0.037$) than NO_2/NO_3, which was not significant ($r = 0.38$, $p = 0.352$). Within P species, TP ($r = 0.91$, $p = 0.002$) significantly correlated most strongly with agriculture, followed by similar patterns in TDP ($r = 0.74$, $p = 0.037$) and SRP ($r = 0.83$, $p = 0.010$).

Storm Events and Nutrient Patterns

Regional rainfall events and monthly precipitation totals in 2017 were exceptional in frequency and intensity compared to precipitation normals defined by NOAA as the 30-year weather normal between 1981 and 2010 (Arguez, et al., 2010; www.ncdc.noaa.gov/data-access/land-based-station-data/land-based-datasets/climate-normals/1981-2010-normals-data; www.usclimatedata.com/climate/rochester/new-york/united-states/usny1232). Monthly precipitation means during this study from April to October of 2017 exceeded the 30-year normal five out of seven months by 0.51 to 10.13 cm, with as much as 6.07 cm of rain for a single storm event within a 24-hour period prior to a sampling event (Table 1). Storm events were successfully captured as evident by a significantly higher API values during storm flow ($F_{1,9} = 7.95$, $p = 0.24$; Appendix D.2). Many storm events brought flooding and severely increased particulate suspension and downstream delivery compared to low flow conditions. High flow events resulted in a significant increase in stream turbidity ($F_{1,60} = 29.778$, $p = 0.0001$), P species ($F_{1,55} > 14.2$, $p < 0.0001$), and TDN ($F_{1,58} = 5.57$, $p = 0.019$) for both restored and unrestored wetlands (Table 3).

Based on API basin wetness values for 7 days prior to sampling, the spring season showed the largest spike in wetness (0.49 event 1 to 1.27 event 2), values suppressed for summer (< 0.28) although only base flow was captured, and fall experienced prolonged high basin wetness for both base and storm flow sampling events (1.05-0.93 events 8-10; Figures 4 and 5). Higher mean TN and TP stream concentrations of both restored and unrestored wetlands were generally observed when there was high basin wetness in relation to high flow from storms at sampling events 2, 4, 8, and 10 (Figures 4 and 5).

Nutrient Reduction over Seasons

With variation across seasons, N and P absolute concentration removal was greater in unrestored than restored wetlands (Tables 1 and 3). However, it is important to note unrestored wetlands received greater nutrient inputs, which may have increased their removal capacity. For total and dissolved forms of N, concentrations seemed to be reduced greatest in the spring season with TN showing greater reduction than NO_2/NO_3 (Figure 3). TN and TDN were significantly removed best under base flow in unrestored wetlands during the spring compared to restored wetlands and other seasons ($F_{2,92} > 0.46$, $p < 0.005$; Table 4). TDN was removed significantly under storm flow ($F_{2,116} = 1.03$, $p = 0.016$) in unrestored wetlands during the spring season when other N species were not. When removal efficiency was considered as a percent change, unrestored wetlands removed a significantly greater percentage of TN at 24 % ($F_{1,40} = 5.15$, $p = 0.028$) than restored wetlands at 15% under base flow, but unlike absolute concentration reduction, no significant differences were detected among seasons or under storm flow conditions for percent removal (Table 4).

Concentrations of total and dissolved forms of P reduction appeared to show the opposite seasonal pattern of N, where most P reduction occurred in summer and fall. As with N, unrestored wetlands removed more P than restored wetlands as TP and SRP in all seasons except for TP in spring (Figure 3). These patterns were similar between storm and base flows, but more significant differences were detected under base flow than storm flow (Table 4). All P species removal as absolute concentration difference was significantly greater in unrestored wetlands ($F_{1,46} > 4.36$, $p < 0.041$) under base flow, where TP removal was greatest (Table 4). P species showed a different pattern under storm flow, where only TP was significantly removed in unrestored wetlands during the fall under storm flow conditions ($F_{1,26} = 7.97$, $p = 0.041$). When TP removal efficiency was considered, unrestored wetlands again removed a significantly greater amount at 17% ($F_{1,40} = 9.16$, $p = 0.006$; Table 4) than restored wetlands at -5% under base flow, but no significant differences in removal efficiency were observed between seasons or at all under storm flow. Overall, more significant N and P removal differences were detected under base flow compared to storm flow and unrestored wetlands under low flow removed more nutrients than restored wetlands.

DISCUSSSION

All stream-to-wetland complexes were eutrophic to hypereutrophic during this study, with chlorophyll a, TN, and TP concentrations over 25 µg/L, 1.2 mg-N/L, and 200 µg-P/L, respectively, for much of the year (Calrson, 1977; Dodds and Whiles, 2010), but lower concentrations of N and P in wetlands than streams, showed nutrient retention services. Nutrient processing in wetlands has been linked to hydrologic controls, including seasonal and episodic weather events (Howard-Williams, 1985; Morrice et al., 2004), daily seiche-driven patterns (Trebitz et al., 2006), long-term lake water-level fluctuations (Steinman et al., 2012), and hydrologic reconnection from stream vectors of landscape inputs (Salk et al., 2018). Human activities (primarily agriculture, and industrial and residential development) degrade water quality in Great Lakes coastal wetlands by significantly increasing TN, chlorophyll a, and TP concentrations in receiving waterbodies, especially within small watersheds of wetland watersheds (Mitsch et al., 2000; Trebitz et al., 2007; Moreno-Mateos, 2008; Morrice et al., 2008).

Over most seasons and flow conditions, nutrient retention in restored and unrestored wetlands was similar, which supports my hypothesis. When differences were detected, unrestored wetlands showed greater nutrient removal than restored wetlands in terms of absolute concentration reduction and removal efficiencies of TN and TP. However, it is paramount to consider that unrestored wetlands received higher nutrient inputs than restored wetlands and may have contributed to their ability to reduce significantly higher nutrient concentrations. Wetlands remove materials at widely different rates from 5% to 100% (e.g., reviews by Verhoeven and van der Toorn, 1990; Mitsch et al., 2000; Fisher and Acreman, 2004; Mitsch and Gosselink, 2007). The average TN and TP removal efficiencies of this study, (15 to 24% and -5 to 17%, respectively) were lower than average removal efficiencies of 203 wetlands analyzed in a review by Land et al. (2016) at 37% for TN and 46% for TP or TN (64%) and TP (40 to 90%) removal efficiencies described in Mitsch and Gosselink (2000) and Suanders and Kalff (2001). These studies, among others, emphasize that removal rate was highly dependent on loading rate (Fleischer et al., 1991; Gale et al., 1993; Jansson et al., 1994).

The environmental variability and numerous influences on nutrient processing (i.e., landscape composition, seasonal and episodic hydrologic controls, ambient physio-chemical characteristics) makes attributing N and P retention to a single control difficult, but I can speculate potential reasons for my results based on conditions known to affect loading and removal. Regardless of mechanism, all wetlands in this study demonstrated the ability to reduce N and P transport to downstream ecosystems and provide a buffering service to Lake Ontario even though restoration did not conclusively improve water quality.

Land Use and Watershed Characteristics

Only two of eight of wetlands in this study were large enough to satisfy suggested 3 to 5% wetland cover of a total watershed area for effective non-point-source pollution control (Mitsch, 1992; Mitsch and Gosselink, 2000) and zero sites had large enough ratios (1:5 to 1:25) for effective water quality improvement according to Woltemade (2000). Watershed size (8.5 to 190.6 km^2) and land use percent cover varied substantially across sites and may have impacted individual wetlands' nutrient loading and retention, but I was not able to test for site-wise differences or block by site for analyses of restoration, season, and flow factors due to a limited sample size, extreme variability in the data, and statistical constraints. I believe watershed areas do not explain differences in nutrient removal between restored and unrestored wetlands because no significant differences in mean watershed size or ratio of watershed area:wetland area were detected between groups of restored and unrestored wetlands.

However, a clear association between agriculture and eutrophication has been established in the literature, which also contributes to harmful algal blooms, hindered nutrient retention abilities, and species diversity loss (Moreno-Mateos et al., 2008; Schock et al., 2014; Alvarez et al., 2017; Delkash et al., 2018).

The ability to use wetlands as a control for nutrient pollution by intercepting inputs from the landscape and reducing exports to downstream aquatic systems has been widely studied (Johnston, 1991; Jansson et al., 1994; Kreiger, 2003), but most research on restored wetlands' effectiveness shows factors at a watershed scale, such as land use cover and landscape composition, likely have a stronger control on retention properties than wetland-scale characteristics (Jordan et al., 1999; Kovacic et al., 2000; Jordan et al., 2003). Sustainable land management practices have documented the potential to reduce erosion and export of nutrients, sediment, and pollutants, which restored wetland ecosystem services when connectivity of a wetland to lake and watershed are considered in the sensitivity of wetlands to changes in nutrient inputs (Morrice et al., 2004: Brinson and Eckles, 2011; Richardson et al., 2011; Salk et al., 2018).

Hydrologic and Seasonal Influences on Nutrient Retention

Coastal wetlands of Lake Ontario are hydrologically connected to the lake and reflect lake water-levels. Due to a combination of high precipitation levels and variable winter ice conditions that disrupted normal water release into the St. Lawrence River, Lake Ontario coastal areas were flooded for much of 2017. During a five-month period

January to May 2017, many locations in the Lake Ontario basin received record-setting precipitation and inflows from Lake Erie via the Niagara River were extreme, making total water supplies to Lake Ontario highest on record in May 2017 and second highest in April 2017 (http://ijc.org/en_/islrbc/LOSLR_QA#One). This made lake water levels in cities such as Rochester, NY peak in May and remain high until the fall, when water was finally able to drain from the lake (tidesandcurrents.noaa.gov/waterlevels.html; Appendix E.1 and E.2). Even with sustained high water levels, new storm events created visible increases in the delivery of suspended solids and P species to streams compared to base flow events. Similar to my findings, Fink and Mitsch (2004) observed that concentrations of SRP and TP in streams increased significantly during precipitation events compared to dry weather flows, but concentrations of NO_3 did not increase significantly. Although streams had increases in nutrients under storm flow, there was no significant difference in wetland retention of these materials under base or storm flow. Additionally, a lack of relationship between API values per event and TN and TP concentrations further suggests that basin wetness as a result of storm flow events did not affect nutrient retention in wetlands.

Because N and P retention in wetlands was not significantly influenced by storm events, these results confirm that flow explained little of the variation in nutrient processing. While there was evidence of N and P retention in these restored and unrestored wetlands in a quantitative sense, with consistently lower nutrient concentrations in wetlands than streams, the data do not allow exact conclusions on the mechanisms. Still, I can speculate that nutrient reduction in the wetland "black boxes" results from a net balance of many processes, including primary producer assimilation, decompositions, denitrification, sedimentation, adsorption, and transport. Higher rates of denitrification have been significantly correlated with warmer soil temperatures and higher inflow NO_3 concentrations in spring and summer (Hernandez and Mitsch, 2007). A review by Fisher and Acreman (2004) showed that generally wetlands reduce N and P loadings, but this largely depends on the degree of waterlogging of sediments. Greater N removal in spring and summer compared to fall in this study may be due to greater N removal in wetter conditions and temperature-dependent denitrification associated with season (Haycock et al., 1997; Spieles and Mitsch, 1999; Hernandez and Mitsch, 2007). Growing vegetation in summer may have assimilated N, held sediment, and produced more organic matter to support denitrification (Spieles and Mitsch, 1999; Mitsch et al., 2000).

Dynamics of P, inferred by concentrations of SRP, TDP, and TP supported my second hypothesis that nutrient removal would be greater under base flow than storm flow, but trends in N did not. P reduction is thought to be greater in drier conditions, and established empirical correlations between inflow and outflow of P in wetlands are consistent with the low P reduction during a rainy spring and high lake-level spring and summer seasons (Haycock et al., 1997; Reddy et al., 1999). The main effect of season is mostly insignificant, but where differences are detected, significantly greater P reduction in the fall season may be attributed to lower water levels in the fall.

The ability of a wetland to retain P depends largely on the physio-chemical properties of the sediment. P adsorption is predicted best by concentrations of amorphous aluminum and iron and P assimilation into microbial biomass increases when preferred electron acceptors involved in decomposition are more available during aerobic conditions (Richardson, 1985; Reddy et al., 1999). Sustained inundated conditions of waterlogged wetland soils can create an anaerobic reduced redox state environment in which P is less likely to sorb to aluminum and iron and more likely to be transported (Rzepecki, 2002). On the other hand, TP has shown patterns of significant removal during drying periods compared to years without drying periods (Jordan et al., 2003).

High lake levels in spring and summer may have decreased P interactions at the water-sediment interface and created anaerobic conditions to explain a lack of P retention and P increase at times. When lake levels finally decreased during the fall to create drier aerobic conditions, P adsorption may have increased with exposed emergent vegetation and soils, as demonstrated by my results. Similar to nutrient fluxes in this study and seasonal water levels in Lake Ontario in 2017, a study by Steinman et al. (2012) on sediment-water nutrient exchange in Great Lakes coastal wetlands of re-wetted sediments showed an exponential decrease in P release from previously desiccated sediment with increasing water-column depth and N release seemed to reach an asymptote at 0.25 cm and greater. Perhaps the wetlands in my study removed nutrients more poorly because flooding caused greater nutrient input from previous exposed sediments that was not measured but speculated to occur with re-wetting.

A large body of literature has demonstrated the control that stream flow and water residence time has on nutrient retention (Howard-Williams, 1985; Reddy et al., 1999; Kovacic et al., 2000; Fisher and Acreman, 2004). For example, a study by Woltemade (2000) observed the greatest ability of restored wetlands to reduce N and P in agricultural drainage catchments under flow conditions that facilitate retention times of at least one or two weeks. However, with this study, I believe that water residence times were likely similar during base and storm flow events because sustained high water-levels in Lake Ontario inhibited water flow from the streams through the wetlands to the lake. Lake water levels remained high throughout the study and did not begin to recede until the fall season. The wetlands under study did not have stage indicators, and the streams were not gauged to measure discharge near their wetland mouth, which prevented us from determining water residence time and exact flow conditions.

Restoration Impacts on Biogeochemistry

I believe as a broad explanation, that unrestored wetlands showed higher nutrient concentrations in their streams and therefore, higher retention could primarily be a response to increased input. However, I offer some influences that restoration may generally have on nutrient retention. The efficiency and longevity of restored wetlands' nutrient removal services are more likely to relate to physio-chemical composition of the water and sediment, nutrient loading, biotic communities, and hydraulic residence time (Woltemade, 2000; Fisher and Acreman, 2004) and less likely to relate to extent of restoration (Hey et al., 2012).

Method of restoration and intensity of activities may vary across projects and sometimes have been used to explain differences between expected and realized N removal (Hoffman et al., 2011). Time since restoration completion can have potential influences on long-term trends in nutrient retention as wetlands age (Spieles and Mitsch, 1999; Mitsch et al., 2000). This study was conducted on relatively new restorations, all of which were completed within the last 4 years. Removal of N may continue indefinitely if converted to gaseous forms in the wetland and released to the atmosphere without limitation (Jordan et al., 2003; Hey et al., 2012). However, Richardson (1985) showed high initial rates of P retention by freshwater wetlands have been followed by large exports of P within a few years when storage compartments become saturated and long-term P retention can be considered controversial if substrate storage capacity is limited. Mitsch and Wilson (1996) suggested that 15 to 20 years might be required to judge the success of a wetland restoration in a freshwater coastal marsh system. Although restoration did not significantly remove more nutrients than unrestored wetlands in this study, all wetlands demonstrated nutrient removal services, and restoration is still valuable to improve other factors making a wetland healthy.

In restorations involving disturbance through habitat modifications via excavation of channels and potholes and planting new vegetation, sediment resuspension may result in an initial release and export of previously buried materials when channels and potholes were excavated (Merrit, 1994). The restored wetlands in this study, like many other coastal wetland restorations in the Great Lakes, did not originally target an improvement in water quality (Mitsch and Wang, 2000). Most wetland restoration projects lack specified targets, complicating efforts to evaluate “success” and the ability of a wetland restoration project to restore a particular function depends on the complexity of the function, its vulnerability to influence of environmental variation, and the ease to which its parameters can be measured (Kusler and Kentula, 2012). For example, habitat quality may be measured through observation of targeted species of vegetation, wildlife, and fish, where fate of pollutants, groundwater recharge, and biogeochemical cycling can be more difficult to evaluate despite measurable metrics. In addition, watershed-level changes in land use and nutrient loading have been suggested to be more important to nutrient retention (Fisher and Acreman, 2004; Trebitz et al., 2007) than small-scale wetland restorations.

This study’s findings generally fit the established predictor between nutrient loading and nutrient retention (Fleischer et al., 1991; Gale et al., 1993; Jansson et al., 1994; Boers and Zedler, 2008; Land et al., 2016). Streams and wetlands of unrestored sites had higher N concentrations than streams and wetlands of restored sites, indicating unrestored wetlands had higher N loading. During spring, unrestored wetlands were associated with greater removal of TN and TDN under base flow conditions. Both restored and unrestored wetlands were likely to have higher rates of N loading in the spring due to high runoff from snow melt and storm events were frequent and severe, which potentially led to higher rates of N reduction in spring regardless of restoration status. Like N, I speculate that P retention was higher in unrestored wetlands than restored wetlands because they received higher loads of P and may have experienced responses to internal eutrophication. Boers and Zedler (2008) studied P retention with the same invasive species of cattail known to have a high affinity for phosphate and established in a monoculture at all sites included in this study. The scientists found that the addition of 2 g P/m^2 to an experimental outdoor mesocosm increased biomass by 23% more than the control that did not receive additional P, suggesting simply that more P is utilized by vegetation when more P is added. Unavailable P in their study may have shifted to a form usable to the plant to increase retention of P as a response to internal eutrophication. Unrestored wetlands of this study may have experienced a similar process, suggested by higher levels of P compared to restored wetlands. However, seasonal conditions of soil moisture appeared to be the strongest control on P retention and considering that all coastal wetlands received the same degree and duration of high lake water levels, true mechanism of higher P retention in unrestored wetlands is unclear. Soil chemical analyses, wetland geomorphology identification, and basin slope analyses would need to be conducted to understand P retention in these wetlands better, in addition to potential effects of wetland restoration efforts.

CONCLUSIONS AND FUTURE RESEARCH

Although wetland restoration did not seem to improve water quality and nutrient retentive properties of these systems, all wetlands still exhibit an ability to remove N and P for part or much of the year and higher nutrient removal may be attributed to increased nutrient loading more so than restoration itself. Perhaps shifting some restoration goals to restoring hydrologic connectivity to stream source and water flow paths throughout the wetland to maximize surface area contact with nutrients and storage compartments would make restorations more successful at water quality improvement in addition to habitat benefits. Determinations of need for future adaptive management, necessity of restoration, and cost-benefit analyses related to water quality and nutrient retention should be based on annual trends in N and P concentrations and shifts in aquatic vegetation. Monitoring could benefit from more frequent sampling and a longer history of trends as wetlands age since time of restoration, but the primary attempts to achieve eutrophication abatement and degraded water quality should be reducing source nutrient loading at the watershed level. This might require wetlands to be created in the watershed and for management of land use in intensive agriculturally dominated catchments, in addition to restoring wetlands. Installing riparian buffers may intercept some high-nutrient runoff before it can be transferred to stream vectors. Wetland creation, in addition to restoration of natural sites, may help regulate stream flow during extreme precipitation events and moderate large pulses of nutrients flushed into the system rapidly. Some biogeochemical and ecological relationships are recognized, but there is a lack of information on the influences of restoration on the ability for coastal wetlands to store and remove nutrient pollutants from waters as they flow into the Great Lakes, thus providing the demand for further research to better inform future management practices.

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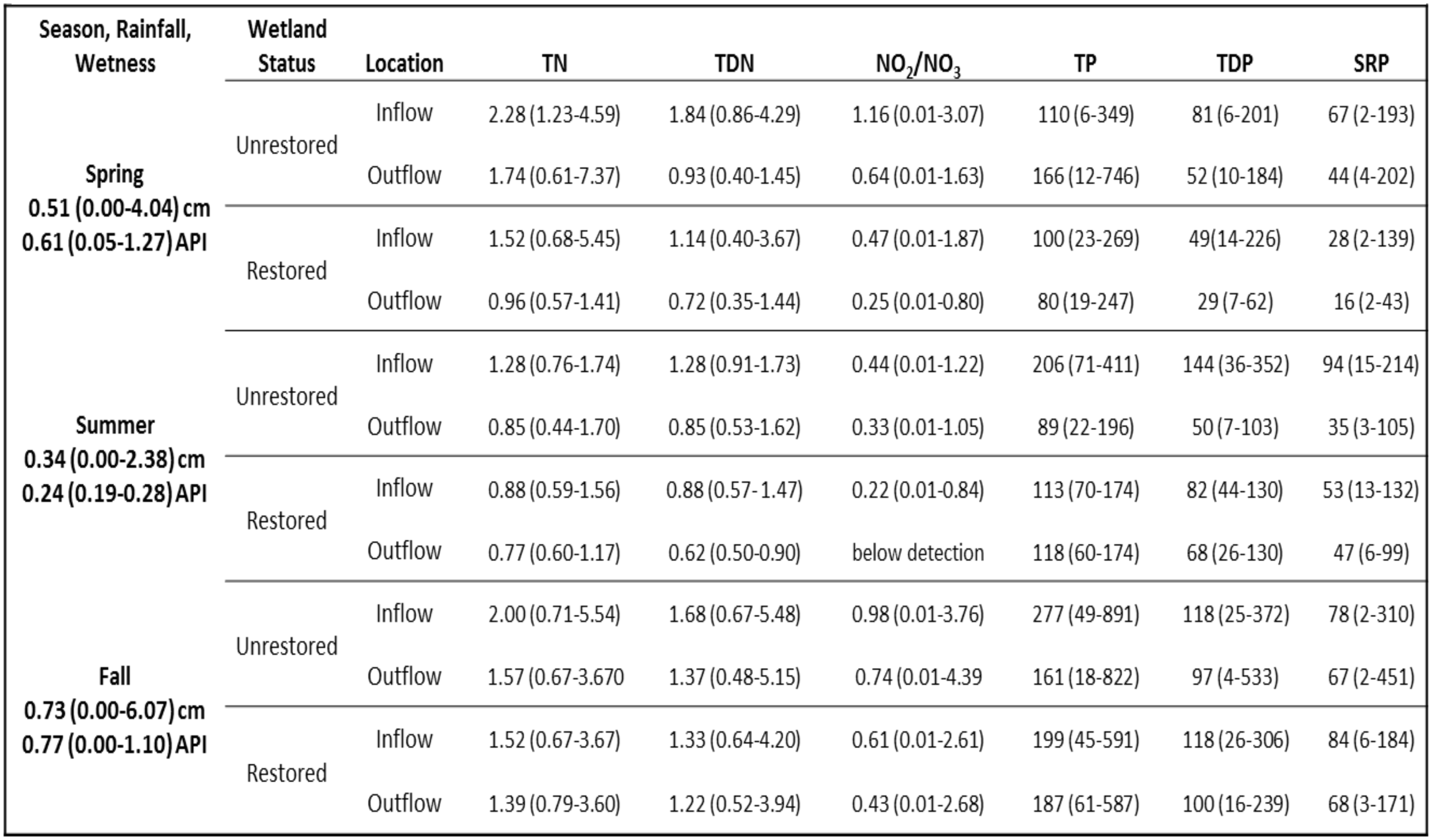
TABLES AND FIGURES

Table 1. Mean (range) concentrations of total and dissolved forms of N (mg/L) and P (µg/L) of inflowing streams and outflowing wetlands throughout the growing season with mean seasonal rainfall (cm) and basin wetness (API).



Season, Rainfall, Wetness	Wetland Status	Location	TN	TDN	NO_2/NO_3	TP	TDP	SRP
Spring **0.51 (0.00-4.04) cm** **0.61 (0.05-1.27) API**	Unrestored	Inflow	2.28 (1.23-4.59)	1.84 (0.86-4.29)	1.16 (0.01-3.07)	110 (6-349)	81 (6-201)	67 (2-193)
		Outflow	1.74 (0.61-7.37)	0.93 (0.40-1.45)	0.64 (0.01-1.63)	166 (12-746)	52 (10-184)	44 (4-202)
	Restored	Inflow	1.52 (0.68-5.45)	1.14 (0.40-3.67)	0.47 (0.01-1.87)	100 (23-269)	49(14-226)	28 (2-139)
		Outflow	0.96 (0.57-1.41)	0.72 (0.35-1.44)	0.25 (0.01-0.80)	80 (19-247)	29 (7-62)	16 (2-43)
Summer **0.34 (0.00-2.38) cm** **0.24 (0.19-0.28) API**	Unrestored	Inflow	1.28 (0.76-1.74)	1.28 (0.91-1.73)	0.44 (0.01-1.22)	206 (71-411)	144 (36-352)	94 (15-214)
		Outflow	0.85 (0.44-1.70)	0.85 (0.53-1.62)	0.33 (0.01-1.05)	89 (22-196)	50 (7-103)	35 (3-105)
	Restored	Inflow	0.88 (0.59-1.56)	0.88 (0.57- 1.47)	0.22 (0.01-0.84)	113 (70-174)	82 (44-130)	53 (13-132)
		Outflow	0.77 (0.60-1.17)	0.62 (0.50-0.90)	below detection	118 (60-174)	68 (26-130)	47 (6-99)
Fall **0.73 (0.00-6.07) cm** **0.77 (0.00-1.10) API**	Unrestored	Inflow	2.00 (0.71-5.54)	1.68 (0.67-5.48)	0.98 (0.01-3.76)	277 (49-891)	118 (25-372)	78 (2-310)
		Outflow	1.57 (0.67-3.670	1.37 (0.48-5.15)	0.74 (0.01-4.39	161 (18-822)	97 (4-533)	67 (2-451)
	Restored	Inflow	1.52 (0.67-3.67)	1.33 (0.64-4.20)	0.61 (0.01-2.61)	199 (45-591)	118 (26-306)	84 (6-184)
		Outflow	1.39 (0.79-3.60)	1.22 (0.52-3.94)	0.43 (0.01-2.68)	187 (61-587)	100 (16-239)	68 (3-171)

Table 2. Land use land cover in each wetland's watershed percent of total, watershed size by area in km^2, and watershed area to wetland area ratio.

	Round Pond	**Sandy Creek**	**Brush Creek**	**East Creek**	**Braddock Bay**	**Long Pond**	**Buck Pond**	**Yanty Creek**
Land Use	Unrestored Wetlands				Restored Wetlands			
Developed (%)	77.4	8.7	5.8	4.2	11.0	19.5	41.5	6.4
Forest (%)	11.7	25.4	12.4	6.4	30.0	29.9	28.3	28.3
Agriculture (%)	8.7	65.1	79.5	88.7	50.8	49.5	21.4	62.1
Wetlands (%)	1.7	0.3	2.1	0.8	5.5	0.4	7.9	2.8
Watershed area (km^2)	53.0	190.6	14.8	8.5	24.5	48.9	34.1	32.1
Watershed : wetland	60.0	378.2	46.5	132.8	18.3	259.0	12.7	36.3

Table 3. Three-way ANOVA on stream water chemistry concentrations between restored and unrestored sites under storm and base flow events using spring and fall data only as to not influence the seasonal significance during the summer when only base flow was captured. P-values considered significant ($p < 0.05$) are in bold and p-values with some statistical support for differences are in italics ($0.10 < p < 0.05$).

	Restoration		Season		Flow		Restoration X Season		Restoration X Flow		Season X Flow		Full Interaction	
	Df = 1		Df = 1		Df = 1		Df = 1		Df = 1		Df = 1		Df = 2	
	F	p	F	p	F	p	F	p	F	p	F	p	F	p
Sp. Cond.	3.75	*0.059*	6.46	**0.013**	8.89	**0.006**	0.69	**0.002**	0.63	**0.001**	0.18	**0.001**	0.45	0.516
DO %	0.39	0.722	2.78	*0.057*	0.02	0.935	0.93	**0.039**	1.13	0.640	0.00	0.097	0.24	0.706
pH	1.82	0.194	0.01	0.907	1.79	0.190	0.24	0.184	0.03	*0.067*	1.29	0.193	0.03	0.864
NTU	0.04	0.841	0.32	0.591	29.78	**0.0001**	0.59	0.558	0.02	**0.0001**	1.70	**0.0001**	0.51	0.493
TN	4.59	**0.033**	0.19	0.667	2.46	0.125	0.34	**0.033**	0.01	**0.010**	1.98	0.106	0.16	0.700
TDN	4.63	**0.036**	0.02	0.892	5.57	**0.019**	0.66	**0.035**	0.17	**0.002**	4.85	**0.017**	0.12	0.741
NO_2NO_3	5.71	**0.019**	0.00	0.962	0.60	0.442	0.54	**0.021**	0.01	**0.012**	4.14	0.444	0.13	0.721
TP	2.96	*0.093*	13.48	**0.0002**	19.53	**0.0001**	0.41	**0.0001**	0.08	**0.0001**	2.18	**0.0001**	0.12	0.746
TDP	1.32	0.264	10.19	**0.002**	17.90	**0.0001**	1.01	**0.001**	0.00	**0.0001**	3.28	**0.0001**	0.91	0.352
SRP	1.82	0.186	5.92	**0.019**	14.20	**0.0002**	2.47	**0.006**	0.05	**0.0001**	1.86	**0.0001**	1.57	0.232

Table 4. Two-way ANOVA with main effects and interaction of restoration status and season on nutrient concentration reduction from stream inflow to wetland outflow. Base flow (top) and storm flow (bottom) sampling events were analyzed independently. Restored wetlands (R) and unrestored wetlands (U) were measured for three seasons: (spring (Sp), summer (Su), and fall (F)) under base flow, and two seasons under storm flow: (Sp and F). NS stands for p-values above 0.10. P-values considered significant ($p < 0.05$) are in bold and p-values with some statistical support for differences are in italics ($0.10 < p < 0.05$). Pattern indicates the direction of higher nutrient reduction. For example, if U>R, a significant reduction in nutrient concentration was observed from stream to wetland and unrestored wetlands had a greater mean difference.

		Restoration (Df = 1)			Season (Df = 2)			Interaction (Df = 2)		
		Pattern	F	p	Pattern	F	p	Pattern	F	p
BASE FLOW	TN (mg-N/L)	U>R	4.83	**0.031**	Sp>F> Su	2.66	*0.077*	USp>	0.46	**0.001**
	TN %	U>R	5.15	**0.028**	All=	2.28	NS	All=	0.01	NS
	TDN (mg-N/L)	U=R	1.86	NS	Sp>F> Su	2.86	**0.045**	USp>	0.56	**0.005**
	NO_2/NO_3 (mg-N/L)	U=R	0.82	NS	All=	1.08	NS	All=	0.48	NS
	TP (µg-P/L)	U>R	12.08	**0.000**	All=	1.03	NS	UF>	1.19	**0.000**
	TP %	U>R	9.16	**0.006**	All=	0.12	NS	UF>	0.70	NS
	TDP (µg-P/L)	U>R	6.66	**0.005**	All=	0.81	NS	UF>	0.91	**0.001**
	SRP (µg-P/L)	U>R	4.36	**0.041**	All=	0.43	NS	UF>	0.72	**0.012**
			(Df = 1)			(Df = 1)			(Df = 1)	
STORM FLOW	TN (mg-N/L)	U=R	0.90	NS	F=Sp	0.00	NS	All=	1.76	NS
	TN %	U>R	0.67	NS	F=Sp	0.00	NS	All=	2.66	NS
	TDN (mg-N/L)	U>R	5.13	**0.018**	F=Sp	0.66	NS	SpU>	1.03	**0.016**
	NO_2/NO_3 (mg-N/L)	U=R	0.14	NS	F=Sp	0.41	NS	All=	0.40	NS
	TP (µg-P/L)	U=R	0.01	NS	F>Sp	4.66	**0.036**	FU>	7.97	**0.041**
	TP %	U>R	0.81	NS	F=Sp	1.44	NS	FU>	4.35	*0.051*
	TDP (µg-P/L)	U=R	1.10	NS	F=Sp	0.38	NS	All=	1.17	NS
	SRP (µg-P/L)	U=R	1.03	NS	F=Sp	0.93	NS	All=	0.74	NS

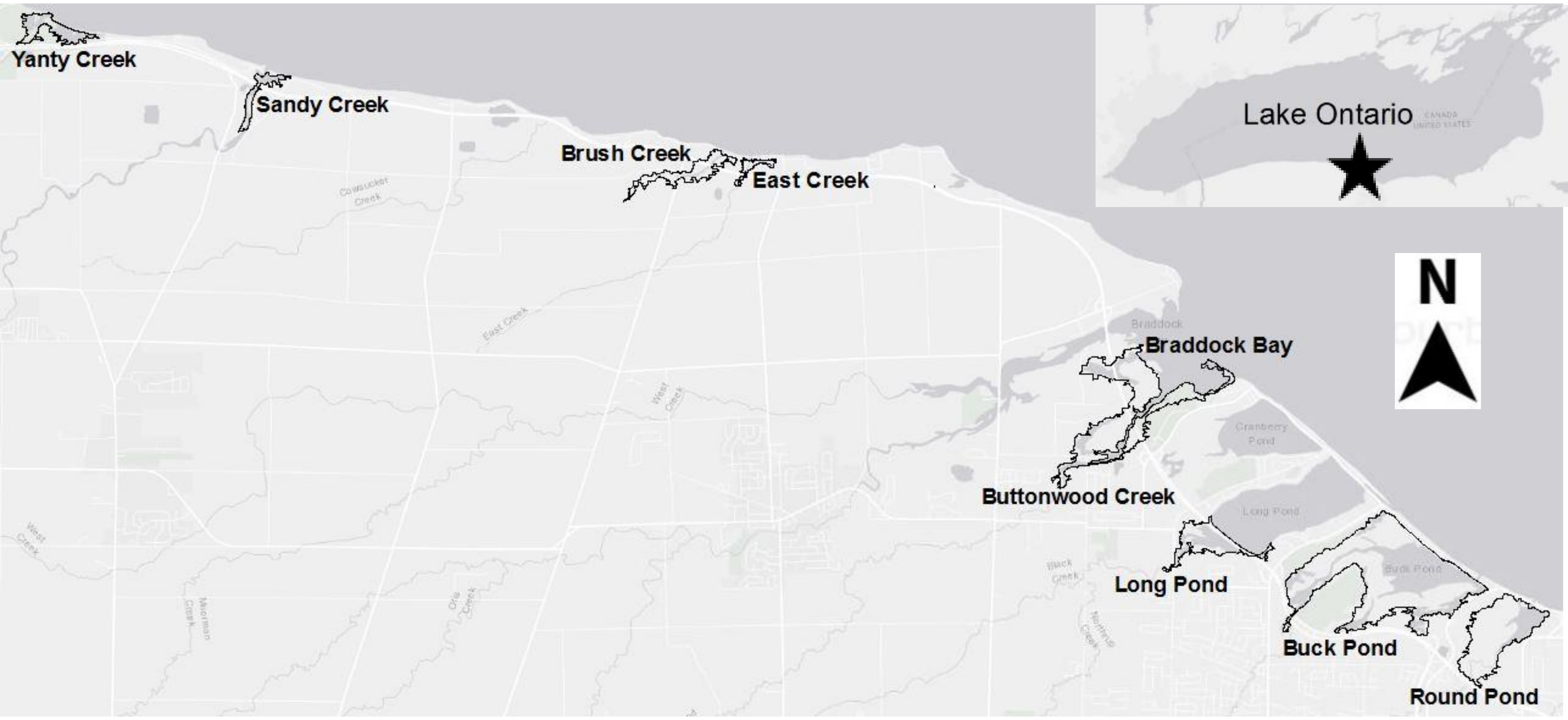


Figure 1. Map of 8 Lake Ontario coastal wetland study sites. Restored wetlands: Yanty Creek, Braddock Bay/Buttonwood Creek, Long Pond, and Buck Pond. Unrestored wetlands: Sandy Creek, Brush Creek, East Creek, and Round Pond.

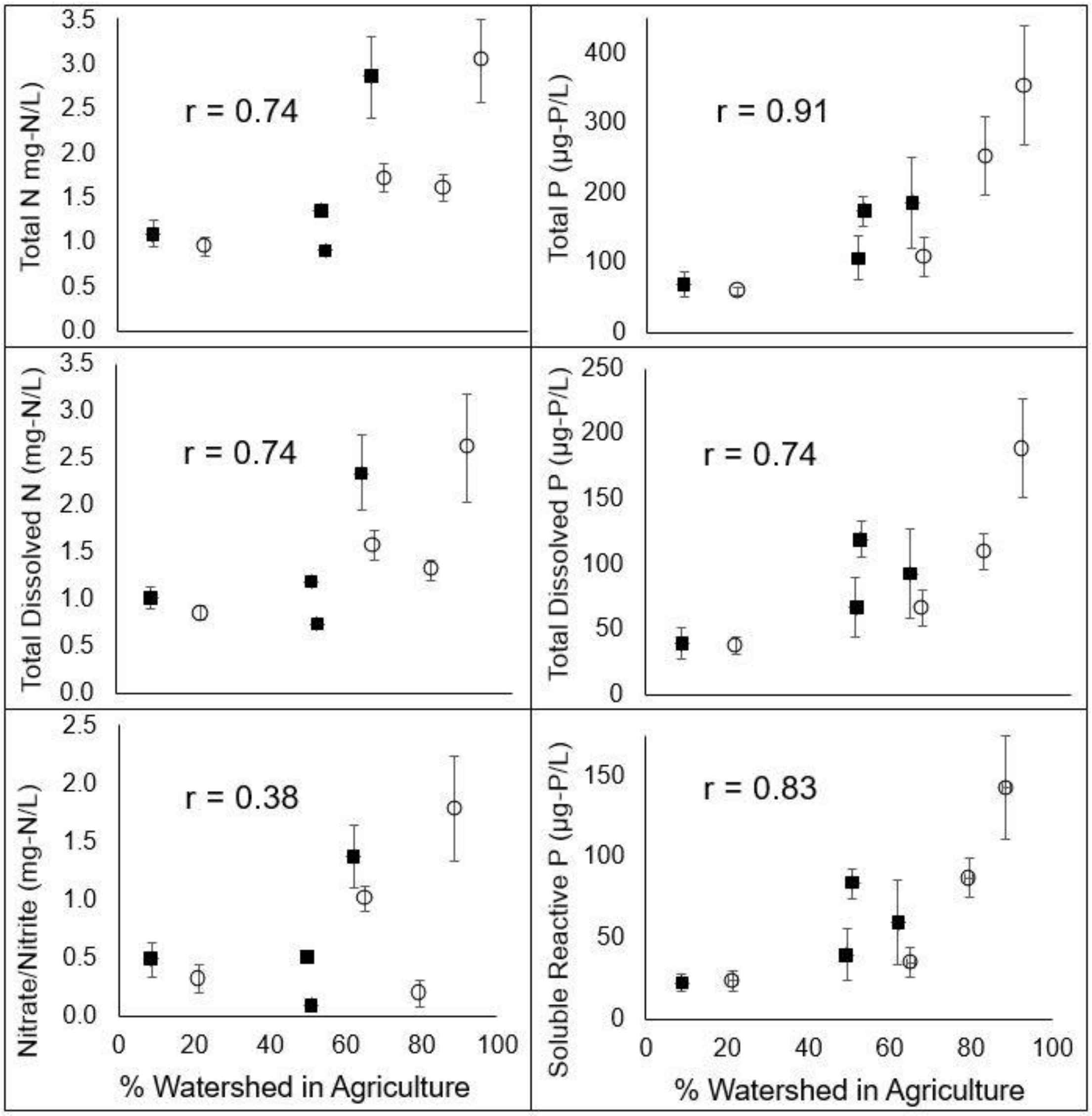


Figure 2. Correlations between the percentage of each watershed that is covered in agriculture and nutrient concentrations of N and P with standard error as TN, TDN, NO_2/NO_3, TP, TDP, and SRP. Restored wetlands are noted as solid black squares and unrestored wetlands as open white circles.

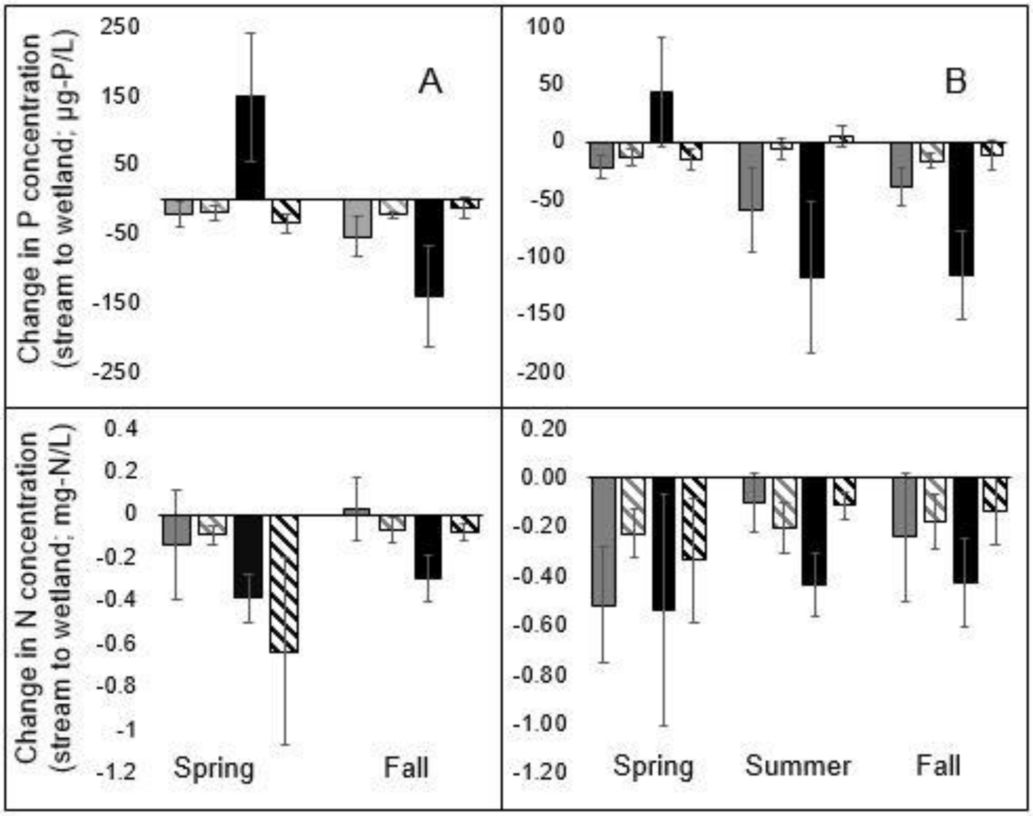


Figure 3. Change in concentrations of TN and TP (black) and NO_2/NO_3 and SRP (grey) between stream and wetland locations of restored (R; striped) and unrestored (U; solid) systems under storm flow (A) and base flow (B). Data are presented as mean seasonal changes and standard error. A negative value indicates a reduction in concentration from stream input to wetland complex.

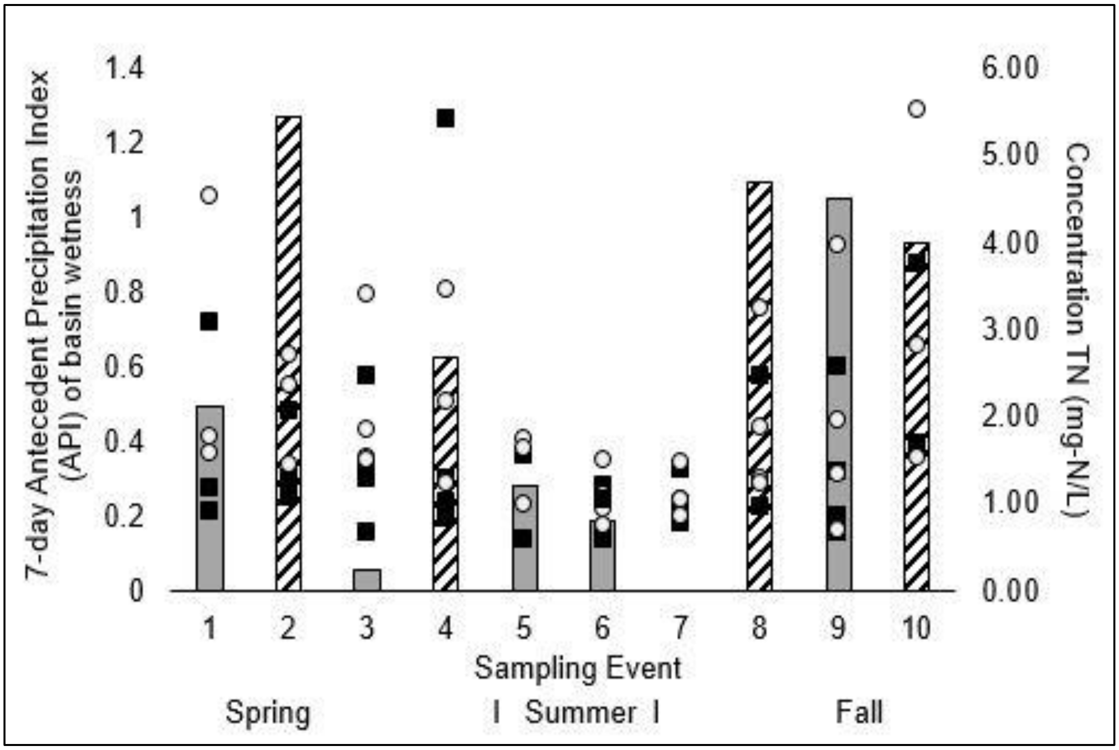


Figure 4. Stream concentrations of TN for each sampling event in restored (black squares) unrestored (white circles) wetlands against changing basin wetness (bars) at 7 days leading up to each sampling event. Base flow events are in solid bars and storm flow events are in striped bars.

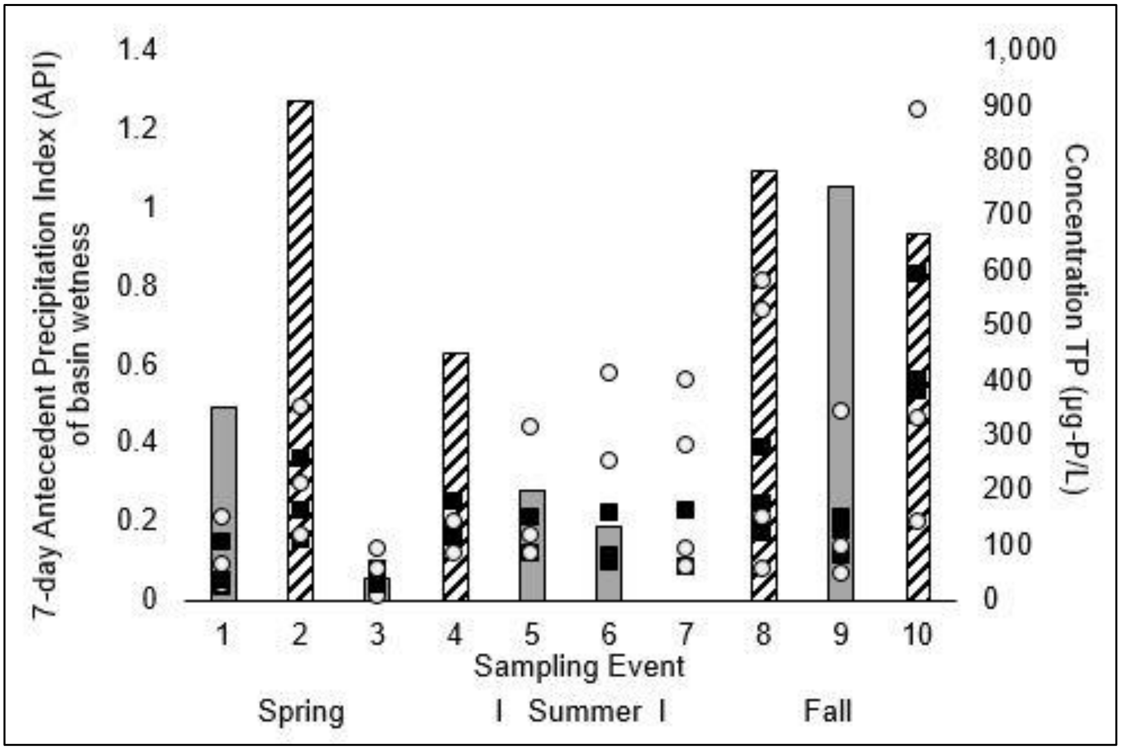


Figure 5. Stream concentrations of TP for each sampling event in restored (black squares) and unrestored (white circles) wetlands against changing basin wetness (bars) at 7 days leading up to each sampling event. Base flow events are in solid bars and storm flow events are in striped bars.

CHAPTER 2: Drivers of dissolved organic matter composition across Lake Ontario coastal wetlands and their tributaries

INTRODUCTION

Dissolved organic matter (DOM) is ubiquitously present in all aquatic environments and is an important biologically active pool of carbon in global carbon cycles (Opsahl and Benner, 1997; Jiao et al., 2010). The origin, composition, and function of DOM has been studied extensively in aquatic systems to understand its role in biogeochemical and ecological processes, as it supports heterotrophic bacterial production, influences ambient physical conditions (e.g., light attenuation, pH, dissolved oxygen), and affects properties and fate of other materials (Thurman, 1985; Keil and Kirchman, 1991; Wetzel, 1992; Morris et al., 1995; Amon and Benner, 1996). Broadly, there are three types of DOM in aquatic systems: 1) externally produced (allochthonous) terrestrial- and soil-derived, 2) internally produced (autochthonous) DOM from biota, and 3) synthetic organic substances from anthropogenic origin. Timing, magnitude, and composition of DOM exported from terrestrial sources to the aquatic environment depends on seasonal temporal patterns and episodic weather events (Petrone et al., 2006; Eimers et al., 2008; Jaffe et al., 2008; Fellman et al., 2009), as well as watershed land use, hydrology, and human activities (Cronan, et al., 1999; Dazell et al., 2007; Wilson and Xenopoulos, 2009; Williams et al., 2010). Autochthonous DOM can be influenced by nutrient availability, solar radiation, temperature, moisture, and substrate quality, among other environmental conditions (Findlay and Sinsbaugh, 2003).

Wetlands, residing at the land-water interface, can often function as sites for decomposition, production, and transformation of organic matter (Reddy et al., 2000; Yamashita et al., 2010), where bacterial transformations of DOM are fundamental to the structure and dynamics of energy and nutrient fluxes (Wetzel, 1992). As such, fluvial and surface-flow wetlands accumulate organic matter and commonly have high concentrations of dissolved organic carbon (DOC), which often appears amber in color and is allochthonous in origin (Biers et al., 2007; Eimers et al., 2008, Graeber et al., 2012). Many wetland systems, however, are degraded by eutrophication, alterations to hydrologic flow, and invasive species (Zedler and Kercher, 2005; Davidson et al., 2014). In human-impacted aquatic ecosystems, DOM tends to have less color and consists of anthropogenic or autochthonous origin, which alters how DOM is processed, cycled, and functions (Fellman et al., 2008; Williams et al., 2010). DOM from anthropogenic and autochthonous sources is sometimes more readily decomposed and preferentially used to meet microbial energy demands (Petrone et al., 2011), and has been linked to increased eutrophication (Seitzinger et al., 2002). As a response to degradation, wetlands are being restored, but little research has examined if restoration returns wetland DOM characteristics to a more natural state. Here, I characterize DOM pools in restored and unrestored coastal wetlands of a Laurentian Great Lake to explore the drivers of DOM composition, with the intention of informing future protection and management in these vulnerable systems with any ecologically meaningful results as it pertains to broader carbon cycling.

Terrestrial-aquatic linkages can be traced through DOM, which tends to be transported from upstream to downstream environments through rivers and eventually reaches the ocean (Opsahl and Benner, 1997; Jiao et al., 2010). This movement of DOM is sensitive to extreme precipitation events such that storm events are associated with increases in surface water DOC concentration and DOM aromaticity, molecular weight, and lignin content (Hinton et al., 1997; Bernal et al., 2002; Jaffe et al., 2008; Vidon et al., 2008). In addition to hydrologic connectivity within the watershed, water levels and hydroperiod are known to influence all biogeochemical processes in wetlands (Miao et al., 2017). Strong temporal trends in DOM character are also shown seasonally by controls of temperature, moisture, and vegetative productivity. DOC concentration is typically highest in warm months and lowest in cold months in association with spring melt and fall wet-up trends (Eimers et al., 2008; Wilson and Xenopoulos, 2008). Internal microbial production of DOM is typically greatest during summer months at peak vegetative productivity, high temperature, and low soil moisture (Jaffe et al., 2008; Wilson and Xenopolous, 2008), but it can also be observed in fall months during decomposition of senesced macrophytes (Lapierre et al., 2009).

Quality and quantity of DOM in aquatic environments has been strongly linked to watershed land use and human activities. Conversion of land use from forest or wetland to agriculture often reduces the chemical complexity of DOM from large, aromatic, humic-like structures to smaller, more recently produced, microbially derived and protein-like DOM with fewer carbon bonds (Wilson and Xenopoulous, 2009). As such, DOM originating from heavily human-impacted watersheds containing anthropogenic pollution from urban development and agriculture can increase bioavailability of DOM, autochthonous microbial production, and DOC concentrations at local to regional scales (Baker and Inverarity, 2004; Williams et al., 2010; Petrone et al., 2011; Stanely et al., 2011; Jaffe et al., 2014).

Various wetland restoration methods have aimed to improve fish and wildlife habitat, reduce invasive species, and increase native species abundance and diversity (Wilcox and Whillans, 1999; Wilcox et al., 2017; U.S.A.C.E., 2018). Yet, the influence of restoration on DOM character is not currently well understood. Wetland restoration methods in coastal wetlands on the southern shore of Lake Ontario included active habitat modification such as excavating channels and potholes in the vegetative complex of a monospecific stand of an invasive cattail species (*Typha* x *glauca*). These methods may have changed the hydrologic connectivity within the wetlands (Wilcox et al., 2008), but it is uncertain if this change operates in a manner that affects DOM availability, transport, and processing. There is often a lag between the completion of a restoration and observable biogeochemical responses, as restoration trajectories are slow for these complex processes (Fenstermacher, 2011; Moreno-Mateos et al., 2015). Some studies on the geological, physical, and biological factors driving DOM character suggest that catchment-scale characteristics (e.g., land use, hydrology, morphology, climate, soil moisture) are the strongest indicators of DOM properties, while other studies suggest that internal processing might outweigh the impact of landscape characteristics in small, high-nutrient systems (e.g., Williams et al., 2013). If catchment-scale controls outweigh the potential impacts of small-scale localized wetland restoration on DOM character or insufficient time since restoration has been allotted to see biogeochemical responses, it is unlikely that restored and unrestored wetlands will exhibit detectably different DOM properties.

Previously, bulk analyses have been used to study changes in DOM concentrations (Hinton et al., 1997), but little information on ecologically relevant details of chemical structure are given with these methods. The DOM pool can be characterized through optical chemistry, providing reliable information on molecular structure and make inferences about source, mobility, state of decomposition, and biological reactivity (Coble, 1996; Fellman et al., 2010). Absorbance combined with fluorescence spectroscopy has been used to identify a broad range of natural (terrestrial-derived plant and soil litter) and anthropogenic (e.g., wastewater, urban, and agricultural runoff) DOM inputs into freshwater ecosystems since the wavelengths at which fluorescence occurs are unique to certain molecular structures (Parlanti et al., 2000; Murphy et al., 2011; Mostofa et al., 2013). Both DOC concentration and chemical composition of DOM influences the intensity and shape of fluorescing spectra. This study used optical chemistry to 1) characterize the DOM pool of restored and unrestored fluvial, coastal wetlands in Lake Ontario and their major tributary, 2) determine if restored coastal wetlands in Lake Ontario have more allochthonous DOM character than that of disturbed, unrestored wetlands, and 3) explore the drivers (e.g., land use, season, and precipitation) of DOM properties in these streams and wetlands.

DOM signatures have not been described previously in this area and it is currently unclear if wetland restoration projects, like those conducted in this study area, influence DOM composition. I hypothesized that 1) DOM in restored wetlands will appear similar in composition to DOM in unrestored wetlands, 2) DOC concentration and humic-like DOM characteristics will be highest under storm flow and high basin saturation, 3) protein-like fluorescence reaches its highest relative abundance during the summer season, and 4) across wetlands, the DOM pool is richer in microbial-like characteristics as amounts of agricultural and urban land use increase. To test these hypotheses, changes in DOC concentration and DOM characteristics were monitored as water flowed into restored and unrestored wetlands and their main tributary ten times over the growing season from April to October 2017, capturing base and storm flow conditions.

METHODS

Study Sites and Sampling Design

Water samples were collected from four restored (Braddock Bay, Long Pond, Buck Pond, and Yanty Creek) and four unrestored (Sandy Creek, Brush Creek, East Creek, and Round Pond) coastal wetlands within 25 km of the Lake Ontario Rochester Embayment Area of Concern (New York, USA) and their main tributaries to characterize the DOM pool during an unusually high lake level year (Figure 1). Sampling was broken up seasonally into spring, summer, and fall, defined by spring and fall equinoxes and summer solstice. Water samples were collected from the largest tributary input close to the up-stream opening of the wetland and within the main flow path of the vegetative wetland complex, but upstream from the mouth of the wetland to the lake. All samples were collected on a single day for each sampling event. Storm flow sampling was defined as samples collected within 48 hours after a rain event that produced $\geq$ 1.5 cm of rain in a 24-hour period.

At each sampling point, a 30 mL glass amber bottle was filled with filtered water collected just below the water's surface for DOM and DOC laboratory analyses. Sample water was filtered on site using a 0.45 µm polycarbonate membrane filter and syringe system. Each filter was rinsed with 30 ml of deionized (DI) water and 10 ml of sample prior to collecting sample filtrate. Prior to filling, each bottle was sample-rinsed with filtered sample water. A 125 mL polycarbonate bottle was also filled with whole sample water for total nutrient analyses. In addition, water temperature (°C) and pH were taken at depths of approximately 20-30 cm from the water surface with a Hydrolab DS5 multi-probe sonde calibrated the day before use. All samples were stored on ice in the dark for transport back to the lab and analyzed within two months of collection.

Precipitation and Lake Ontario water level, as indicators of water transfer and flow through each catchment, were used to understand potential influences of season, episodic weather, and environmental condition on DOM. Daily rainfall totals (mm) for the duration of the study were used from standard rain gauges at the nearby Rochester International Airport weather station (Greater Rochester International, 2017; https://wunderground.com/calendar/us/ny/rochester). Daily rainfall was compared to the 30-year normal for precipitation levels in this region from 1980 to 2010 (www.ncdc.noaa.gov/data-access/land-based-station-data/land-based-datasets/climate-normals/1981-2010-normals-data). Lake Ontario water levels for 2017 and height above the low water datum were obtained from the Rochester, NY station monitored by NOAA (tidesandcurrents.noaa.gov/waterlevels.html). Finally, an antecedent precipitation index (API; McDonnel et al., 1991) was used as a means to describe basin wetness over a pre-determined 7-day period prior to sampling (see methods, Chapter 1 for equation).

Stream watersheds were delineated and basin characteristics generated with the United States Geological Survey (USGS) StreamStats tool version 4.0 (http://streamstats.usgs.gov/). GIS ArcMap version 10.4 was used in tandem with 2011 edition Northeast National Land Cover Database files provided by USGS to produce percent land use classifications for each stream watershed. These land use and cover data were grouped into development, forest, agriculture, and wetland categories and used to compare watersheds among streams in reference to size, land use, and watershed-to-wetland area ratio. For more detail, see Chapter 1 methods.

Laboratory Analyses

All analytical procedures were done in the Limnology Laboratory of SUNY—The College at Brockport. Total nitrogen (TN) and total phosphorus (TP) samples were measured colorimetrically after persulfate oxidation/digestion using a Technicon Auto Analyzer II (SM 4500-P-F, APHA 1992). DOC concentration was measured as nonpurgeable organic carbon (NPOC) using a Shimadzu TOC-L analyzer and the Shimadzu ASI-L Autosampler via high temperature combustion of total dissolved carbon after acid sparing and measured as carbon dioxide with an infrared gas analyzer (SM 5310, APHA 1998). The instrument and method detection limit was between 0.1 and 0.3 mg-C/L. Optical chemistry of DOM was analyzed using an Aqualog® spectrofluorometer (Horiba; Hansen et al., 2018), which simultaneously measured absorbance and fluorescence spectra of DOM. Using a 1-cm path-length quartz cuvette, UV-Visible absorbance spectra were collected at a 3-nm interval and excitation and emission matrix (EEM) scans were made from excitation (Ex) 500 to 239 nm at a 3-nm interval and from emission (Em) 245.6 to 836.2 nm at a 2.33-nm interval, later trimmed to max Em 499.8 nm. EEM scans were adjusted for instrument variation, corrected for inner filter effects, blank-subtracted using laboratory-grade nanopure deionized (DI) water, and normalized by the Raman Peak area (RU) at 350 nm (Murphy et al., 2010; Harold, 2013). First-and second- order Raleigh scatter were removed at 25-nm intervals and negative fluorescence readings were set to zero as a preliminary treatment of EEMs. Samples with absorbance at 254 nm greater than 45 m^{-1} were diluted by 50% and rescanned. The scans were used to generate three-dimensional contour plots of fluorescence as a function of Ex and Em wavelengths.

From these pre-treated optical chemical data, a variety of commonly used diagnostic DOM indices were calculated to help describe the DOM pool’s source and composition. I used the following indices: a modified florescence index (FI; McKnight et al., 2001; Cory and McKnight, 2005, Cory et al., 2010), a freshness index (β:α ratio;

Parlanti et al., 2000; Wilson and Xenopoulos 2009), a modified humification index (HIX; Zsolnay et al., 1999; Ohno 2002), a spectral slope and ratio (S_R; Helms et al., 2008), and a specific UV absorbance (SUVA; Weishaar et al., 2003; Appendix F). FI was calculated as the ratio of Em wavelengths 470 nm and 520 nm obtained at Ex 370 nm (Cory and McKnight, 2005). FI yields information on source of DOM and is inversely related to lignin content. One of two sources is indicated: dominantly terrestrial-derived (low FI around 1.2 from plant or soil organic matter) or microbial-derived (high FI around 1.8 from extracellular release and leachate from bacteria and algae; McKnight et al., 2001; Cory and McKnight, 2005, Cory et al., 2010). β:α was calculated as the ratio of Em intensity at 390 nm divided by the Em intensity maximum observed between 420 and 436 nm, obtained at Ex 370 nm (Parlanti et al., 2000; Wilson and Xenopoulos, 2009). β:α ratio gives information on the relative contribution of recently produced DOM compared to degraded DOM, where higher fluorescence intensities in the β region (Em 390 nm at Ex 310 nm) have been associated with recently produced protein-like DOM and fluorescence intensities in the α region (Em 420 to 436 nm at Ex 310 nm) have been associated with more degraded and decomposed humic-like compounds (Parlanti et al., 2000; Wilson and Xenopoulos, 2009). HIX was calculated as the area under the Em spectra 435 to 480 nm divided by the peak area 300 to 345 nm + 435 to 480 nm obtained at Ex 254 nm. HIX is an indicator of humic substance content or extent of humification of the material; lower values (<0.75) indicate less humified plant material and higher values (>0.90) indicate fulvic acid extracts based on the assumption that Em spectra of fluorescing molecules will shift toward longer wavelengths as humification proceeds (Zsolnay et al., 1999; Ohno, 2002). S_R gives information about the size of the compounds via molecular weight (MW), source, and extent of photobleaching, where the S_R value is inversely related to MW (Helms, et al., 2008). Finally, SUVA was calculated as the absorbance at 254 nm divided by DOC (mg/L) concentration. SUVA can be used to suggest chemical composition and reactivity of DOC by normalizing the UV absorbance of the water sample for DOC concentration and strongly correlates with percent aromaticity of the carbon compound (Weishaar et al., 2003).

Finally, sample EEM scans (n = 173) were modeled using parallel factor analysis (PARAFAC) to decompose DOM fluorophore signatures, reduce EEM spectra, and separate them into individual components (Stedmon and Bro, 2008). This estimated each component's contribution to the total DOM fluorescence. Prior to modeling, EEMs were visually inspected for scanning errors. PARAFAC modeling was conducted in MATLAB (version 2017a) using the DOMFLuorv1 7 toolbox (Stedmon and Bro, 2003). The most likely PARAFAC model was selected stepwise after examining sum of squares error, model loadings, and model residual plots. The selected model was then validated using a split half analysis and Tucker congruency coefficient. A five-component PARAFAC model was selected as the best model and validated in all splits. The model produced a fluorescence intensity maximum (F_{max}) for each component. To analyze quantitative changes in concentration as they relate to flow conditions, I used fluorescence intensity in Raman Units (RU), but to reduce the influence of concentration on the model scores when analyzing relative shifts in DOM character, percent of F_{max} is presented for each component (i.e., [$F_{max}Cx/\Sigma F_{max}$ C1 to 5] × 100%). To determine the tentative identity of each PARAFAC component, the five components were compared to models previously described in the literature using OpenFluor set at 95% similarity (Murphy et al., 2014; Table 1; Figure 2) and compared visually to peaks identified by Coble (1996; 1998). The tentative component identities were as follows: terrestrial/humic-like (C1), microbial/humic-like/unknown (C2), soil/fulvic-like (C3), anthropogenic/humic-like (C4), and protein-like/tryptophan-like (C5; Table 1).

Statistical Analyses

DOM characteristics were observed to reflect a univariate normal distribution after evaluation for normality and homogeneity of variance using Shapiro-Wilk and Kolomogrov-Smirnov tests in IBM SPSS version 24. DOC concentration data were not normally distributed, however. Means and ranges for each variable were calculated in Microsoft Excel. Stream and wetland DOM properties were analyzed independently from each other to determine drivers of DOM character within habitat type. Univariate relationships between DOM characteristics (i.e., PARAFAC components as %, S_R, $\beta:\alpha$ ratio, FI, HIX, and SUVA), land use, and API values were compared using Pearson's bivariate correlations (r) in SPSS and a Holm-Bonferroni significance correction was applied with the Gaetano (2013) calculator to account for multiple test error inflation (Holm, 1979). DOC concentration, DOM characteristics, and API were correlated using Spearman's Rank. Basin-wide analyses used stream and wetland data together, so before variables were correlated with land use, the combined stream and wetland data were averaged for each site since streams and wetlands share the same watershed and land use did not change over any other factor tested. Before variables were correlated with API, the combined stream and wetland data were averaged for each event across sites and other factors since API only changed with sampling event. All other correlations were generated using event and site-specific values.

To compare differences in stream and wetland DOC concentrations, a related-samples Wilcoxon signed rank test was run on stream and wetland DOC paired by sites and event. For further DOC analyses, the full dataset was split into stream and wetland concentration subsets and analyzed independently. Univariate, unrestricted full factorial permutation analysis of variance (ANOVA) were run on land use (see methods, Chapter 1) and DOC data in R version 3.5.0 using the RStudio (2015) interface. These data were analyzed using a randomized permutation approach appropriate for non-parametric testing (Manly, 2007) to generate an F-statistic distribution from 9999 permutations of the original data instead of comparing the test statistic to a theoretical F distribution (Howell, 2009; http://www.uvm.edu/ ~dhowell/StatPages/ Permutation%20Anova/ PermTestsAnova). To generate a probability factor, the resampled F-distribution was compared to the F-statistic of the original data for the ANOVA model's main effects (season and flow for streams; restoration, season, and flow for wetlands) and their interactions.

For multivariate analysis, all data were Z-score standardized and scaled to make a distance matrix using the Euclidean method for each measurement variable.

Permutation MANOVA with resampling pairwise comparison (10,000) was run in R using the adonis function (Anderson, 2001) with the vegan package (Oksanen et al., 2006). This determined if stream DOM pools differed from those of wetlands, then DOM characteristics were split into stream and wetland subsets for further analyses, independently. Permutation MANOVA was run on wetland DOM differed among restoration status, season, and flow and also run on stream DOM differed among seasons and flow condition. Storm flow was not captured during the summer season, but I included data from the summer during base flow in analyses even though it was an unbalanced model design in order to test my hypothesis specifically regarding protein-like characters in the summer. The remaining statistical analyses were run using PRIMER v.6. Principle component analyses (PCA) was used on stream and wetland subsets to visualize factors that influenced the data and differences in DOM composition based on linear combinations of the variables using correlation matrices. PCs with eigenvalue above 1.0 were retained. Finally, two-way analyses of similarity (ANOSIM) with replication (10,000 permutations) were applied to a similarity matrix underlying the ordination of samples for pairwise comparisons of season and flow test factors.

RESULTS

DOM Characteristics

S_R ranged from 0.77 to 1.16 in streams and 0.76 to 1.54 in wetlands, showing a mixture of large and small sized compounds across sites and events. $\beta:\alpha$ in both habitats indicated generally more contribution of decomposed DOM than recently produced DOM, with streams ranging from 0.64 to 0.75 and wetlands 0.64 to 0.77. HIX values ranged from 0.83 to 0.94 in streams and 0.81 to 0.93 in wetlands, suggesting a moderate to high humic nature to the DOM pool. FI values indicated a mixture of microbial- and terrestrial-derived DOM in streams and wetlands (Table 2). SUVA ranged from 2.6 to 4.2 in streams and 2.0 to 4.3 in wetlands, meaning the DOM pool was a mixture of aliphatic to aromatic humic-like substances.

The terrestrial, humic-like component, C1, was the largest contributor to F_{max} in both streams and wetlands, accounting for an average of 47% (range 36% to 53%) of DOM fluorescence intensity throughout the study (Table 2). Mean contribution of microbial humic-like C2, and soil fulvic-like C3 was 23% (range 19.2% to 27.4%) and 12% (range 7.8% to 16.2%), respectively, in streams and wetlands. Anthropogenic C4 and protein-like C5 were the smallest overall contributors to DOM fluorescence, each less than 10% on average relative intensity. Streams tended to have slightly more C2 and C3 than wetlands but slightly lower amounts of C4 and C5 than wetlands (Table 2).

Small, fresh, microbial indices (S_R, $\beta:\alpha$, and FI) tended to correlate positively with each other. Humic and aromatic indices (HIX and SUVA) correlated positively with each other, but opposite to S_R, $\beta:\alpha$, and FI. C1 and C3 were correlated with HIX and SUVA ($r > 0.52$, $p < 0.001$), C2 was correlated with FI ($r > 0.72$, $p < 0.001$), and C4 and C5 were correlated with S_R and $\beta:\alpha$ in both streams and wetlands ($r > 0.44$, $p < 0.001$; Tables 3 and 4). C5 was more microbial-associated (FI) in streams ($r = 0.41$, p

<0.001), while C4 was terrestrial-associated in wetlands ($r = -0.31$, $p < 0.001$). In both streams and wetlands, DOC concentration was negatively correlated with S_R, β:α, C4, and C5 but positively correlated with C1 and HIX (Appendix G.1). In wetlands only, DOC was positively correlated with C2.

Despite some similar patterns between habitat types, stream and wetland DOM pools significantly differed in quality (MANOVA, $F_{1,149} = 4.75$, $p = 0.009$). Streams appeared to consist of larger terrestrial-humic aromatics than wetlands based on mean DOM index values (Table 2). Stream and wetland principle component analyses explained 90.1% and 91.0 % of the variation, respectively, in the DOM pools with three principle components. Aromatic and humic indices (SUVA, HIX) and terrestrial and soil C1 and C3 negatively loaded with PC 1. Small compound size (S_R), freshness (β:α) and anthropogenic and protein-like C4 and C5 positively loaded with PC1. Microbial source (FI) and microbial C2 positively loaded with PC2, but neither loaded strongly with PC1 in a positive or negative direction (Figure 3; Appendix G.2). In both stream and wetland systems, HIX and SUVA loaded negatively with PC2, while C1 and C3 loaded positively with PC2. However, unlike streams, C4 loaded dissimilarly to other variables in wetlands (Figure 4; Appendix G.3).

Environmental variables and DOC concentrations

Mean temperature and pH for the duration of the study were 16.3 (7.9 to 24.8) ˚C and 7.3 (6.1 to 8.4), respectively, but seasonal mean temperature was highest in summer, as expected. Mean specific conductance measured 574 (224 to 1667) µS/cm.

For both streams and wetlands, temperature and pH were significantly correlated with small, freshly produced anthropogenic and protein-like components (SR, β:α, C4, and C5; $r > 0.27$, $p < 0.05$), and negatively correlated with terrestrial humic-like characteristics and components (HIX, SUVA, C1 and C3; $r < -0.29$, $p < 0.05$; Tables 3 and 4).

TN and TP concentrations in most stream-to-wetland complexes in this study commonly measured in eutrophic ranges over 1.2 mg-N/L (0.44 to 7.37 mg-N/L) and 200 µg-P/L (6 to 891 µg-P/L), respectively, for much of the year, with stream concentrations often exceeding wetland concentrations. Over the duration of the study, unrestored wetlands showed higher concentrations of TN and TP compared to restored wetlands. However, across all wetlands, nutrient concentrations appeared to be elevated under storm flow, with mean seasonal TN highest in spring and mean seasonal TP highest in fall (see results, Table 1, Chapter 1).

Wetlands had significantly lower median DOC concentration than their tributaries (Wilcoxon, $Z = -3.41$, $p = 0.001$; Appendix G.4). Mean concentration of DOC in wetlands was slightly lower than in streams (Table 2). Restored wetlands had a significantly higher mean DOC concentration than unrestored wetlands (ANOVA, $F_{1,65} = 8.59$, $p = 0.005$; Appendix G.5). When considering all streams and wetlands regardless of restoration status across seasons and flow conditions, the overall mean concentration of stream DOC was relatively consistent across seasons ($F_{2,71} = 0.08$, $p = 0.919$), but there was marginal evidence that DOC concentration was elevated in streams under storm flow conditions ($F_{1,71} = 3.00$, $p = 0.086$), especially in the spring during storm flow conditions ($F_{1,71}$ = 1.44, p = 0.072; Appendix G.6). In wetlands, DOC concentration also tended to be higher under storm flow ($F_{1,65}$ = 3.11, p = 0.088; Appendix G.5).

Restoration, Season, and Flow Influences on DOM Character

Stream DOM (based on characteristic indices and component contribution as a percent of F_{max}) was significantly different among seasons (MANOVA, $F_{2,71}$ = 17.92, $p<0.001$) and flow condition ($F_{1,71}$ = 22.63, $p<0.001$), with a significant interaction between season and flow observed ($F_{1,71}$ = 4.27, p = 0.012; Table 5). When considering fluorescence intensity as RU, stream DOM was again found to be significantly different among seasons ($F_{2,71}$ = 5.28, p = 0.001) and flow ($F_{1,71}$ = 10.65, $p < 0.001$; Table 6). In the PCA ordination of the MANOVA results, samples reflected large, terrestrial humic-like, aromatic composition during the spring season, then shifted to a small, fresh, microbial- and protein-like composition through the summer and fall (Figure 3). DOM character during the spring appeared most similar within seasonal group compared to DOM within other seasons; fall had the most variability (Figure 3). Pairwise comparisons among seasons indicate that spring and fall are statistically most dissimilar (ANOSIM, R = 0.505, p = 0.001; Appendix G.7). PCA analysis also illustrated a separation of DOM composition between flow events across all seasons, where DOM sampled under storm events is terrestrial humic-like aromatics loading almost entirely negative with PC1. Stream DOM was different between storm and base flows based on ANOSIM (R = 0.321, p = 0.001).

Wetland DOM characteristics and component contribution did not differ significantly between restored and unrestored wetlands (MANOVA, $F_{1,65} = 1.95$, $p = 0.124$), but significantly differed between seasons ($F_{2,65} = 10.58$, $p< 0.001$) and flow ($F_{1,65} = 12.85$, $p < 0.001$; Table 7). MANOVA of wetland DOM fluorescence intensity showed the same patterns in season ($F_{2,65} = 2.86$, $p = 0.032$) and an increase under storm flow ($F_{1,65} = 8.04$, $p = 0.002$; Table 8). However, contrary to insignificant differences in DOM character between wetlands of different restoration status, restored wetlands showed significantly higher fluorescence intensity ($F_{1,65} = 10.19$, $p < 0.001$; Table 8). Therefore, source and composition of DOM did not differ between restored and unrestored wetlands, but restored wetlands supported higher DOC concentrations.

In conjunction with MANOVA results, relatively similar but weaker seasonal and flow-related patterns that were present in streams also appeared in wetlands, but there was greater overall variation in wetland data compared to streams. Storm flow and spring season were most associated with terrestrial humic-like aromatic composition. However, there was more seasonal and flow condition overlap in wetlands compared to streams, with a mixture of terrestrial humic-like and microbial protein-like DOM across most seasons and flows (Figure 4). Fall and spring seasons were again least similar (ANOSIM, $R = 0.35$, $p = 0.\ 0.001$; Appendix G.8), but summer and fall DOM composition overlapped ($R = 0.00$, $p = 0.403$) in wetlands. Wetland DOM seemed to be less variable within flow group under base flow than under storm flow (Figure 4).

Drivers of DOM Properties at the Watershed Scale

Watershed size and watershed area-to-wetland area ratios were variable across sites and between groups of restored and unrestored wetlands (see chapter 1). All catchments contained some extent of each land use category (agriculture, forest, wetland, and urban development). Percent land use cover in forest was significantly greater in restored wetlands than unrestored wetlands (ANOVA, $F_{1,7} = 13.82$, $p = 0.010$; Chapter 1, Appendix D.1), but no other significant differences in land use were observed. Wetlands made up a small fraction of land use and cover in all watersheds (0.3 to 7.9%; Chapter 1, Table 2).

DOM composition showed relationships to agriculture, urban development, and forest cover but not wetland cover (Table 9). Forest cover was significantly associated with aromatic structures (SUVA, $r = 0.83$, $p = 0.012$) and agriculture was found to be associated with higher concentrations of total nutrients, HIX, and terrestrial-humic C1 and microbial-humic C2 ($r = 0.74$ to 0.88, $p = 0.044$-0.04; Table 9). As urban developed land cover increased, fresh, microbial-like, anthropogenic DOM also increased significantly, showing correlations with $\beta:\alpha$ and C4 ($r = 0.87$ to 0.96, $p = 0.005$ to 0.001). Anthropogenic influence on water quality was further demonstrated, as urban development cover correlated strongly with specific conductance ($r = 0.97$, $p = 0.001$; Table 9).

Basin wetness values given with the API significantly differed between storm and base flow events (ANOVA, $F_{1,9} = 7.947$, $p = 0.024$; see Chapter 1, Appendix D.2) and were significantly correlated to component contributions. API, which can be associated with higher flows, significantly correlated positively with DOC (r = 0.661, p 0.038) and C3 (r = 0.76, p = 0.010), but negatively with C4 (r = -0.87, p = 0.001; Appendix G.9). Basin wetness associated with storm flow events and the increase in soil DOM signatures (C3) is supported by PCA of stream and wetland data, where C3 loaded toward the direction where storm flow event data points congregate most (Figures 3 and 4). However, fall data load positively with PC2 and spring data negatively with PC2, suggesting that the influence of API on C3 contribution was more apparent in fall. HIX and C2 were correlated with API.

Land use cover and basin wetness influences on DOM that cannot be explained by characteristic indices or percent component contribution can be observed through quantitative changes in intensity of fluorescence shown in EEM-PARAFAC contour plots of the data. For example, during the fall season, I compared stream and wetland contour plots of unrestored East Creek, which contained the greatest watershed cover in agriculture at 88.7% and the restored Braddock Bay, which contained the greatest watershed cover in forest at 30.0% (Figure 5, Chapter 2; Table 2, Chapter 1). I examined patterns under a base flow event (7), when basin wetness was low at API 0.00 and under a storm flow event (10), when basin wetness was high at API 0.93. RU intensity was significantly different between the streams and wetlands (MANOVA, $F_{1,149} = 4.41$, p = 0.0133), supporting the significant difference between habitat types reported by the qualitative tests but yield more quantitative patterns. In this example of the contour plots, maximum intensity of fluorescence measured higher in streams (about 3.0 to 4.0 RU) than in wetlands (about 1.0 to 3.0 RU) for both land use types.

DISCUSSION

DOM plays a critical role in the dynamics of aquatic environments (Keil and Kirchman, 1991; Wetzel, 1992; Driscoll et al., 1995; Morris et al., 1995), and wetlands can be considered a DOM focal point, with high rates of production, decomposition, and transformation (Findlay and Sinsabaugh, 2003; Yamashita et al., 2010). In natural systems, hydrological regimes and landscape geology and morphology are strong predictors of terrestrial accumulation and transfer of DOM. Spring snow melt and heavy precipitation events typically increase DOC concentration and the delivery of humic-like compounds (Eiemers et al., 2008; Vidon et al., 2008), and microbial, protein-like characteristics of DOM pools typically increases in warmer seasons and drier conditions (Jaffe et al., 2008; Wilson and Xenopoulos, 2008; Fellman et al., 2009). In human-dominated systems, DOM quality and quantity can be modified and subject to change, as increased agricultural and urban development activities have been linked to shifts in more bioavailable, freshly produced, microbial-like and protein-like signatures (Wilson and Xenopoulos, 2009; Williams et al., 2010; Williams et al., 2016). Compared to historical conditions, DOM export is thought to have increased in many ecosystems and DOM pools now tend to contain unique anthropogenic markers, such as synthetic compounds of trace pesticides, growth hormones, and antibiotics routinely used in intensive agriculture land use practices (Dalzell et al., 2007; Tank et al., 2010). Although many biogeochemical and ecological processes are influenced by DOM character, the matter is rarely incorporated into mainstream water quality analysis or considered as a major criterion for restoration and management practices.

My findings report a DOM pool in eight coastal wetlands of Lake Ontario with broad ranges of sources and structural/chemical properties. Consistent with previous works (Coble et al., 1998; Murphy et al., 2011; Osburn et al., 2011, 2012, 2016; Williams et al., 2013; Kothawala et al., 2014; Gueguen et al., 2015; Lambert et al., 2016), the terrestrial humic-like component represented the most abundant fluorophore group in this study (Table 1). The microbial-humic, soil-fulvic, anthropogenic, and protein-like groups previously described were also identified here, which means that DOM characteristics of these systems are not entirely unique from pools studied in freshwater systems to date. These systems generally fall within typical ranges for DOC concentration, HIX, S_R, and SUVA values described in wetland DOM pools (Ohno et al., 2002; Weishaar et al., 2003; Helms et al., 2008; Fellman et al., 2008; Yamashita et al., 2010). DOM character differed by stream and wetland even though similar patterns in season and flow were shared by both habitat types. Restoration did not seem affect the DOM pool. Warmer conditions presented an association with smaller, freshly produced, anthropogenic DOM, and wetter conditions were linked to increases in soil-derived DOM. Agricultural land use tended to be associated with nutrients, terrestrial, and microbial humic-like components, and an anthropogenic signature was linked to urban developed land use.

Storm Events and Seasonal Influences on DOM

DOC concentration normally increases with stream discharge during storm flow, and these high export episodes typically contribute to a large portion of total annual DOC export (Hinton et al., 1997; Bernal et al., 2002). Although there was only marginal evidence for elevated DOC concentrations after storms, precipitation events are still widely known to trigger large pulses of release in terrestrial DOM and a significant elevation in RU intensity identified pulses not observed in concentration. I was not able to measure stream velocity directly or discharge rates in these study sites due to limitations of equipment and resources, nor was I able to use data from preexisting stream gauges since they were too-far-removed upstream from the sampling sites. The calculated API values of basin wetness can, in part, be associated with storm events.

In most cases, the literature reports an association with storm events and temporary shifts in DOM character through increases in aromaticity and average molecular weight in DOM as enhanced signal of humic-like fluorescence (Jaffe et al., 2008; Vidon et al., 2008). Precipitation during this study for the year 2017 was extreme in intensity and frequency compared to data on 30-year precipitation normals for the region (www.usclimatedata.com/climate/rochester/new-york/united-states/usny1232), resulting in relatively wet conditions at the watershed level and in the wetland sites themselves, with record high water levels in Lake Ontario for much of the year (https://tidesandcurrents.noaa.gov/waterlevels.html?id=9052058; see *Hydrologic and Seasonal Influences on Nutrient Retention*, Chapter 1). Wet, flooded conditions, in combination with heavy rain, may explain why wetlands appeared slightly more humic in nature than streams, considering the patterns between landscape flushing and terrestrial humic-like material. Since dissolved humic substances typically account for a bulk of fluorescence in natural waters (Del Vecchio and Blough, 2004), a significantly higher fluorescence intensity observed under storm flow supports my hypothesis that DOC concentration would significantly increase under storm flow.

When comparing the relationship with basin wetness (API) and humic-like compounds and DOM characteristics in this study, the relationships are less clear than the MANOVA flow results. Yet, significant correlations with soil, fulvic-like C3 and HIX in streams and wetlands indeed suggested flushing of terrestrial DOM with rain events and supports my hypothesis that larger, humic-like, more aromatic DOM signatures would increase under storm flow. These data further support this pattern with PCA for streams and wetlands, as samples measured during storm flow across seasons were best described by terrestrial, humic-like, aromatic index values and components. However, unexplained significant correlations of HIX and microbial-like C2 to API are contrary to other results and my hypothesis, meaning that the extent of humification/decomposition and contribution from humic-like components may have been higher under wet conditions and storm events. A lack of relationship between API and humic-like C1 can potentially be explained by the ubiquitous presence for this terrestrial fluorophore group and its large contribution to the DOM under most circumstances, depreciating any significant changes during storms.

Seasonally, DOC concentrations typically decrease in temperate zones during spring from snow melt and frequent rain/basin wetness dilution and show highest concentrations in warm months with lower soil moisture conditions (Eimers et al., 2008; Wilson and Xenopoulos, 2008). The data in this study showed no significant difference in DOC concentration among seasons in streams or wetlands, but significant seasonal differences were observed for DOM characteristics. Hence, DOM changed in composition but not concentration across seasons. Temporal trends in DOM seasonally are associated with temperature, moisture, and vegetative productivity (Petrone et al., 2006; Fellman et al., 2009; Lappiere et al., 2009; Williams et al., 2010). Here, I use temperature to further explore seasonal patterns, when highest mean seasonal temperature occurred during summer, as expected. Temperature correlated positively with indicators of small and freshly produced DOM characteristics and protein-like and anthropogenic components, but correlated negatively with terrestrial-humic indices and components (Tables 3 and 4). In conjunction with the literature and my hypothesis, protein-like fluorescence reached its highest relative abundance during the summer season based on temperature (Jaffe et al., 2008, 2014). This may be due to internal production of DOM increasing during summer conditions that permit high primary productivity. When considering moisture conditions, these data arguably show small, fresh, protein-like DOM composition in the fall according to PCA. Over the course of the study, basin and wetland conditions were wettest in the spring and driest in the fall based on data of precipitation and high lake water levels. This difference in flooding between spring and fall could be responsible for the greatest pairwise difference in overall DOM composition observed between spring and fall and drier conditions may account for protein-like contribution in the fall.

The Effects of Land Use and Basin Wetness Trends on Composition of DOM

Quantity and quality of terrestrial DOM entering aquatic recipients depends largely on hydrologic flow paths (Petrone et al., 2006; Fellman et al., 2009), geology (Yamashita et al., 2010), and soil type (Fellman et al., 2008). Given that terrestrial-derived DOM is mobile and hydrologically connected to the landscape, it is reasonable to assume that land use within a watershed strongly affects DOM delivered downstream. Natural land cover, such as forest and wetland, usually coincide with terrestrial humic-like DOM and increases in DOC concentration (Xenopoulous et al., 2003; Mostofa et al., 2013). Agricultural and other intensive anthropogenic land uses tend to increase nutrient loading more than would naturally occur in forest or wetland dominated catchments (see chapter 1; Trebitz et al., 2007) with application of nutrient fertilizers and intense management of upper soil layers with tillage and drainage. Wilson and Xenopoulos (2009) made clear the connections between nutrient enrichment from agricultural land use and microbial humic-like DOM, which supports a nutrient-driven transformation of DOM character. Williams et al. (2010) suggested that DOM exported from agriculture-dominated watersheds is likely more labile and accessible to the microbial community.

Anthropogenic DOM from urbanized streams tends to be more protein-like, aliphatic, and photoreactive (Murphy et al., 2011; Meng et al., 2013; Williams et al., 2016). These patterns have ecological implications because DOM from anthropogenic and autochthonous sources at times are more readily decomposed and preferentially used to meet microbial energy demands (Petrone et al., 2011), has been linked to increased eutrophication (Seitzinger et al., 2002), and provide aquatic organisms less protection from damaging ultraviolet radiation than compounds with higher humic substances (Del Vecchio and Blough, 2004).

These data display evidence to support my hypothesis that increases in agricultural and urban land uses would increase the contribution of smaller, recently produced microbial-like, and protein-like components to the total DOM pool. High nutrient-associated, agricultural land use increased contributions of the microbial component (2) and urban development land cover was significantly related to specific conductance and small, freshly produced compounds of anthropogenic and protein-like sources with greater C4 and C5 contribution. Significant relationships between wetland cover and DOM character may be lacking due to the small percentage of each watershed that wetlands occupy (less than 8%). Although DOM characteristics can vary within aquatic ecosystem type, wetland DOM is typically characterized by structurally complex, high molecular weight aromatics that are less bioavailable for microbial use (Fellman et al., 2008; Graeber et al., 2012; Inamdar et al., 2012). In this study, streams reflected more of these properties than wetlands. This could potentially be due to a dilution effect of exceptionally wet basin conditions and the coastal wetlands' position in the landscape with intimate hydrological contact with Lake Ontario, which differ from other stagnant and isolated wetland types.

Noting the influence that hydrology has on wetland environments and biogeochemical processes (Miao et al., 2017), I believe that basin wetness and lake water levels worked in conjunction with land use to affect the data. Particularly when I examined the relationship between HIX and basin-wide wetness, I found some variation in the data that could be explained by API. I suspect that, despite the role land use played in DOM quality for this study, some microbial DOM signal I would expect to see from agricultural watershed draining might have been undermined by an unusually wet year with record precipitation and high lake water levels, causing flooding in wetland sites above normal. These conditions may have permitted a lake effect that mixed coastal lake water into the wetlands and diluted the signal that would be observed under average basin wetness conditions. Verification of this will require sampling for much longer times than the short duration of this study and sampling under contrasting conditions for reference.

Restoration as a Small Player in Drivers of DOM

Most upland and stream management practices have the potential to influence DOM delivery due to a large portion of aquatic DOM that originates from the terrestrial landscape. Some studies have suggested that riparian buffer zones intercepting harmful, unnatural DOM between terrestrial source and stream vector connecting to downstream ecosystems as the most practical solution as it allows upland land use to continue (Stanley et al., 2012). Others have offered that increased watershed cover in wetland and construction of multiple wetlands, if even small in size, scattered throughout the watershed would improve water quality as a function of reducing landscape homogeneity (Mitsch and Gosselink, 2000; Moreno-Mateos et al., 2008). However, localized downstream wetland restorations, like those conducted in these sites, are small in scale compared to the size of the watershed and are likely constrained in their ability to influence delivery. Time since restoration, seasonal changes in temperature and moisture, as well as episodic precipitation events and watershed land use composition were likely stronger constituents to drivers of DOM character in both restored and unrestored wetlands, although differences in DOM intensity/concentration were observed between restored and unrestored wetlands.

Wetland restoration efforts implemented at these sites aimed to improve habitat quality and biodiversity by excavating channels and potholes within the vegetative complex of a dense cattail monoculture. These methods may have influenced the hydrologic connectivity in some manner (Wilcox et al., 2008) but not to the point at which processes affecting DOM composition were altered significantly. DOC concentration was marginally higher and fluorescence intensity of DOM was very significantly higher in restored wetlands than unrestored wetlands despite no marked differences between wetlands of either status when considering DOM quality. A change in concentration without a change in composition, suggests that these coastal wetlands are building carbon of the same type regardless of restoration status. This finding supports my hypothesis that restored and unrestored wetlands would show similar DOM character. Wetland restoration at these sites did not significantly impact DOM compound size, extent of decomposition, source, humification, or aromaticity. However, these results might suggest that restored wetlands were better isolated from lake mixing, or the restoration caused dissolution of particulate organic matter (POM) to DOC, or the restored wetland somehow increased organic matter production and DOM leaching. The reason for the impact is likely well outside the scopes of this study and differences between restored and unrestored wetlands may not have to do with restoration itself but, instead, upland processes or geomorphic characteristics of the systems.

A lack of difference in DOM composition between restored and unrestored wetlands may be attributed to the relatively young age of these restorations, which were between only one and four years at the time of the study. Consistent with research showing a lag between restoration and biogeochemical responses on the scale of decades or more (Mitsh and Wilson, 1996; Fenstermacher, 2011; Moreno-Mateos et al., 2015), I found little evidence that composition of DOM in restored wetlands could be distinguished from that of unrestored wetlands. Both restored and unrestored wetlands in this study are impacted by eutrophication with high nutrient concentrations (see chapter 1), originating from inputs from the landscape. Although restoration did not appear to affect DOM composition in this context, restoration is still useful in the discussion of ecological implications of DOM. Parlanti et al. (2000) found that the contribution of recently produced DOM was high in coastal zones characterized by nutrient enrichment and algae growth. Biological processes of DOM production can be environmentally important when considering that contaminants (i.e., metals, pesticides, nutrient pollutants) are often concentrated in wetland areas and adsorb to the surface of algae. Some water quality parameters were monitored in restorations conducted at these study sites, but a reduction in nutrient loading was not a target and any changes to nutrient or DOM loading must likely come from the upland processes.

CONCLUSIONS AND FUTURE RESEARCH

The intent of this study was to understand better the DOM characteristics of restored and unrestored coastal wetlands of Lake Ontario. A major theme of this work emphasized that, despite the critical role DOM plays in biogeochemical and ecological processes and the fact anthropogenic activities can shift DOM away from natural characteristics, management for DOM is largely lacking and the effects current restoration efforts aimed at other habitat targets have on DOM processing are unclear. Rates of production and decomposition are highly variable between wetlands, depending on soil type, vegetation, hydrology, nutrient inputs, solar radiation, length of growing season, morphology, and disturbance, among other factors (Reddy et al., 2000; Fisher and Acreman, 2004). Organic matter storage can be important in protecting downstream ecosystems because storage as POM immobilizes nutrients such as N and P and utilization of DOM by heterotrophs influences productivity.

I used optical water chemistry to test for DOM character and DOC concentration differences between restored and unrestored wetlands and for changes across season, flow regimes, and watershed land use. I found DOC concentrations to be higher in restored wetlands but found few other differences in DOM properties between restoration status. Humic content of DOM increases with flow and protein-like DOM was likely highest in summer months, but hydrological conditions of high basin wetness and frequent precipitation events were more likely drivers of DOM quality than watershed land use. This study adds to the existing database on DOM character in freshwater systems, but there is still a need for further research on the role and ecological consequences of human-caused changes in DOM composition, magnitude, and timing. Further, some important questions regarding the effectiveness and success of restoration and management on biogeochemical cycles are beyond the scope of this study (e.g., What intensity of restoration is enough? What targets are appropriate? What time scale do these changes operate on?). Therefore, more attention needs to turn to management efforts that might improve the natural composition of DOM and natural processes occurring in these systems for health and biodiversity in higher trophic levels.

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TABLES AND FIGURES

Table 1. Excitation (Ex) and emission (Em) peak location (2nd peak) and tentative description of five-component EEM-PARAFAC model, referenced to other fluorophore groups previously identified in the literature.

Component	Ex maximum (nm)	Em maximum (nm)	Osburn et al., 2011	Gueguen, et al., 2015	Lambert et al., 2016	Kothawala et al., 2014	Osburn et al., 2016	Williams et al., 2013	Murphy et al., 2011	Osburn et al., 2012	Coble et al., 1998	Origin/Description
C1	<255	445	C1	C1	C1	C1,C4	C1	C3	C1		A	Terrestrial, humic-like
C2	<255	380-400	C2		C3		C2	C6	C4		A, M	Microbial, humic-like, unknown
C3	270 (390)	497		C3		C3					A, C	Soil, fulvic-like
C4	340	386								C2	C, M	Anthropogenic, humic-like
C5	280 (<255)	331	C5	C4	C5	C6	C4	C7	C5	C5	T, N	Protein-like, tryptophan-like

Table 2. Mean and range DOM index values (dimensionless), dissolved organic carbon (DOC; mg-C/L), and PARAFAC component as intensity (RU) and percent (%) for streams and restored and unrestored wetland.

	Streams	Wetlands	
	All	Restored	Unrestored
S_R	0.88 (0.77-1.16)	0.94 (0.80-1.28)	0.97 (0.76-1.54)
β:α	0.64 (0.56-0.75)	0.64 (0.58-0.78)	0.65 (0.57-0.73)
FI	1.50 (1.51-1.72)	1.57 (1.52-1.67)	1.58 (1.54-1.66)
HIX	0.91 (0.83-0.94)	0.90 (0.82-0.92)	0.90 (0.83-0.93)
SUVA	3.6 (2.6-4.2)	3.5 (2.2- 4.2)	3.3 (2.0-4.4)
C1 %	47.7 (35.7-52.9)	47.5 (35.8-51.7)	47.1 (37.5-52.3)
C2 %	23.3 (20.4-27.4)	22.6 (19.2-26.3)	22.9 (20.5-26.9)
C3 %	12.2 (7.8-16.0)	11.5 (8.1-16.2)	11.9 (8.1-15.8)
C4 %	8.9 (0.2-26.7)	9.9 (2.9-19.6)	8.9 (2.2-21.2)
C5 %	8.0 (5.0-17.0)	8.8 (6.2-17.2)	9.5 (6.0-18.3)
DOC	8.4 (3.4-15.7)	7.9 (2.8-11.9)	6.3 (2.8-13.3)
C1 RU	2.08(0.36-3.39)	1.98 (0.33-2.23)	1.57 (0.32-3.56)
C2 RU	1.01 (0.18-1.74)	0.94 (0.15-1.30)	0.76 (0.16-1.75
C3 RU	0.54 (0.07-0.99)	0.48 (0.09-0.80)	0.41 (0.07-0.82)
C4 RU	0.36 (0.00-1.27)	0.39 (0.0-8.33)	0.24 (0.00-0.60)
C5 RU	0.33 (0.05-0.51)	0.34 (0.10-0.52)	0.27 (0.07-0.48)

Table 3. Pearson's bivariate correlation (r) between DOM absorbance and fluorescence indices*, PARAFAC components, and environmental variables for streams. Only significant correlations ($p < 0.05$) are listed with correlations that remain significant after Holm-Bonferroni correction are in bold. Comparisons were made pairwise by site and event for each variable.

	Temperature	pH	TN	TP	β:α	FI	HIX	SUVA	C1 %	C2 %	C3 %	C4 %	C5 %
S_R	**0.63**	0.30	**-0.38**	-0.24	**0.78**	0.31	**-0.86**	**-0.71**	**-0.73**		**-0.66**	**0.59**	**0.79**
β:α	**0.47**	**0.46**	-0.27	-0.29	**-**	**0.48**	**-0.85**	**-0.78**	**-0.92**		**-0.58**	**0.69**	**0.69**
FI				0.29		-	-0.31	**-0.59**		**0.73**			**0.41**
HIX	**-0.42**	-0.35	0.23				**-**	**0.67**	**0.87**		**0.53**	**-0.59**	**-0.93**
SUVA	**-0.45**	-0.29						-	**0.55**	-0.26	**0.58**	-0.35	**-0.65**
C1 %	-0.39	**-0.42**	0.34	0.35					-	0.26	**0.52**	**-0.81**	**-0.67**
C2 %			**0.41**	**0.53**						-	0.24	**-0.55**	
C3 %	**-0.72**		**0.49**	0.27							-	**-0.77**	-0.30
C4 %	**0.52**	0.27	**-0.56**	**-0.51**								-	0.27
C5 %	0.31	0.31											-

Table 4. Pearson's bivariate correlation (r) between DOM absorbance and fluorescence indices*, PARAFAC components, and environmental variables for wetlands. Only significant correlations ($p < 0.05$) are listed with correlations that remain significant after Holm-Bonferroni correction are in bold. Comparisons were made pairwise by site and event for each variable.

	Temperature	pH	TN	TP	β:α	FI	HIX	SUVA	C1 %	C2 %	C3 %	C4 %	C5 %
S_R	**0.43**	0.39	-0.39	**-0.40**	**0.67**		**-0.90**	**-0.85**	**-0.71**	**-0.42**	**-0.60**	**0.44**	**0.88**
β:α	**0.56**	**0.66**		-0.33	-	0.31	**-0.77**	**-0.68**	**-0.92**		**-0.63**	**0.67**	**0.64**
FI						-		-0.25		**0.72**		-0.31	
HIX	**-0.47**	**-0.45**	0.32	0.34			-	**0.82**	**0.85**	**0.49**	**0.62**	**-0.54**	**-0.96**
SUVA	-0.29	**-0.33**	0.32	0.33				-	**0.65**	0.24	**0.52**	-0.36	**-0.79**
C1 %	**-0.54**	**-0.57**	0.30	0.37					-	**0.39**	**0.63**	**-0.78**	**-0.72**
C2 %			**0.41**	**0.46**						-	**0.43**	**-0.58**	**-0.43**
C3 %	**-0.72**		**0.52**	**0.52**							-	**-0.82**	**-0.47**
C4 %	**0.59**	0.38	**-0.47**	**-0.55**								**-**	0.32
C5 %		0.38	-0.24	-0.23									-

Table 5. Two-way permutation MANOVA output on stream DOM index and PARAFAC components as percent tested by factors of season (spring, summer, and fall) and flow (storm and base).

STREAMS	Df	Sum of Squares	Mean Square	F	p
Season	2	200.98	100.49	17.92	<0.001
Flow	1	126.92	126.923	22.63	<0.001
Season X Flow	1	23.94	23.942	4.27	0.012
Residuals	71	398.16	5.608		
Total	75	750			

Table 6. Two-way permutation MANOVA output on stream DOM RU intensities tested by factors of season (spring, summer, and fall) and flow (storm and base).

STREAMS	Df	Sum of Squares	Mean Square	F	p
Season	2	33.89	16.95	5.28	0.001
Flow	1	34.18	34.18	10.65	<0.001
Season X Flow	1	4.08	4.08	1.27	0.278
Residuals	71	227.85	3.21		
Total	75	300.00			

Table 7. Three-way permutation MANOVA output on wetland DOM index and PARAFAC components as percent tested by factors of restoration (restored or unrestored), season (spring, summer, and fall), and flow (storm and base).

WETLANDS	Df	Sum of Squares	Mean Square	F	p
Restoration	1	13.57	13.57	1.95	0.124
Season	2	147.60	73.80	10.58	<0.001
Flow	1	89.65	89.65	12.85	<0.001
Restoration X Season	2	8.49	4.24	0.61	0.695
Restoration X Flow	1	4.26	4.26	0.61	0.581
Season X Flow	1	13.16	13.16	1.89	0.135
3- way Interaction	1	9.91	9.91	1.42	0.223
Residuals	65	453.35	6.98		
Total	74	740.00			

Table 8. Three-way permutation MANOVA output on wetland DOM RU intensities tested by factors of restoration (restored or unrestored), season (spring, summer, and fall), and flow (storm and base).

WETLANDS	Df	Sum of Squares	Mean Square	F	p
Restoration	1	31.85	31.48	10.19	<0.001
Season	2	17.69	8.84	2.86	0.032
Flow	1	24.85	24.85	8.04	0.002
Restoration X Season	2	7.27	3.63	1.18	0.309
Restoration X Flow	1	1.46	1.46	0.47	0.619
Season X Flow	1	5.73	5.73	1.85	0.152
3- way Interaction	1	6.65	6.65	2.15	0.119
Residuals	65	200.87	3.09		
Total	74	296.00			

Table 9. Pearson’s bivariate correlations (r) between land uses, environmental variables, and DOM characteristics using stream and wetland data averaged by site. Only significant correlations (p <0.05) are listed with correlations that remain significant after Holm-Bonferroni correction are in bold. Comparisons were made pairwise using the mean value at each.

	Agriculture	Developed	Forest
Specific Conductance	-0.84	**0.97**	
TN	0.72		
TP	0.88		
S_R		0.74	
β:α	-0.78	0.87	
HIX	0.74	-0.85	
SUVA			0.83
C1 %	0.88	**-0.96**	
C2 %	0.86	-0.80	
C3 %			
C4 %	-0.91	**0.96**	
C5 %			

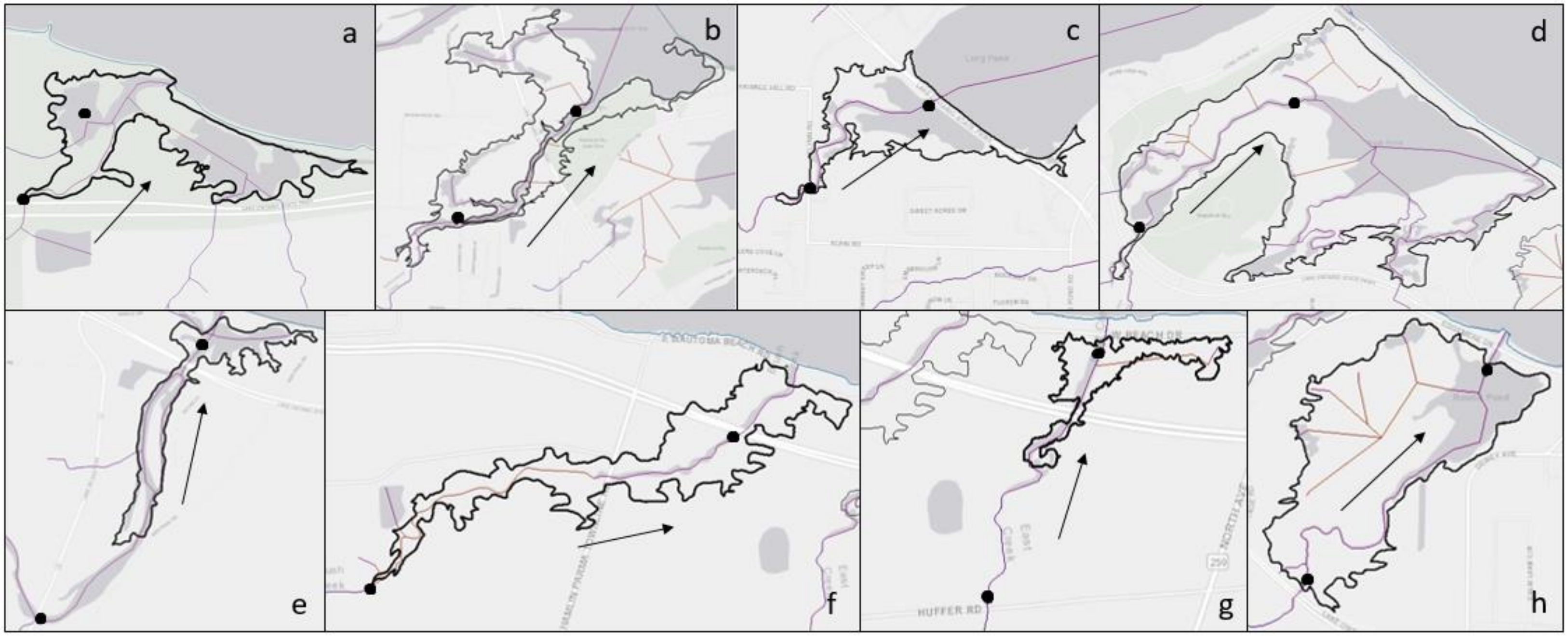


Figure 1. Map of 8 Lake Ontario coastal wetland study sites (see chapter 1 for reference) outlined by emergent vegetation cover (not to same scale). Restored wetlands (top row) from west to east: Yanty Creek (a), Braddock Bay/Buttonwood Creek (b), Long Pond (c), and Buck Pond (d). Unrestored wetlands (bottom row) from west to east: Sandy Creek (e), Brush Creek (f), East Creek (g), and Round Pond (h). Stream and wetland sampling points (black circles) are indicated with the surface water flow path (grey line) and direction (arrow).

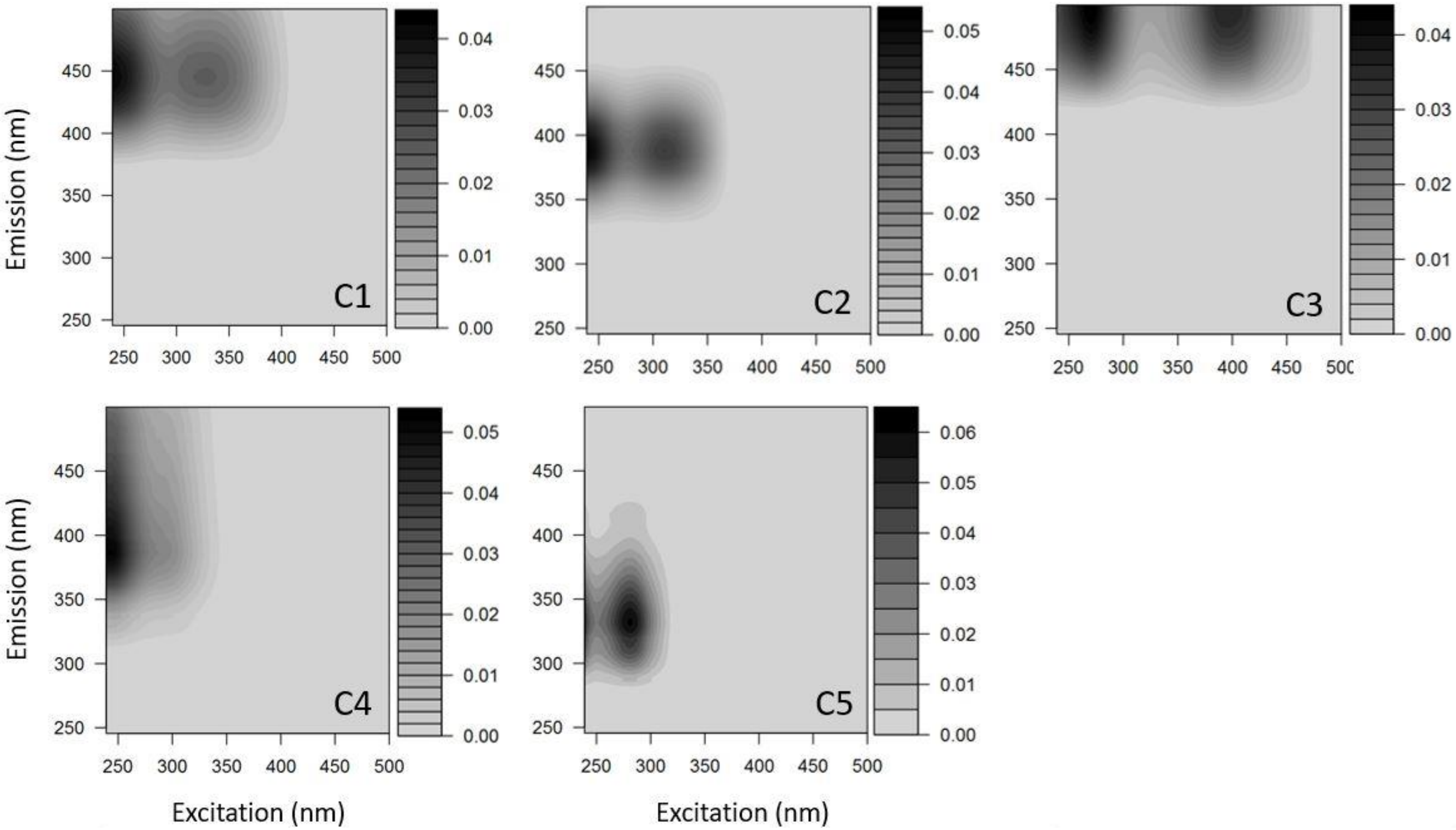


Figure 2. Contour plots of five EEM-PARAFAC components. Excitation (nm) on x-axis, Em (nm) on primary y-axis, and absorbance/fluorescence intensity (Raman units) on secondary y-axis. See Table 1 for origin.

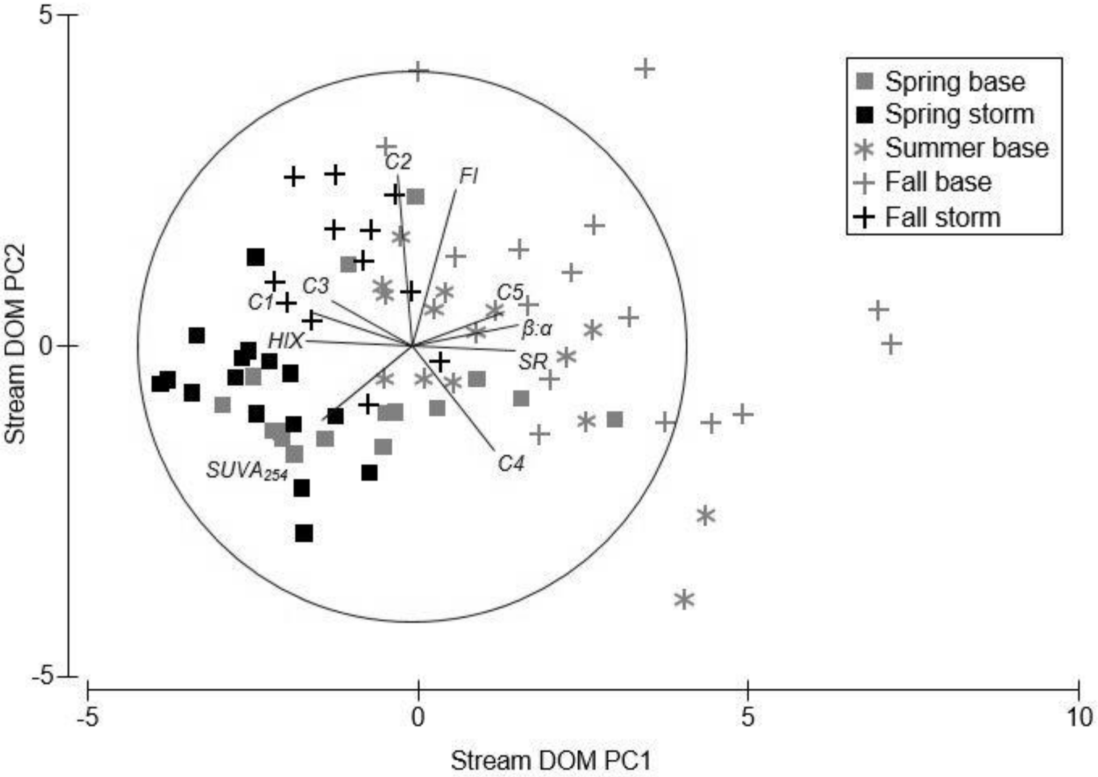


Figure 3. Principle component analysis ordination based on Euclidean distance matrix for stream DOM. All variables used in the analysis are labeled as vectors.

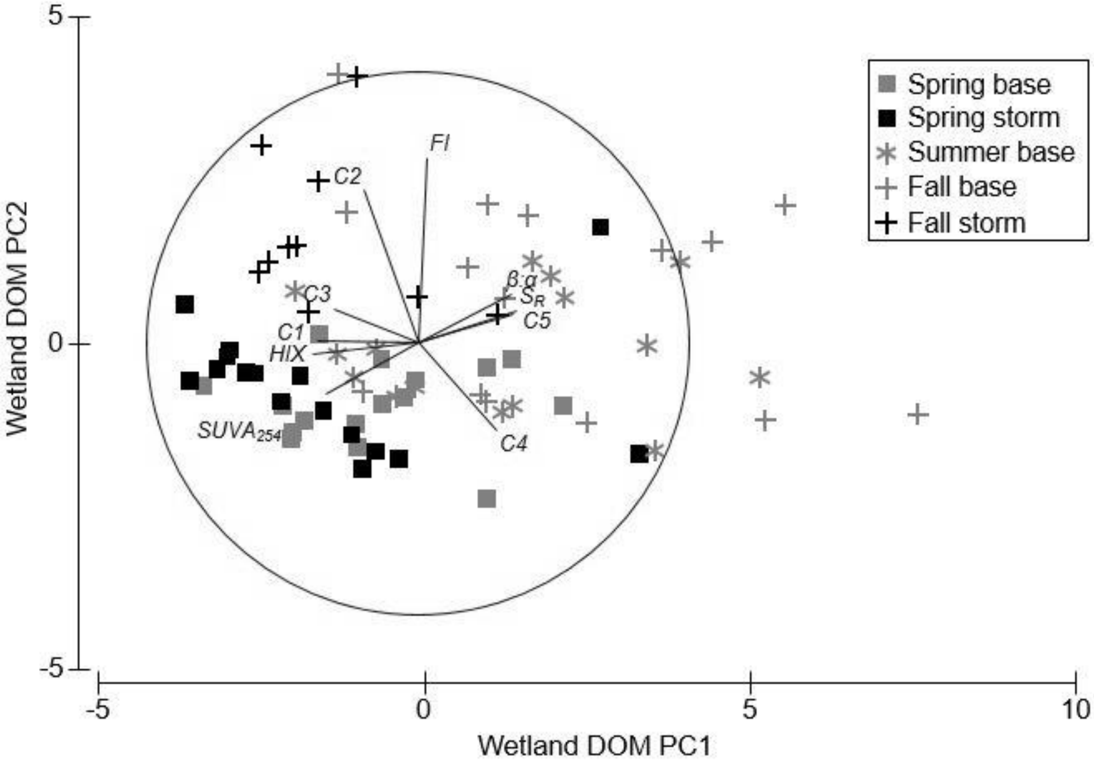


Figure 4. Principle component analysis ordination based on Euclidean distance matrix for wetland DOM. All variables used in the analysis are labeled as vectors.

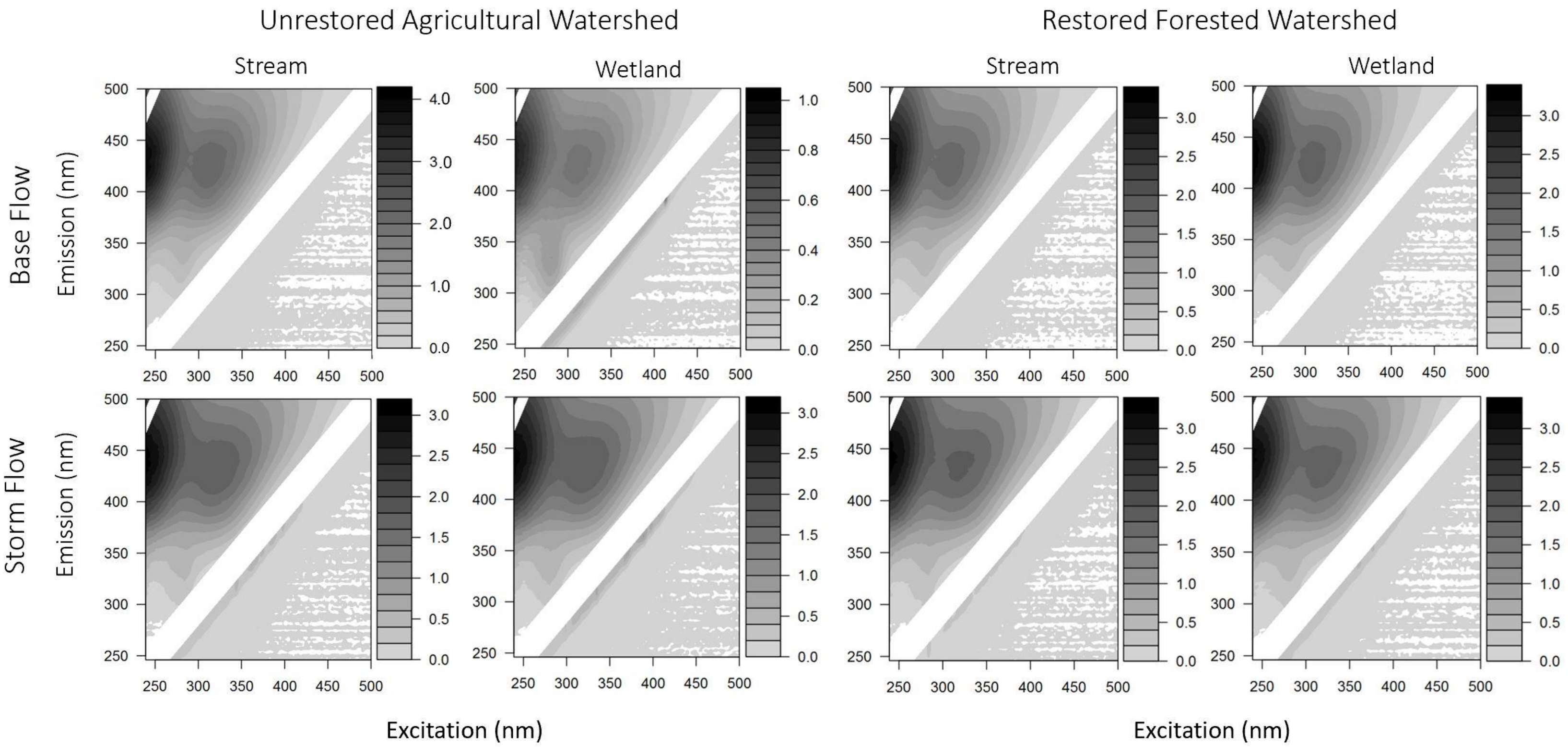


Figure 5. Examples of EEM contour plots for stream and wetland samples in an agriculture-dominated watershed (East Creek-left two columns) and an urban development-dominated watershed (Round Pond-right two columns) under a base flow event (event 7-top row) and a storm flow event (event 10-bottom row) during the same season (fall).

APPENDICES

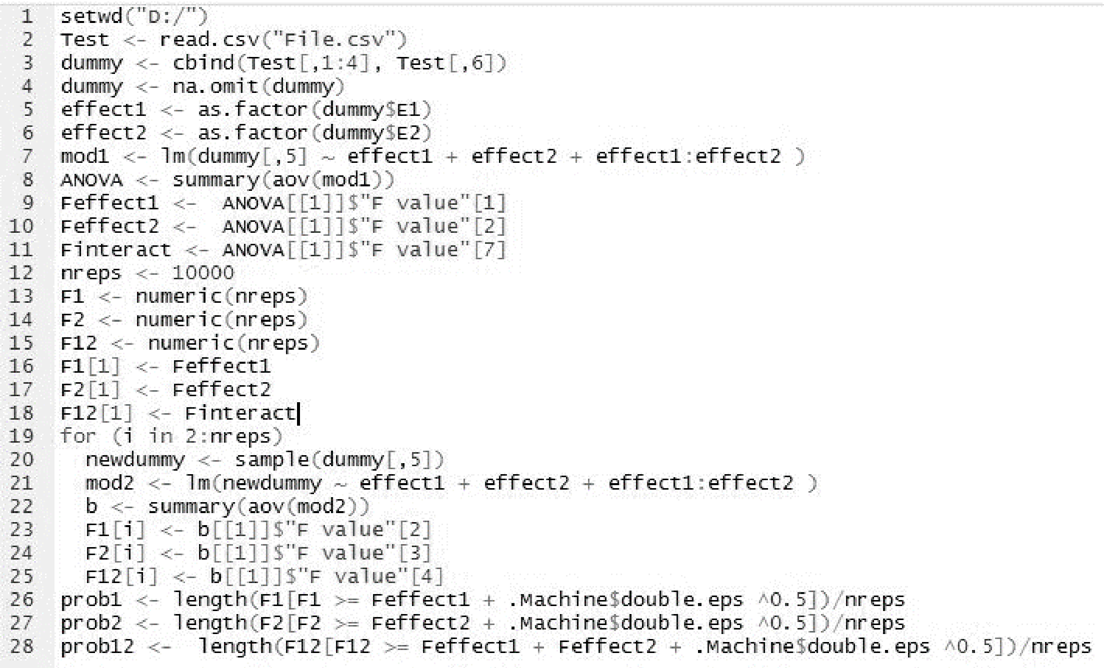
APPENDIX A

A.1 List of restoration methods, year of completion, and agencies conducting projects: U.S. Army Corps of Engineers (USACOE), Ducks Unlimited (DU), The Nature Conservancy (TNC), SUNY Brockport, US Fish and Wildlife Service (FWS), and New York State (NYS) Parks. Channels and potholes were excavated in *Typha* mats, *Typha* control involved cutting and herbicide application, and vegetation was seeded in sedge/grass meadow (SGM) and planted in emergent zones.

Site	Year	Agency	Channels	Potholes	Cattail Control	SGM seeding	Emergent Planting
Braddock Bay	2016	USACOE	Yes- wide	Yes-Large	Yes	Yes	Yes
Buck Pond	2014	DU/TNC	Yes- narrow/shallow	Yes- shallow	No	No	Yes
	2015	DU/Brockport	Yes- wide/deep	Yes- large	Yes	Yes	Yes
	2016	FWS	Yes- narrow/shallow	Yes	Yes	No	Yes
Long Pond	2016	FWS	No	Yes- isolated	Yes	No	Yes
Yanty Creek	2017	NYS Parks	No	Yes	Yes	No	No

APPENDIX B

B.1 Generic code for a 10,000 permutation two-way ANOVA used in RStudio to generate F statistic and p-value.



```r
setwd("D:/")
Test <- read.csv("File.csv")
dummy <- cbind(Test[,1:4], Test[,6])
dummy <- na.omit(dummy)
effect1 <- as.factor(dummy$E1)
effect2 <- as.factor(dummy$E2)
mod1 <- lm(dummy[,5] ~ effect1 + effect2 + effect1:effect2 )
ANOVA <- summary(aov(mod1))
Feffect1 <-  ANOVA[[1]]$"F value"[1]
Feffect2 <-  ANOVA[[1]]$"F value"[2]
Finteract <- ANOVA[[1]]$"F value"[7]
nreps <- 10000
F1 <- numeric(nreps)
F2 <- numeric(nreps)
F12 <- numeric(nreps)
F1[1] <- Feffect1
F2[1] <- Feffect2
F12[1] <- Finteract
for (i in 2:nreps)
  newdummy <- sample(dummy[,5])
  mod2 <- lm(newdummy ~ effect1 + effect2 + effect1:effect2 )
  b <- summary(aov(mod2))
  F1[i] <- b[[1]]$"F value"[2]
  F2[i] <- b[[1]]$"F value"[3]
  F12[i] <- b[[1]]$"F value"[4]
prob1 <- length(F1[F1 >= Feffect1 + .Machine$double.eps ^0.5])/nreps
prob2 <- length(F2[F2 >= Feffect2 + .Machine$double.eps ^0.5])/nreps
prob12 <-  length(F12[F12 >= Feffect1 + Feffect2 + .Machine$double.eps ^0.5])/nreps
```

APPENDIX C

C.1 Mean and range water chemistry for restored and unrestored wetlands.

Water Chemistry Parameter	Restored Wetlands	Unrestored Wetlands
Temperature (°C)	16.3 (7.9-24.8)	16.3 (8.0-24.1)
Specific conductance (µS/cm)	569 (224-940)	599 (225-1667)
pH	7.2 (6.1-8.2)	7.4 (6.3-8.4)
DO % saturation	72.7 (2.5-141.3)	74.9 (1.2-155.3)
Chlorophyll a (µg/L)	34.2 (4.6-199.7)	34.0 (5.9-288.8)
Turbidity (NTU)	19.5 (2.7-156.0)	19.8 (2.3-116.0)

APPENDIX D

D1. One-way ANOVAs testing for significant difference of mean land use categories (% cover of a watershed), area, and watershed:wetland ratio between restored and unrestored wetlands for basin comparison. For all tests, Df effect = 1, Df error = 7.

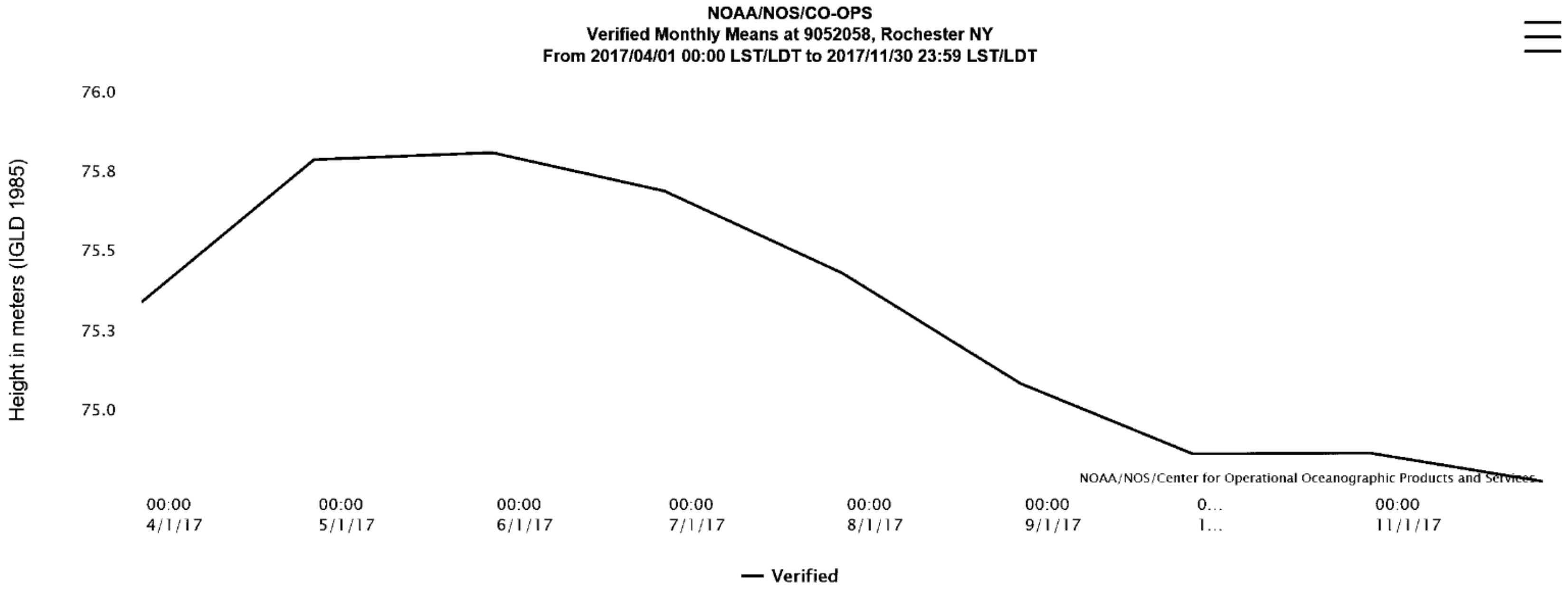
Land Use Category	Pattern	F	p
Developed	=	0.05	0.938
Forest	U<R	13.82	**0.010**
Agriculture	=	0.53	0.432
Wetlands	=	3.00	0.113
Total Watershed area	=	0.56	0.713
Watershed:wetland ratio	=	0.56	0.473

D.2 One-way ANOVA of basin wetness (API) 7 days prior to a sampling event between storm (S) and base (B) flows. Df effect = 1, Df error = 9.

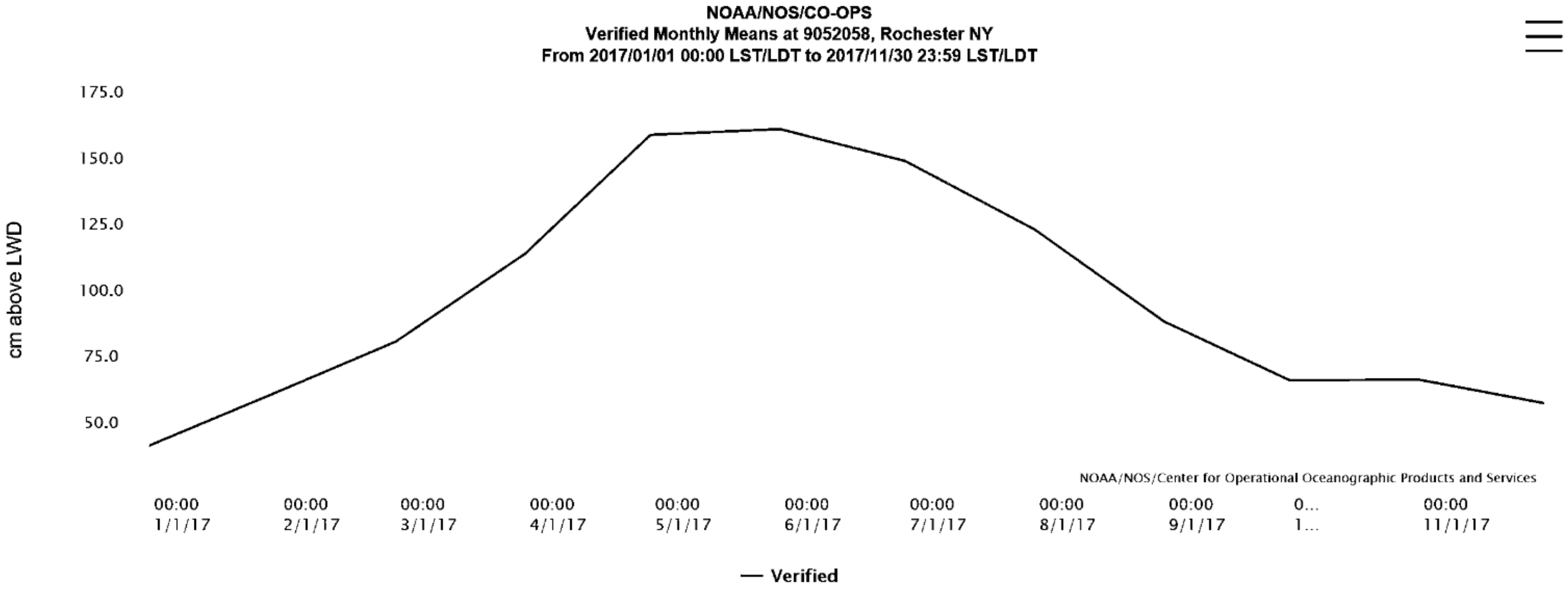
	Pattern	F	P
Flow	S>B	7.95	**0.024**

APPENDIX E

E.1 Lake Ontario water level height (m) in Rochester, NY for the duration of the study from the NOAA recording station on Great Lakes water levels.



E.2 Lake Ontario water level in cm above low water datum (LWD) for 2017 based on mean low water levels obtained from the Rochester, NY NOAA recording station database on Great Lakes water levels in reference to 1980-2010 normals.



APPENDIX F

DOM index calculations and descriptions, adapted from Fellman et al., 2010.

Index	Calculation	Description	Reference
S_R	$\frac{\text{slope of} \ln(275 - 295 \text{ nm})}{\text{slope of} \ln(350 - 400 \text{ nm})}$	Spectral slope ratio indicates size. Higher S_R indicates smaller size.	Helms et al., 2008
FI	At Ex 370 nm $\frac{\text{fluorescence intensity at Em 470 nm}}{\text{fluorescence intensity at Ex 520 nm}}$	Fluorescence index indicates source of either microbial (high FI ~ 1.8) or terrestrial (low FI ~ 1.2) origin.	McKnight et al., 2001; Cory and McKnight, 2005; Cory et al., 2010
β:α	At Ex 310nm $\frac{\text{fluorescence intensity at Em 390 nm}}{\text{maximum fluorescence intensity between Em 420–436nm}}$	Freshness index indicates contribution of recently produced DOM (β recent; α decomposed).	Parlanti et al., 2000; Wilson and Xenopoulos, 2009
HIX	At Ex 254 nm $\frac{\text{area under Em spectra 435–480 nm}}{\text{peak area under 300–345 nm + 435–480 nm}}$	Humification index indicates direct humic substance content and extent of decomposition.	Zsolnay et al., 1999; Ohno 2002
SUVA	$\frac{\text{A } (\text{m}^{-1}) \text{ at 254 nm}}{\text{DOC } (\text{ mg L}^{-1})}$, where A = absorbance	Specific ultraviolet absorbance index indicates compound aromaticity, complexity, and molecular weight.	Weishaar et al., 2003

APPENDIX G

Statistical outputs.

G.1 Spearman's rank correlations between stream and wetland DOC concentrations and DOM characteristics and components. Only significant correlations ($p < 0.05$) are listed with correlations that remain significant after Holm-Bonferroni correction are in bold.

	S_R	β:α	FI	HIX	C1	C2	C3	C4	C5
Stream DOC	**-0.43**	**-0.68**		**0.56**	**0.71**			**-0.45**	**-0.43**
Wetland DOC	**-0.55**	**-0.49**		**0.63**	**0.59**	**0.36**		-0.27	**-0.58**

G.2 Principle component analysis for stream loading scores (coefficients in the linear combinations of variables making up principle components), eigenvalues, and variation explained.

STREAMS	PC1	PC2	PC3	PC4	PC5
S_R	-0.374	0.014	0.116	-0.368	-0.211
β:α	-0.388	-0.078	-0.081	0.365	0.211
FI	-0.161	-0.572	-0.131	0.144	-0.525
HIX	0.388	-0.019	-0.318	0.02	0.09
SUVA	0.329	0.269	0.186	0.297	-0.731
C1	0.37	-0.122	-0.075	-0.53	-0.026
C2	0.054	-0.625	-0.238	0.153	0.037
C3	0.29	-0.164	0.594	0.431	0.279
C4	-0.298	0.381	-0.346	0.293	-0.071
C5	-0.336	-0.125	0.541	-0.214	-0.085
Eigenvalues	5.9	2.23	0.88	0.533	0.21
% Variation	59.0	22.3	8.8	5.3	2.1
Cumulative % Variation	59.0	81.3	90.1	95.4	97.5

G.3 PCA loading scores for wetlands.

WETLANDS	PC1	PC2	PC3	PC4	PC5
S_R	-0.361	-0.119	0.293	-0.194	-0.05
β:α	-0.346	-0.182	-0.346	0.329	-0.146
FI	-0.035	-0.682	-0.138	-0.075	0.358
HIX	0.39	0.037	-0.21	-0.113	-0.189
SUVA	0.34	0.19	-0.215	0.273	0.747
C1	0.371	-0.006	0.22	-0.484	0.005
C2	0.196	-0.564	-0.315	-0.054	-0.175
C3	0.309	-0.128	0.358	0.718	-0.28
C4	-0.291	0.323	-0.502	0.019	-0.057
C5	-0.354	-0.106	0.396	0.094	0.378
Eigenvalues	6.07	1.95	1.08	0.44	0.23
%Variation	60.7	19.5	10.8	4.4	2.3
Cumulative %Variation	60.7	80.2	91.0	95.4	97.7

G.4. Non-parametric related samples Wilcoxon signed rank test on stream and wetland DOC concentrations paired by site and event.

Paired samples		N	Mean Rank	Sum of Ranks	Z	p
Stream-Wetland DOC	Negative Ranks	46[a]	38.66	1778.5	-3.41[b]	0.001
	Positive Ranks	23[b]	27.67	636.5		
	Total	69				

a. Wetland DOC < Stream DOC, negative ranks.
b. Wetland DOC > Stream DOC, positive ranks; Z is based off b.

G.5 Three-way permutation ANOVA output on wetland DOC concentrations tested by factors of restoration (restored or unrestored), season (spring, summer, and fall), and flow (storm and base).

WETLANDS	Df	Sum of Squares	Mean Square	F	p
Restoration	1	45.7	45.8	8.59	**0.005**
Season	2	2.7	1.4	0.25	0.776
Flow	1	16.6	16.6	3.11	*0.088*
Restoration X Season	2	4.8	2.4	0.45	**0.640**
Restoration X Flow	1	1.0	1.0	0.19	**0.667**
Season X Flow	1	0.4	0.4	0.08	*0.774*
Interaction	1	11.0	11.0	2.07	0.159
Residuals	65	346.3	5.3		
Total	74	428.5			

G.6 Two-way permutation ANOVA output on stream DOC concentrations tested by factors of season (spring, summer, and fall) and flow (storm and base).

STREAMS	Df	Sum of Squares	Mean Square	F	p
Flow	1	19.3	19.3	3.00	*0.086*
Season	2	1.0	0.5	0.08	0.919
Interaction	1	9.3	9.3	1.44	*0.072*
Residuals	71	456.5	6.4		
Total	75	486.1			

G.7 ANOSIM- 9999 permutations; differences between test groups across all other groups in streams.

STREAMS	Global R	p	NP
Season	0.359	0.0001	0
Flow	0.321	0.0001	0

Where NP is the number of permuted statistics greater than or equal to Global R

Pairwise tests for season

			Permutations		NP
Groups	R	p	Possible	Actual	Observed
Spring, Summer	0.269	0.03	300540195	9999	2
Spring, Fall	0.505	0.01	Very large	9999	0
Summer, Fall	0.131	0.8	300540195	9999	78

G.8 ANOSIM- 9999 permutations; differences between test groups across all other groups in wetlands.

WETLANDS	Global R	p	NP
Restoration	-0.011	0.6245	6245
Season	0.232	0.0001	0
Flow	0.142	0.003	27

Where NP is the number of permuted statistics greater than or equal to Global R

Pairwise tests for season

			Permutations		NP
Groups	R	p	Possible	Actual	Observed
Spring, Summer	0.199	0.2	300540195	9999	20
Spring, Fall	0.353	0.01	Very large	9999	0
Summer, Fall	0	40.3	77558760	9999	78

G.9 Pearson's bivariate correlation (r) between API basin wetness and environmental and DOM variables and Spearman's rank correlation between API and DOC for streams and wetlands together, averaged by event. Only significant correlations (p <0.05) are listed with correlations that remain significant after Holm-Bonferroni correction are in bold.

		TN	TP	S_R	β:α	FI	HIX	DOC	SUVA	C1	C2	C3	C4	C5
API	r						0.67	0.66			0.73	0.76	**-0.87**	
	p						0.034	0.038			0.017	0.01	0.001	