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Assessment of Water Quality Index, Light Attenuation, and Nutrient Sequestering by Submerged Aquatic Vegetation in the Detroit River

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By

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ABSTRACT

This thesis assessed water quality – submerged aquatic vegetation interactions in the Detroit River. Submerged aquatic vegetation provides essential ecosystem services that support aquatic biodiversity and regulating ecosystem services such as carbon sinks, purifying water and nutrient cycling. Chapter 2 explored how degraded water quality in the Detroit River limits submerged aquatic vegetation via light limitation. A water quality index and light extinction coefficients were measured at 21 sites along with installation of in-situ water quality sondes at 4 sites to measure water quality at high temporal resolution. The river wide median euphotic depth was estimated to be 1.30 m, higher (1.34 m) at sites without tributary inflow compared sites that receive tributary inflow (0.83 m). Measured light extinction coefficients were correlated with water quality index scores. However, a multivariate PCA model predicting light extinction coefficient from chlorophyll *a*, turbidity and specific conductivity yielded the best prediction. Light attenuation appears to be driven by different water quality constitutes at different sites and over time. Chapter 3 tested nutrient drawdown by submerged aquatic vegetation at 5 wetlands. There was no evidence for phosphorus drawdown but nitrogen drawdown was apparent at one bed site. This thesis supports a conclusion for light limitation of submerged aquatic macrophytes at tributary influenced locations implying actions to improve tributary water quality will benefit the Detroit River. However, expanding macrophyte bed coverage is unlikely to address phosphorus reduction targets mandated for the Detroit River.

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LIST OF ABBREVIATIONS/SYMBOLS

AOC	Area of concern
BUI	Beneficial Use Impairments
ECCC	Environment and Climate Change Canada
ε	Light Extinction Coefficient
IBI	Index of Biotic Integrity
IJC	International Joint Commission
PAR	Photosynthetically active radiation
RAP	Remedial Action Plan
SAV	Submerged aquatic vegetation
SAV-IBI	Submerged Aquatic Vegetation Index of Biotic Integrity
TP	Total Phosphorus
WQI	Water quality index
$Z_{EU(SAV)}$	Submerged Aquatic Vegetation Euphotic Depth

CHAPTER 1

General Introduction

1.1 Detroit River Area of Concern

The Detroit River is a 52 km connecting channel linking the upstream Lake St. Clair and the western basin of Lake Erie and a component of the Huron-Erie corridor (UGLCCS, 1988). The international boundary between Canada and the U.S. runs along the Detroit River's length following navigation channels over the course of the waterway. The river supports two major metropolitan centres, the City of Detroit, Michigan, U.S.A. located along its north-west shoreline and Windsor, Ontario Canada along the southeast shoreline. Both cities draw their drinking water from the Detroit River as well as release their treated wastewaters into it via three wastewater treatment plants situated along the upper and middle reaches of Canadian and U.S. sides of the system. The Detroit River also supplies water for a variety of industrial uses within the region.

The Detroit River's watershed drains 1800 km^2 of Michigan and Ontario, but the majority of water entering the river is derived from Lake St. Clair and ultimately Lake Huron (Van Alstyne, 2015). Its outflow, averaging 5600 m^3/s, is the largest water source and a major source of nutrient loads to Lake (Scavia et al., 2019; UGLCCS, 1988). The Detroit River has undergone large historical changes beginning with early European colonization in the 1700's which cleared much of the surrounding forests for agricultural lands and drained wetlands in support of shoreline development, massive industrialization which commenced with the dawn of the auto industry in the 1920's that was greatly expanded as part of the U.S. war effort in World War II coupled with extensive navigational dredging conducted in parallel with industrialization in support of

Great Lakes and trans-Atlantic shipping (ERCA, 1998). These changes coupled with human population increases caused crashes in the river's cold water fisheries such as lake whitefish that previously supported commercial fishing, accumulation of toxic pollutants such as metals and organic chemicals in its sediments and extensive loss of coastal marshes estimated to be more than 97% loss from pre-European colonization and 53.4% of the historical wetland coverage assessed in 1876 (Roseman et al., 2007; Hartig and Bennion, 2017).

The Detroit River was designated as a Great Lakes International Area of Concern (AOC) by the International Joint Commission (IJC) in 1996 on account of multiple beneficial use impairments assessed in the initial Stage 1 Remedial Action Plan (RAP) report and re-affirmed under the Stage 2 RAP process (Green et al., 2010). The AOC boundary stretches from the flashing navigation light at Peche Island to the middle of the Detroit River, near the Huron River's mouth. Both the U.S. and Canada operate separate implementation committees for this AOC, with the Canadian waters of the Detroit River being managed by the Detroit River Canadian Clean-up Committee (Green et al., 2010).

Each AOC is assessed against fourteen standard beneficial use impairments, the last of which is identified as BUI #14: Loss of Fish and Wildlife Habitat. According to the Canadian Stage 2 RAP report, BUI #14 is listed as impaired (Green et al., 2010). Delisting the AOC may commence after all BUIs are re-assigned as unimpaired. BUI #14 has been a prime focus in restoration plans conducted in the Detroit River and other AOCs (Hartig et al., 2019; Turner, 2017). The Detroit River Canadian Clean-Up committee identifies four components of BUI #14 that include protection of coastal wetlands, aquatic and riparian habitat, improvement of shoreline softening and protecting terrestrial habitat. Submerged aquatic vegetation (SAV) is a vital part of coastal wetlands that support aquatic biodiversity including benthic invertebrates, fish, and marsh birds. Therefore, the monitoring, protection, and restoration of SAV in the Detroit River is a component of the restoration initiatives adopted by Canada in support of BUI #14.

1.2 Submerged Aquatic Macrophytes

Submerged aquatic vegetation consists of rooted underwater plants which are also referred to as submerged macrophytes. They are composed of mixed communities of flowering plants (angiosperms), ferns (pteridophytes) and bryophytes (mosses, hornworts and liverworts) that form complex three dimensional structure in the water column providing rich habitat in support of microbial communities, invertebrates, fish, amphibians, turtles and coastal marsh birds (Wetzel, 2001; Cho and May, 2006; Tursi et al., 2009; Hill et al., 2021; Blumenfeld et al., 2009; Csák, 2019; Adame et al., 2019; Gómez-Baggethun et al., 2019). As primary producers, SAV contribute to annual carbon production and energy flow at the base of the food web (Wetzel, 2001). Their leaves provide large surface areas that further support epiphytic plankton and microbial biofilms (Han et al., 2018), their roots translocate oxygen into sediments enriching increasing the diversity and function of microbial communities (Kemp and Murray, 1986) while macrophyte surface area and condition increases invertebrate abundance (Beckett et al., 1992). The complex structure around SAV beds provides habitat and predator refuges for zooplankton, benthic invertebrates and juvenile fish while also supporting rich food resources supportive of economically important fish species, amphibians, reptiles and marsh birds (Scheffer, 2004; Tursi et al., 2009).

Beyond provisioning services, wetlands and SAV provide regulating ecological services related to hydrological processes and nutrients (Walker et al., 2020; Barbier et al., 2011; Daily, 2003). These attributes can produce a series of feedback loops that reinforce the clear water state when macrophyte production dominates in shallow lake environments and in coastal embayment's (Scheffer, 2004). For example, wetlands attenuate water flow due to friction of water flowing between macrophyte surfaces which in turn attenuates wave action and stream flow resulting in decreased sediment resuspension and lower turbidity of the water column (Zhu et al., 2015). Macrophytes can compete with and reduce overlying phytoplankton populations in a number of ways. First, by drawing down and sequestering nutrients from the water column they can potentially limit phytoplankton production (Quiliam et al., 2015; Wang et al., 2021). Second, several species of macrophytes can release allelopathic substances that inhibit phytoplankton growth, including cyanobacteria responsible for harmful algal blooms (Nezbrytska et al., 2022). Finally, their ability to function as predator refuges and habitat for large grazing zooplankton such as *Daphnia magna* facilitates top-down control of phytoplankton biomass (Scheffer, 2004; Nezbrystska et al., 2022).

SAV beds are sensitive indicators of water quality and strongly responsive to altered hydrology and inputs of pollutants that compromise water transparency and light penetration (Dennison et al., 1993; Eisemann et al., 2021; Stankelis et al., 1999; Orth et al., 2010). Changes to hydrology can increase input of dissolved and suspended solids to water that attenuate light through a combination of light scattering and light absorption (Wetzel, 2001). The soils, terrain, temperature, hydrology, water chemistry, flora, and other watershed landscape elements, including human disturbance, all influence hydrodynamics to varying degrees. Addition of nutrients further contributes to eutrophication which increases phytoplankton biomass in water that attenuates light transmission initiating the shift from clear to turbid-water state (Dorgham, 2014; Scheffer et al., 2001). The rapid increase of industrial, urban, and agricultural activity and subsequent increase in nutrient loads to aquatic systems have been identified as primary contributors to wetland losses (Rothenberger et al., 2009; Wang et al., 2021). At a global scale, significant decreases in coastal wetland coverage have been observed across marine and freshwater environments (Clark and O'Connor, 2019; Guimarães et al., 2022). Lotze found that since colonial settlement, seagrasses and other submersed angiosperms declined by 65 and 48 percent in twelve estuaries and coastal waters, respectively (Lotze et al., 2006). A recent worldwide quantitative assessment of seagrass abundances revealed accelerated rates of decline since 1990, with current loss rates (seven percent per year) being comparable to reported rates of decline for mangroves, coral reefs, and tropical rainforests (Pandolfi et al., 2003, Orth et al., 2010; Waycott et al., 2009). Changes in submersed vegetation in shallow lakes subject to human-induced eutrophication and associated increased phytoplankton and turbidity are highlighted by Scheffer et al. (2001) as "one of the best-studied and most dramatic shifts". As previously stated for the Detroit River, the most recent assessment of coastal wetland coverage is estimated to be less than 3% of its natural state and only 57% of the coastal wetland coverage documented in 1876 (Hartig and Bennion, 2017).

Because it serves as both a home and a source of food, loss of aquatic vegetation has the potential to not only affect the abiotic conditions of wetlands but also the biota at numerous trophic levels (Budria, 2017; Stasko et al., 2012). The significance of wetlands has been brought into sharper focus in modern times because of the vast potential production, untapped resources, and productive sustenance resources that they provide for a great many different organisms.

1.3 Water Quality Index and Submerged Aquatic Macrophytes Assessment in AOCs

Across Canadian AOCs, two indices are routinely applied to assess wetland and SAV quality. These include: (1) Water Quality Index (WQI) and (2) Submerged Aquatic Vegetation Index of Biotic Integrity (SAV-IBI) (Chow-Fraser, 2006; Grabas et al., 2012). In addition, other lines of evidence include an assessment of SAV coverage, invertebrate, fish, and marsh bird indices of biotic integrity (Uzarski et al., 2021). This thesis focuses on water quality – SAV interactions, starting with the premise that degraded water quality limits SAV distribution within the Detroit River (Chapter 2) followed by a separate assessment of how SAV potentially modifies and mediates water quality in water overlying macrophyte beds (Chapter 3).

The WQI is used by Environment and Climate Change Canada and was developed by Chow Fraser (Chow-Fraser, 2006). The index was calibrated from 110 Great Lakes coastal wetland sites and is used as part of an expert weighted index to assess wetland disturbance (Chow-Fraser, 2006). The initial model assesses wetland status across 12-parameters that included turbidity (NTU), temperature (°C), pH, conductivity (µS/cm), chlorophyll-*a* (µg/L), total suspended solids (mg/L), total inorganic suspended solids (mg/L), total phosphorus (µg/L), soluble reactive phosphorus (µg/L), total ammonium nitrogen (µg/L), total nitrate nitrogen (µg/L) and total nitrogen (µg/L). However, following multivariate ordination and accounting for water quality parameter covariates, the authors were able to simplify the WQI to include four major parameters that explained more than 80% of the original 12 parameter model. The simplified WQI model includes turbidity, conductivity, temperature (^{o}C), and pH and is calculated as:

WQI = -1.37·log Turbidity – 1.58·log Conductivity – 1.63 log Temp – 2.37 log pH + 9.27 (Eq 1)

Individual wetland WQI scores are generated at monitored wetland locations and the generated score is used to assign a quality category for wetland classification purposes. Scores in the range of +2 to +3 are classified as excellent, +2 to +1 very good, +1 to 0 good, 0 to -1 moderately degraded, -1 to -2 degraded and -2 to -3 very degraded.

However, it should be emphasized that the WQI model was not built on an ecologically theoretical model, but rather formulated through statistical approaches that rely on the investigator's initial characterization of individual wetland sites and their predetermined health status used in the model calibration process (Chow-Fraser, 2006; Hawkins et al., 2010). Some of the parameters included in Eq 1 still may be covariates of one another within a given system or may conflict with theoretical principles relating to wetland limiting conditions and/or wetland function. For example, conductivity is influenced by nearshore erosion and urban runoff including road salts and storm drain runoff which are likely to correlate with suspended solids concentrations. Turbidity measures light scattering by suspended particles including living cells and is therefore expected to be partially related to conductivity and a better proxy of suspended solids concentration (Rügner et al., 2014). The key resource limitation experienced by macrophytes is light which is expected to be jointly determined by conductivity and turbidity on account of the role that suspended solids play in light transmission through the water column (Binzer et al., 2006; Franklin et al., 2008; Hilton et al., 2006). Other parameters in Eq 1 are more difficult to interpret with respect to wetland health on theoretical grounds. Seasonally averaged temperature has utility for resolving between site differences when sites are compared across broad geographic regions but will unlikely resolve site differences within the same local water body (Gilman et al., 2006; Roberts et al., 2021). Water pH is largely a function of buffering capacity of the water body, e.g., alkalinity and, like temperature, is expected to generate larger variation across water bodies than within water bodies. There are also confounding interpretations about the role of pH in assessing macrophyte function. At one level, pH can mediate nutrient speciation influencing nutrient bioavailability (Wetzel, 2001, Scheffer, 2004). Alternatively, macrophytes can alter water pH at a local level during photosynthesis (Wetzel, 2001). During periods of high photosynthesis, macrophytes draw down CO_2, increasing bicarbonate ion abundance which increases pH over the SAV bed (Dolui et al., 2021; Sand-Jensen et al., 2018). This can be accompanied by supersaturated oxygen concentrations generated as part of photosynthesis. Yet the coefficient for pH in the WQI is negative, implying high pH, which can occur as a temporary condition of high production, is assessed as a sign of negative wetland health.

Another issue to consider when using the water quality index as a means of assessing SAV health involves the frequency and timing of observations used within a monitoring program. Some parameters such as turbidity and associated light transmission can be highly variable over time leading to inaccurate WQI assessments if measurements are constrained to a limited number of sample events. Typical surveys in Canadian AOCs to determine WQI involve suitable sampling events completed during a couple of weeks in the open water season and may involve compilation of multiple years of data. If the monitoring program does not capture seasonal patterns of water quality, then year to year comparisons or impact vs reference site contrasts of WQI may be obscured.

Since light limitation is a major driver of SAV distribution, I will adopt additional measures of light attenuation to compare against WQI-SAV health inferences. Euphotic depth (Z_{eu}) is defined as the maximum depth at which net photosynthesis (i.e., carbon dioxide uptake by photosynthesis exceeds carbon dioxide release by respiration) can occur. For phytoplankton, euphotic depth is generally defined as the depth at which the light intensity is 1% of the light intensity at the water surface (Wu et al., 2021; Zhang et al., 2006). However, rooted SAV have higher light requirements compared to phytoplankton. This is because pelagic algae remain suspended in the water column, but most cells are constantly changing their depth in the water column due to turbulence in the epilimnion. Thus, phytoplankton cells integrate light over a given day due to their constant movement in space and vertical position. In contrast, macrophytes must grow from the sediment up and therefore require sufficient light impinging on the sediment surface to permit initial vegetative growth. According to Scheffer (2004), the euphotic depth for SAV ($Z_{eu(SAV)}$) can be estimated as the depth where light intensity is 10% of the light intensity impinging on the surface. However, the actual light requirements are variable across different macrophyte species and can range from 2-4% for *Chara* beds (stonewarts) to 21% for flowering angiosperms (Chambers and Kalf, 1985; Schwarz et al., 2000; Sondergaard et al., 2013). Once $Z_{eu(SAV)}$ is established for a given water body, the maximum SAV potential coverage can be estimated based on bathymetry information to identify locations where sediment depths are equal or less then $Z_{eu(SAV)}$.

Euphotic depth is most accurately estimated from the light extinction coefficient (ε) measured directly in each body of water. Although the light extinction coefficient of pure water is a constant, natural waters vary in their composition of dissolved chemicals coupled with presence of suspended solids that contribute to scattering and absorption of photosynthetically active radiation (PAR) in the wavelength range of 400-700 nm (Wetzel, 2001). To calculate the light extinction coefficient in a water body, light intensity measurements of PAR wavelengths are determined at a series of depths using a PAR-light meter. A linear regression of natural log of light intensity against depth is performed and ε is set as the slope of the regression relationship. Beer's Law is used in conjunction with ε to extrapolate the amount of light at a given depth relative to the surface. Based on the 10% of surface light criteria, $Z_{eu(SAV)}$ is estimated according to:

$$Z_{eu(SAV)} = [-1 \cdot \ln(0.10)]/\varepsilon_{PAR} \quad \text{(Equation 2)}$$

1.4 Submerged Aquatic Macrophytes as Nutrient Sinks

SAV beds are capable of sequestering nutrients from the water column and therefore enhancing water quality (Quiliam et al., 2015; Wang et al., 2021). The removal of nitrogen and phosphorus from water is one of the primary reasons aquatic macrophytes are employed extensively in artificial wetlands all over the globe (Kumar & Dutta, 2019; Srivastava et al., 2008). Macrophytes composed of vascular plants can accept nutrients directly from water and/or sediments (Barko et al., 1988; Ozimek et al., 1993). However, because sediments offer a far richer source of phosphorus and nitrogen, most macrophytes appear to obtain a majority of their nitrogen and phosphorus from the sediments as opposed to the water column (Cargnan and Kalff, 1980). Rooted submerged macrophytes, even those with relatively small root systems, are capable of significantly depleting pools of nitrogen and phosphorus from sediments (Alahuhta et al., 2021; Dhir et al., 2009; Reddy and De Busk, 1985). Barko found that the contents of exchangeable nitrogen and acid-extractable phosphorus decreased by more than 90 percent and more than 30 percent, respectively, from sediment on which *Hydrilla verticillata* was cultivated (Barko et al., 1988). The ability to jointly exploit sediment and water sources of nutrients is one reason macrophytes can competitively dominate phytoplankton under low nutrient, oligotrophic conditions.

However, beyond macrophyte biomass itself, SAV beds also support rich periphyton and biofilm growth that must acquire nutrients directly from water and therefore can compete with suspended phytoplankton for dissolved nitrogen and phosphorus (Dierberg et al., 2002; Levi et al., 2015). Indirectly, the diurnal cycle of oxygenation of sediments via roots and diffused from leaf surfaces can alter redox of water and sediments that can reverse with respiration at night (Han et al., 2018). This cycling is thought to be important to nitrogen biogeochemistry and nitrogen removal via denitrification (Rysgaard et al., 1994). Therefore, establishing and promoting plentiful SAV bed coverage in an aquatic system can be an important tool for generating ecosystem resistance and stability of the clear water state, one that favours low lake trophic status and supports healthy and vibrant fisheries.

1.6 Thesis Objectives

The objective of my thesis is to explore water quality – submerged macrophyte associations across wetlands sites within Canadian waters of the Detroit River. Chapter 2 examined differences in WQI scores and light attenuation across several wetland sites including those previously identified as wetlands of significant provincial interest and at several sites designated as prospective wetland restoration sites. Water quality and light attenuation was measured at 21 locations in the Detroit River throughout May to October of 2017 at two week intervals while high resolution in situ water quality sondes were deployed at four selected stations. This information was used to determine light extinction coefficient and submerged aquatic macrophyte euphotic depth to contrast light availability across sample locations and determine if light constraints affect some regions of the Detroit River more than others. Such information could inform macrophyte restoration initiatives given that locations with greater light availability should be prioritized for restoration efforts over those which are likely to be light stressed given that such sites would require additional remedial actions to further control sources of suspended solids, turbidity or excessive algal growth at the localized area of remediation interest.

Prior work by Environment and Climate Change Canada (ECCC, 2017) demonstrated that Detroit River wetlands located downstream of tributaries at Turkey Creek and River Canard had low water quality index scores compared to other wetlands of the Detroit River not influenced by tributary inflows. Since the water quality index used by ECCC consists of water quality measurements such as turbidity and conductivity that are known to affect light transmission (Scheffer, 2004), differences in water quality scores between sites should reflect between site differences in light availability. However, ECCC limits its sampling efforts to five wetlands within Canadian waters of the Detroit River and these sample areas are typically visited for only short periods of time of one to two weeks in a given year. Given that water quality parameters measured by ECCC are also highly variable through time, higher temporal resolution sampling is needed to verify the interpreted between site differences in water quality.

A recent habitat feasibility assessment study identified seven prospective wetland restoration sites in Canadian waters of the Detroit River where feasible construction improvements such as extending break walls, creation of deflector zones or creation of shallow islands could be performed to enhance submerged aquatic macrophyte coverage in the Area of Concern (ERCA, 2017). However, this study did not index water quality at the identified wetland restoration sites to water quality present at established wetlands in the Area of Concern. Neither the habitat feasibility study or ECCC's wetland monitoring program directly measured light availability or its linkage to water quality parameters included in the water quality index (WQI). Additional research to determine which water quality parameters contribute most strongly to light attenuation in the Detroit River and whether the relative contribution of such parameters are similar between locations and/or across time is needed.

Chapter 2 builds off of the ECCC and ERCA Detroit River studies by 1) expanding the number of sampling locations to increase spatial extent of water quality observations to include both existing and prospective wetland restoration stations, 2) conducting higher temporal resolution sampling of water quality and light availability to extent temporal observations 3) establish statistical associations between light availability, ECCC's water quality index scores and individual water quality parameters and 4) to determine if light availability is driven by similar contributions of water quality parameters at different locations and through time within the system. Based on literature and prior system specific studies conducted in the Detroit River described above, I generated the following hypotheses to for testing in Chapter 2:

H1: Wetland sites adjacent or downstream of tributary inputs have lower seasonally averaged WQI scores and greater light limitation than wetland sites not associated with tributary inputs in the Detroit River.

H2: Water quality scores and light limitation at proposed wetland restoration sites are similar to water quality and light limitation at established wetland locations in the Detroit River.

H3: The ECCC water quality index is strongly correlated to light attenuation and light extinction coefficients and therefore predictive of light constraints of submerged aquatic macrophyte growth.

H4: Light limitation in the Detroit River is driven by a subset of water quality parameters and that the major drivers of light limitation are similar across locations and through time.

Chapter 3 takes a different perspective, moving from characterization of light constraints on macrophyte habitat and depth limitations towards understanding of wetland function. In Chapter 3, I ask the question of whether macrophyte beds can improve water quality in the Detroit River via nutrient drawdown. If wetlands are shown to increase water quality, then the enhancement of macrophyte areal extent supported by the completion of proposed habitat restoration efforts could potentially represent a nutrient mitigation strategy which improves water quality in both the Detroit River and the downstream receiving waters of western Lake Erie. Chapter 3 focused on the five established wetland sites previously designated as wetlands of significant provincial interest and routinely monitored by ECCC in their wetland monitoring program for the Detroit River Area of Concern (ECCC, 2017). At each wetland, water quality sonde measures and water samples for nutrients were determined at replicated upstream and downstream bed margin locations and at five random locations overlying the macrophyte bed. Samples were taken across nine sampling points over the open water season of 2018. Under the prediction that Detroit River wetlands result in significant drawdown of key nutrients such as phosphorus and nitrogen, I formulated the following hypothesis to test in Chapter 3:

H1: Nutrient concentrations in water overlying submerged aquatic macrophyte beds are lower than nutrient concentrations at their upstream bed margin.

Given that ECCC (2017) has previously designed some wetlands as stressed (i.e. Turkey Creek and River Canard influenced wetlands) and others as good quality (e.g. Peche Island), I further predict that the wetland stress status will interact with degree of nutrient drawdown generated by a given wetland bed. In other words, healthy wetlands have improved wetland function over stressed wetlands. Based on this prediction I formulated a second hypothesis to test in Chapter 3:

H2: Nutrient drawdown over the macrophyte bed is higher in wetlands designated as better quality based on WQI scores compared wetlands designated as degraded according to the water quality index.

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CHAPTER 2

Water Quality Index and Light Limitation of Submerged Aquatic Vegetation in the Detroit River

2.1 Introduction

The Detroit River is a connecting channel between Lake Huron and Lake Erie. The system has seen significant deterioration in both the quality and quantity of the aquatic habitat it provides (Hartig et al., 2009; Manny et al., 2015). Losses of wetland coverage in the system are estimated at 97% along the US shoreline based on historical maps of wetland coverage generated in 1796 and 53.4% of the historical wetland coverage assessed in 1876 (Roseman et al., 2007; Hartig and Bennion, 2017). The Detroit River was included on the list of Great Lakes Areas of Concern (AOCs) after 1995 as a result of these losses as well as a result of impairments arising across several other beneficial uses caused by industry (Leney and Haffner, 2006), urbanization, and agriculture (Snell, 1987; Green et al., 2010).

Coastal wetlands in this system serve as important nursery habitat for over sixty five different species of fish (ERCA, 2022). However, in spite of the degradation and loss of habitat that has been observed, the Detroit River and its tributaries continue to support some of the highest levels of fish biodiversity in Canada (Stephenson et al., 2014; Tsuboi et al., 2022). The importance of aquatic macrophytes which form the basis of submerged aquatic vegetation (SAV) beds as habitat of small-bodied and early life stage fishes was highlighted in a prior study of the fish community for the Detroit River (Hilling et al., 2021). These findings bring attention to the significance of SAV within these systems.

Submerged aquatic vegetation is an essential component of nearshore freshwater ecosystems because it not only stabilises substrates, filters nutrients, and oxygenates the water, but it also provides critical habitat supporting aquatic biodiversity (Midwood, 2020; Midwood et al., 2021). Given the significance of SAV, a large number of studies have been conducted in an effort to develop models of SAV distribution and cover (Moyle et al., 2016; Valley et al., 2004). Many such models, however, tend to have a regional focus and may be difficult to transfer to other areas due to differences in the environmental conditions across broad geographic areas that support different species indicative of SAV macrophyte communities (Lazzari & Stone, 2006; Wilson et al., 2014).

Environment and Climate Change Canada adopted a water quality index (WQI) tailored to Great Lakes Coastal wetlands based on statistical models calibrated against water quality parameters measured at110 Great Lakes coastal wetland sites over a gradient of disturbed and reference locations (Chow-Fraser, 2006). The WQI is co-interpreted with several independently derived biotic integrity indices (IBI's) that focus on macrophyte composition, benthic invertebrates, fish, and marsh bird communities (Grabas et al., 2012; Uzarski et al., 2001). Together, the WQI and biotic integrity indices form the basis for the Canadian approach to coastal wetland assessment used to address the fish and habitat loss beneficial use impairment in Great Lakes AOCs. The WQI and associated IBI's have been utilized throughout Lake Ontario, Lake Erie, and the Huron-Erie Corridor (Grabas et al., 2012; ECCC, 2017).

The WQI consists of 4 main water quality parameters: turbidity, conductivity, temperature, and pH (Chow-Fraser, 2006; Grabas et al., 2012). Two of these parameters, turbidity and conductivity, are indirectly related to water transparency which is expected to be an important determinant of macrophyte quality given that macrophyte distributions are frequently constrained by light limitation (Orth et al., 2010; Eisemann et al., 2021; Manzoor et al., 2021). Alternatively, light attenuation in water can be determined by direct empirical approaches. Secchi disc, first described in 1865 (Wernand, 2010) is a near universal limnological standard for measuring water transparency in rivers, lakes, and oceans. However, utilization of a Secchi disk in coastal wetlands often fails because the disc becomes obstructed by the macrophyte canopy or it may still be visible when the disk is lowered to the bottom precluding an of estimate of degree of light attention. Direct measures of light intensity using an irradiance meter such as a LiCor PAR meter involves taking light intensity readings as a function of depth and calculating the light extinction coefficient (ε) according to Beer's Law (Scheffer, 2004). For photosynthetic organisms inclusive of macrophytes, light intensity measures are preferably taken across the photosynthetically active radiation (PAR) spectrum which consists of light wavelengths in the range of 400-700 nm utilized by chlorophyll a and accessory pigments during photosynthesis (Wetzel, 2001). Generally, the euphotic depth capable of supporting macrophytes (Z_{EU_SAV}) is estimated as the depth at which the light intensity is 10% that of the surface intensity (Scheffer et al., 2001). Measures of light extinction coefficient (ε) and Z_{EU_SAV} are expected to correlate more strongly with macrophyte depth limitations compared to water quality parameters but are less frequently available owing to the need for use of specialized equipment, e.g., PAR irradiance meters necessary to take such measurements. It is therefore of interest to determine if light extinction coefficient measurements collected at individual wetland sites are correlated with WQI and to tease out the relative contributions of different water quality parameters which contribute to increased light attenuation in waters overlying SAV beds.

Environment and Climate Change Canada performs routine monitoring of the water quality index at 5 established wetland sites in Canadian waters of the Detroit River in support of the habitat beneficial use impairment designated for this Great Lakes AOC (ECCC, 2017). Their observations demonstrate that two of the five routinely monitored wetlands receiving input from smaller tributaries discharging to the Detroit River had moderate to highly degraded water quality scores compared to the other wetlands that are not influenced by tributary inputs. However, ECCC limits its sampling efforts to five wetlands within Canadian waters of the Detroit River and these sample areas are typically visited for only short periods of time in a given year. Other research in the AOC identified prospective SAV restoration areas for remedial actions to increase SAV abundance to help resolve the BUI (ERCA, 2016). However, the water quality at these restoration sites were not determined or compared to water quality at established wetlands of the Detroit River and therefore it is not known if proposed habitat restoration initiatives would lead to successful SAV establishment or not.

Chapter 2 provides enhanced spatial and temporal monitoring of water quality index scores and light attenuation in Canadian waters of the Detroit River. One objective of this research was to verify if Environment and Climate Change Canada's designation of degraded wetland sites persists when samples are taken at higher temporal resolution and to match these results with new site specific measures of light attenuation leading to the hypothesis: wetland sites adjacent or downstream of tributary inputs have lower seasonally averaged WQI scores and greater light limitation than wetland sites not associated with tributary inputs in the Detroit River. A second objective was to determine if water quality and light availability at identified wetland restoration sites is similar to established wetlands according to a second tested hypothesis: water quality scores and light limitation at proposed wetland restoration sites are similar to water quality and light limitation at established wetland locations in the Detroit River.

The third objective for chapter 2 focuses on uncovering predictive relationships to estimate light extinction coefficient. Assuming Environment and Climate Change Canada's water quality index can serve as a proxy for the light attenuation coefficient, it is hypothesized that water quality index will be strongly correlated with site specific measures of light extinction coefficient and therefore the index can be shown to be predictor of light constraints of submerged aquatic macrophyte growth. In addition to the water quality index, other multivariate models calibrated to predict light extinction coefficient are explored. Finally, Chapter 2 will provide a more detailed examination of individual water quality parameter contributions to light attenuation using high temporal resolution data in order to test a final hypothesis that light limitation in the Detroit River is driven by a subset of water quality parameters and that the major drivers of light limitation are similar across locations and through time.

2.2 Methods

2.2.1 Sample Stations in the Detroit River

Twenty-one sampling locations distributed throughout the Canadian portions of the Detroit River area of concern (AOC) were established. Light penetration and water quality parameters at each station were measured at two-week intervals between May 3 to Oct 17, 2017. The wetland monitoring sites consisted of 21sample locations encompassing Ontario designated Significant Wetlands utilized by Environment and Climate Change Canada as part of its SAV monitoring plan (Peche Island, Turkey Creek, Grass Island, Detroit River Marshes, and River Canard estuary) as well as prospective wetland restoration sites identified by Essex Region Conservation authority as priority SAV restoration areas (ERCA, 2016). Site locations and coordinates are provided in Table 2.1 and location positions graphically represented in Figure 2.1. The distribution of these sites included six locations in the upper and middle reach of the Detroit River, three stations near tributary inputs around Turkey Creek and River Canard and ten stations in the lower portion of the Detroit River. Ten of the stations were located offshore in the vicinity of Canadian islands of the river, six were situated along the Canadian mainland shoreline and four were within the mixing zone of a tributary inputs.

2.2.2. Water Quality Parameter Measurements

Spot measures of water quality were taken during 2-week site visitations using an RBR water quality profiler (RBR Global, Ottawa, Ontario, Canada) equipped with probes capable of measuring turbidity, chlorophyll *a*, temperature, conductivity, pH, and dissolved oxygen. Profiler measures were taken at the 0.5 m depth during each site visitation. Water samples (1 L) were also taken at each site and time point to determine total suspended solids (TSS) by filtering and determining dry filtered residues by weighing at the laboratory. Water Quality Index (WQI) was calculated as described by

Table 2.1. Coastal wetland monitoring sites used for water quality measures in the Detroit River

Station	Coordinate (UTM)	Location Descriptor	Station Type
North Peche Island	17T0341156, 4689928	Non-Tributary	SAV Restoration Site
South Peche Island	17T0341156, 4689928	Non-Tributary	ECCC Monitoring Site
East Peche Island	17T0340820, 4690090	Non-Tributary	SAV Restoration Site
Abars Marina	17T0339556, 4689970	Non-Tributary	SAV Restoration Site
Chewitt Bay	17T0341156, 4689928	Non-Tributary	SAV Restoration Site
Ojibway Shores	17T0326860, 4682271	Non-Tributary	SAV Restoration Site
Upstream Turkey Creek	17T0326269, 4679551	Tributary	Upstream of ECCC Site
Turkey Creek B	17T0326257, 4679295	Tributary	ECCC Monitoring Site
Turkey Creek A	17T0326153, 4679191	Tributary	ECCC Monitoring Site

Upstream Grass Isl.	17T0325880, 4676930	Non-Tributary	SAV Restoration Site
West Grass Isl.	17T0325928, 4676743	Non-Tributary	ECCC Monitoring Site
Island View Marina	17T0326187, 4676271	Non-Tributary	SAV Restoration Site
West Fighting Isl.	17T0324991, 4673382	Non-Tributary	SAV Restoration Site
South Fighting Isl.	17T0325335, 4673075	Non-Tributary	SAV Restoration Site
Upstream Turkey Isl.	17T0325420, 4672722	Non-Tributary	Upstream ECCC Site
Downstream Turkey Isl.	17T0325543, 4672310	Non-Tributary	ECCC Monitoring Site
Upstream River Canard	17T0325092, 4671172	Non-Tributary	Upstream ECCC Site
River Canard	17T0324826, 4669888	Tributary	ECCC Monitoring Site
Boblo Island	17T0324848, 4661823	Non-Tributary	SAV Restoration Site
Boblo Dock	17T0325237, 4661421	Non-Tributary	SAV Restoration Site

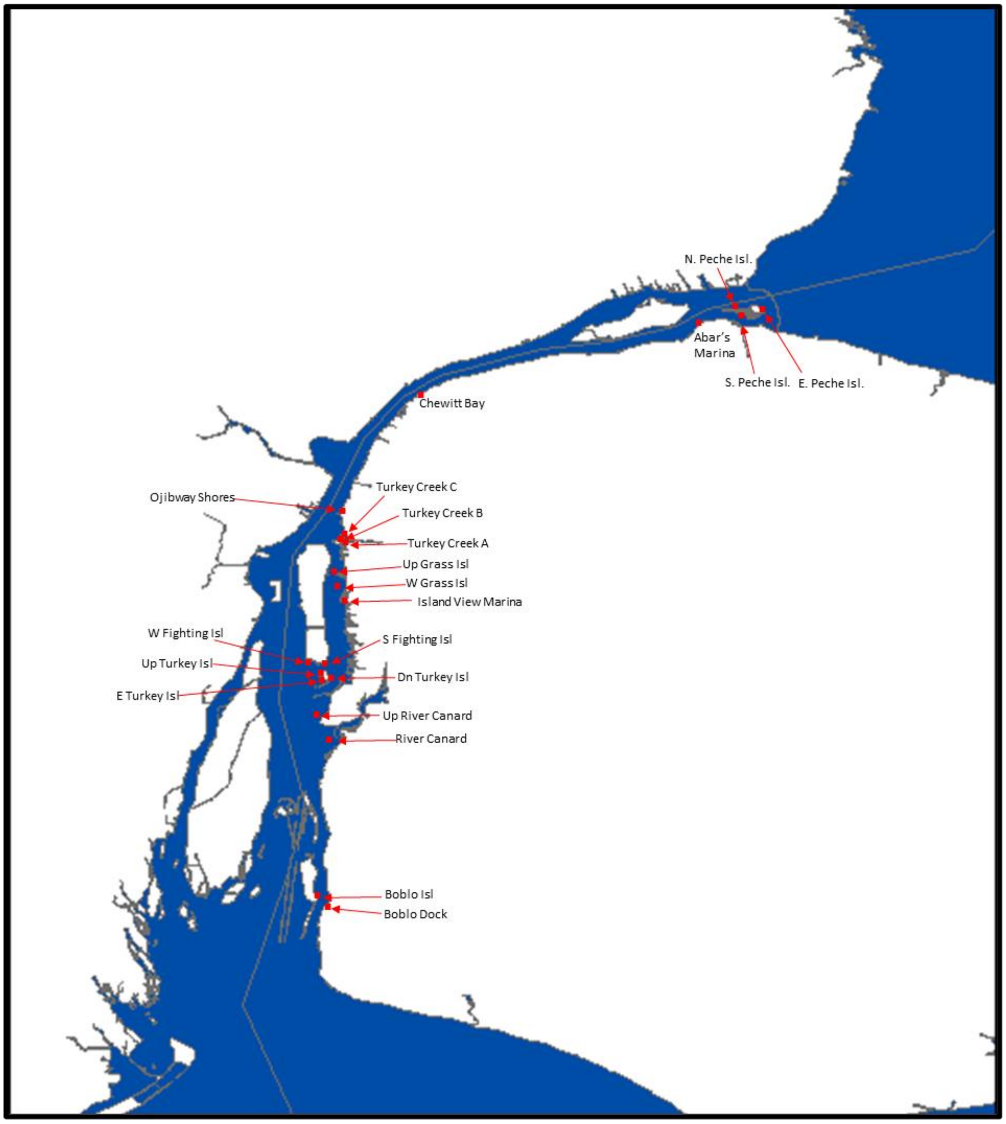

Figure 2.1. Water quality monitoring sites in the Detroit River.

Chow-Fraser (2006) according to:

$$WQI = -1.37 \cdot \log Turbidity - 1.58 \cdot \log Conductivity - 1.63 \log Temp - 2.37 \log pH + 9.27$$

Given that all locations of monitoring were from the same water body and subject to seasonal temperature change, time point specific measures of WQI at each site used the seasonally averaged site-specific temperature to generate the WQI score. All other parameters used in the WQI calculation used the site and time-specific measured parameter value. The WQI typically ranges from – 3 to +3 reflective of highly degraded up to excellent quality sites. The WQI was used to compare relative differences in water conditions between sites for stations categorized as tributary influenced or non-tributary influenced or based on whether the site supports an established wetland or represents a prospective wetland restoration area (Table 2.1).

High resolution sampling of water quality parameters was also performed at four selected stations. The four selected locations included: South Peche Island, East Turkey Island, River Canard and Boblo Dock (Figure 2.1). High resolution sampling at these sites was limited to four locations due to the limited availability of water quality sondes capable of being deployed and taking pre-programmed time-interval measurements. RBR *In-situ* Sondes outfitted with probes capable of measuring depth, turbidity, chlorophyll a, temperature and conductivity were used. The sondes were moored in place by tying each sonde to an angle iron inserted into the sediment so that the sonde probes were between 0.5 – 1 m below the surface and marked with a large buoy. The sondes were programmed to take timed interval parameter readings every 2 minutes. The sondes were visited every two weeks to download logged data, clear the sensors and re-deploy them to collect data over the subsequent 2-week interval. Individual water quality parameters were used to correlate with spot and high-resolution extrapolated measures of ε_{PAR}. The high-resolution sonde data was also used to estimate WQI as described above. In this case, both the seasonally averaged site-specific temperature and pH (derived from 2-week profiler measures) were used instead of time-specific parameter measures.

2.2.3 Light Attenuation Measurements

Light intensity with depth readings at each site were taken using a light meter (LI-COR LI-192 Underwater Quantum Sensor with LI-1500 Light Sensor Logger; Li-COR Environmental, Lincoln, Nebraska, USA) capable of equal sensor response for wavelengths in the PAR range. Light intensity readings were in units of µmol photons/m^2/s. At each site and time point, the first light reading was taken just below the water surface and subsequent readings were taken by lowering the sensor at 0.5 m depth intervals until a final depth of 3 m or until the sensor reached bottom. Macrophytes were pushed out of the way to keep them from blocking the sensor when lowing the probe. Light intensity data were used to determine the light extinction coefficient (ε_{PAR}; m^{-1}). The ratio of light intensity at depth was standardized to the near surface light intensity reading taken just below the water surface. A linear regression was performed on natural transformed light reading ratios (y-axis) against depth (m; x-axis) at each site/time point and ε_{PAR} was set equal to the slope of the above regression. In cases where the decline of light intensity with depth was non-significant, i.e., due to changes in cloud cover during readings, the data were censored from the final dataset. The euphotic depth (Z_{eu}) for macrophytes was estimated as:

$$Z_{eu(SAV)} = 2.31/\varepsilon_{PAR}$$

2.2.4. Macrophyte Composition and Community Composition Metrics

Macrophyte composition and relative abundance was determined at each of the twenty-one locations during 4-time intervals: July 10-12, July 24-26, Aug 9-10 and Sep 16-17. Macrophyte biomass was collected by heaving a weighted double-sided rake attached to a rope overboard to scour approximately 5 m of the SAV field in front of the anchored boat. All plant material retrieved from five rake throws were pooled. Rake throws that came back empty were excluded from the standard five throw count. The pooled material was stored in plastic Ziplock bags and returned to the lab for identification and sorting.

At the laboratory, plants were identified to species using taxonomic keys and Canadian Wildlife Service's SAV biomonitoring reports as a guide to species present. Species identification was completed by GLIER technician Joanne Ching. Each plant type was sorted, dewatered by centrifugal force, and then dehydrated in a food dehydrator overnight. The dry biomass of each species was determined by weighing and percent biomass of each species was determined as a relative abundance metric.

Macrophyte community metrics of species richness, species diversity and species evenness were calculated based on relative dry biomass composition. Species richness was measured as the total number of species collected at a given location. Species diversity was calculated using the Shannon-Weiner Index and species evenness by Pielou's J using relative biomass rather than species count within the sample. Shannon-Weiner index (H') was calculated as:

$$H' = \sum_{i=1}^{S} p_i \cdot ln(p_i)$$

where S is the total number of species and p_i is the proportion of dry biomass of species is relative to the total dry biomass retrieved at a site. Pielou's J was calculated as:

$$J = \frac{H\prime}{\ln{(S)}}$$

Collected macrophyte species were also identified as light sensitive or low light tolerant species according to Albert and Minc (2004). A light sensitivity composition index was generated by dividing the proportion of dry biomass of all plants categorized as light sensitive species by the proportion of dry biomass of plants categorized as low light tolerant species. Values of light sensitivity index approaching or greater than one indicates a preponderance of light sensitive species suggestive of high light quality at the site. Species that were identified but not ranked by light tolerance were excluded from this metric.

A macrophyte conservation score was calculated based on species scores described by Oldham et al. (1995). Each species within the index is given a conservation score ranging from 0 to 10 with the highest scores applied to species with lower disturbance tolerance. A cumulative conservation score was generated by multiplying the species conservation score by the proportion of dry biomass of the given species and summing across the species identified in the sample. Species identified that had no conservation score associated with them were excluded from the conservation score index.

Macrophyte composition metrics including species richness, diversity (H'), evenness (J) light sensitivity index and conservation score were contrasted against ε_{PAR}, individual water quality parameters and WQI by Pearson's correlation analysis to determine if light limitations and water quality impacted SAV quality and function.

2.2.5 Data Interpretation and Statistical Analysis

Hypotheses 1 and 2 were tested by analysis of variance (ANOVA) using empirically measured water quality index score data or light extinction coefficient (ε) measurements determined for samples grouped across time points and classified into treatment or control groups. Prior to ANOVA, data were first tested for normality by Lilefor's test. Where data failed normality, even after logarithmic transformation, non-parametric Kruskall-Wallis was used in place of ANOVA. Pairwise comparisons were performed by Tukey's Test where data were normal or Convover-Inman's Test where data failed normality. For normal data, measures of central tendency and variation are expressed as mean±standard error of data. For non-normal data, measures of central tendency and variance are expressed as median and the 5 to 95th percentiles. For Hypothesis 1, water quality index scores or light extinction coefficient measurements were tested to examine for differences between tributary influenced sites (treatment) and other sites (controls) within the Detroit River (See Table 2.1 Location Descriptor Column). For Hypothesis 2, water quality index scores or light extinction coefficient measurement differences were tested between sites grouped as prospective restoration sites (treatments) or established wetland sites (controls; See Table 2.1 Station Descriptor Column). Broader spatial differences were also examined using either by ANOVA or Kruskall-Wallis tests for samples grouped by individual collection locations after combining data across time points.

In order to test Hypothesis 3, a linear regression analysis was performed between light attenuation coefficients (ε) and water quality index scores (WQI scores). ANOVA was used to determine if the slope of the above relationship was significantly different from zero and the coefficient of determination (R^2) was interpreted as a metric of the quality of model fit. The above model is referred to subsequently as the WQI model.

In addition to the WQI model, an independent multivariate model was trained using the water quality parameter data available from both the water quality profiler sonde and the in-situ water quality sondes. The water quality data matrix was composed of log10 transformed data on temperature, specific conductivity, chlorophyll a concentration and turbidity. The data were first reduced in dimensionality by principal components analysis (PCA) using a variance-covariance matrix. Individual parameters with high correlations to one another will load together on a given PCA axis. Parameters which load to different PCA axes are not correlated to one another. As such, PCA scores across different significant PCA axes can be used as an alternate set of predictors incorporated into multiple regression analysis to generate a model. The number of significant PCA axes was chosen to include those with eigenvalues greater than 1 and which also had water quality parameters with strong loadings associated with it (correlation coefficient to a given PCA axis must be greater than 0.6). This alternative model is subsequently referred to as the multivariate PCA model and was contrasted in its performance to the WQI model.

Hypothesis four used the high resolution temporal monitoring data generated by the in-situ water quality sondes to identify major drivers of light limitation at the four deployment locations and determine whether or not such drivers were consistent between sites and/or across time. To accomplish this. the WQI or multivariate PCA model, whichever performed best, was used in conjunction with the in-situ water quality sonde data to predict light extinction coefficients at the 4 sonde deployment stations. High resolution temporal patterns of light extinction coefficient estimates were visually examined across sites by scatter plots to determine major temporal consistencies between locations.

Subsequently, the model (WQI or multivariate PCA model) was then used to estimate each parameter's relative contribution to each light extinction coefficient estimate generated for the high temporal resolution dataset. This was performed by estimating the light extinction coefficient according to the selected model using only one parameter at a time for a given deployment site and time point and setting the other parameters within the model to zero. The % contribution of that parameter was estimated as the ratio of light extinction estimate for the single parameter estimate to the multi-parameter estimate multiplied by 100. Percent contributions of individual water quality parameters as a function of time were then plotted by scatter plot at each site to determine major similarities between sites and or across time points.

Each in-situ water quality sonde also contained a pressure sensor capable of measuring water depth during each 2 minute interval. This data was used to estimate maximum daily wave height and wave intensity at each of the deployment sites. The maximum daily wave height was estimated as the deepest depth measured in a given 24 h period against the minimum sonde depth recorded for that day. The wave intensity was estimated from the coefficient of variation (%) of water depths measured by each sonde over a 24 h period in a given day. Maximum daily wave height and wave intensity were contrasted against WQI- or the multivariate PCA model predictions of light extinction coefficient by linear regression analysis.

Finally, macrophyte composition indices on species richness, species diversity, light sensitive species and conservation score described in section 2.2.4 were contrasted against light extinction coefficient and water quality index score using linear regression analysis. These analyses attempted to determine if macrophyte composition was influenced by water quality or light attention.

2.3. Results

2.3.1. Light Extinction Coefficients and Water Quality Index Scores

During processing PAR light extinction coefficients, twenty-six estimates had to be censored due to poor regression relationships between light intensity and depth. After censoring the above there were 163 light extinction coefficient measurements remaining across the stations and time points. The median (5-95 percentiles) river wide light extinction coefficient (ε) for the Detroit River was 1.78 (0.46 – 4.23) m^{-1}. When individual ε measures were converted to macrophyte euphotic depth ($Z_{EU\text{-}SAV}$), the median (5-95 percentile) ($Z_{EU\text{-}SAV}$) was 1.30 (0.55-4.70) m.

There were highly significant differences between light extinction coefficient measurements across individual sample sites (Kruskal-Wallis test with Conover Inman's pairwise comparisons; $p<0.001$). Table 2.2 provides a summary of mean annual light extinction coefficient measurements at each of the 21 sampling stations. Boblo Dock had the lowest light extinction coefficient indicative of high light availability whereas Island View Bay and Chewitt Bay had the greatest magnitude of light attenuation.

To test Hypothesis 1, sample sites were grouped into tributary versus non-tributary influenced locations across time points (see Table 2.1 and 2.2). Light extinction coefficients at sites with tributary influence were significantly higher (Kruskal-Wallis test due to non-normality of data; $p<0.001$) than non-tributary categorized sites. The median (5-95 percentiles) of light extinction coefficients were 1.72 (0.45-4.61) m^{-1} and 2.78 (0.47-3.99) m^{-1} for non-tributary compared to tributary influenced sites, respectively. Similarly, the median (5-95 percentiles) of $Z_{EU\text{-}SAV}$ was 1.34 (0.50-4.96) m and 0.83 (0.58-5.51) m for non-tributary versus tributary influenced sites, respectively. Hypothesis 2 compared light availability at established wetland locations compared to prospective wetland restoration sites (see Table 2.1). Light extinction coefficients at established wetland areas were not significantly different (Kruskal-Wallis test; $p>0.05$) compared to prospective wetland restoration sites.

A total of 161 water quality index scores were calculated based on water quality profiler measurements of temperature, conductivity, turbidty and pH. The river wide water quality index score was -0.41±0.6 corresponding to a moderately degraded ranking. Similar to light extinction coefficient measurements, there were highly significant differences (ANOVA, $p<0.001$) between water quality scores across sampling stations when data were combined across time points. Table 2.2 provides a summary of mean and standard error water quality scores from each station. North Peche Island and East Peche Island sites had the highest water quality scores approaching +0.5 and were categorized as good. Lowest water quality scores were observed at the River Canard outlet corresponding to a highly degraded designation (< -1).

When Hypothesis 1 was tested for water quality index score, tributary influenced sties were highly significantly (ANOVA, $p<0.001$) lower in their water quality scores compared to sites not influenced by tributary inputs. The mean±standard error water quality index scores for tributary and non-tributary sites was -0.94±0.1 and -0.32±0.06, respectively. However, both site categories would be designated as moderately degraded according to the Chow-Fraser (2006) grading scheme. For Hypothesis 2, there were no significant differences (ANOVA; $p>0.2$) in water quality index scores between established wetland sites and sites designated as prospective wetland restoration areas. Figure 2.2 provides box and whisker plots of light extinction coefficients and water quality index scores tested via hypothesis 1 and 2.

Table 2.2. Median (5-95 percentiles) light extinction coefficient and mean±standard error water quality index score values across Detroit River locations.

Site	Position Category	Light Extinction Coefficient	WQI Score (Category)
North Peche Island	Non-Tributary, Restoration	0.74 (0.40-1.53)	0.52±0.0.13 Good
East Peche Island	Non-Tributary, Established	0.87 (0.35-2.42)	0.48±0.17 Good
South Peche Island	Non-Tributary, Established	1.54 (0.47-2.95)	-0.15±0.24 Mod. Degraded
Abar’s Bay	Non-Tributary, Restoration	1.47 (0.50-2.61)	-0.30±0.16 Mod. Degraded
Chewitt Bay	Non-Tributary, Restoration	2.54 (1.37-6.77)	-0.92±0.27 Mod Degraded
Ojibway Shores	Non-Tributary, Restoration	1.76 (1.42-4.86)	-0.89±0.21 Mod. Degraded
Upstream Turkey Creek	Non-Tributary, Established	2.32(0.69-2.86)	-0.53±0.28 Mod Degraded
Turkey Creek B	Tributary, Established	2.01 (0.66-4.16)	-0.96±0.27 Mod. Degraded
Turkey Creek A	Tributary, Established	2.73(0.91-3.72)	-0.78±0.25 Mod. Degraded

Upstream Grass Isle	Non-Tributary, Established	1.87(1.31-3.05)	-0.29±0.24 Mod. Degraded
West Grass Isle	Non-Tributary, Established	1.56 (0.67-4.51)	-0.58±0.20 Mod. Degraded
Island View Bay	Non-Tributary, Established	4.61 (1.65-6.62)	-0.85±0.16 Mod. Degraded
West Fighting Isle	Non-Tributary, Established	0.79 (0.51-2.02)	-0.30±0.17 Mod. Degraded
South Fighting Isle	Non-Tributary, Established	2.13 (0.95-3.54)	-0.51±0.26 Mod. Degraded
Up Turkey Isle	Non-Tributary, Established	1.88 (0.54-3.30)	-0.12±0.15 Mod. Degraded
Dn Turkey Isle	Non-Tributary, Established	1.08 (0.48-2.10)	-0.41±0.20 Mod. Degraded
East Turkey	Non-Tributary, Established	3.00 (1.42-3.94)	-0.32±0.20 Mod. Degraded
Up Riv. Canard	Non-Tributary, Established	1.03 (0.65-2.03)	-0.06±0.34 Mod. Degraded
River Canard	Tributary, Established	2.83 (2.15-3.79)	-1.24±0.10 Very Degraded
Boblo Island	Non-Tributary, Restoration	0.62 (0.47-1.57)	0.03±0.38

			Good
Boblo Dock	Non-Tributary, Restoration	0.92 (0.48-3.89)	-0.40±0.19 Mod. Degraded

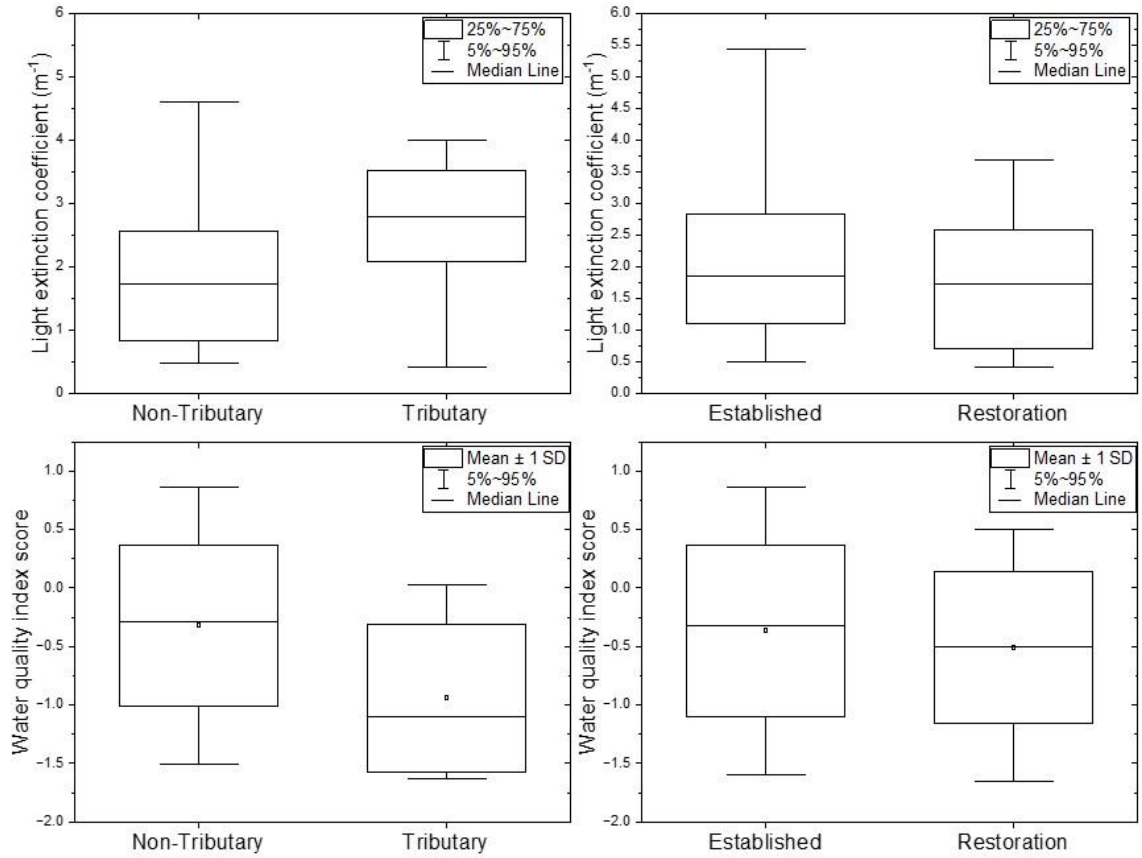

Figure 2.2. Light extinction coefficients (m^{-1}) and water quality index scores at sample stations grouped by non-tributary influenced vs tributary and established wetland vs those designated for restoration actions.

2.3.2. Models to Predict Light Extinction Coefficient

Hypothesis 3 tested whether water quality score can be used as a predictor of light extinction coefficient. Linear regression analysis demonstrated a highly significant (ANOVA, $p<0.001$) negative relationship between water quality index score and light extinction coefficient (Figure 2.3). The coefficient of determination (R^2) of the above relationship was 0.24. The generated WQI model is given by:

$$\text{Light extinction coefficient} = -0.95 \pm 0.14 \cdot WQI_{score} + 1.70 \pm 0.11;\ p<0.001;\ R^2=0.24$$

A multivariate PCA model was generated as an alternative predictor to the WQI model. After removing samples with missing data for some of the parameters, a complete data matrix was available for 121 records across sites and time points. The initial PCA generated two significant PCA axes with eigenvalues greater than one which in combination explained 96.7% of the profiler generated water quality data variation. Parameters loading onto PCA 1 included specific conductivity, chlorophyll a and turbidity. Temperature loaded strongly onto PCA 3 but this axis was not deemed significant owing to its very low eigenvalue. Given that temperature did not load strongly onto a significant PCA axis, another PCA was performed excluding temperature as a variable. The second PCA explained 99.6% of the variation of the data across the first two PCA axes.

Multiple regression analysis was performed using PCA1 and PCA2 scores as predictors of light extinction coefficient. There were 105 matched cases where both light extinction coefficient and a complete matrix of detected water quality parameters (specific conductivity, chlorophyll a and turbidity) were available. The multiple

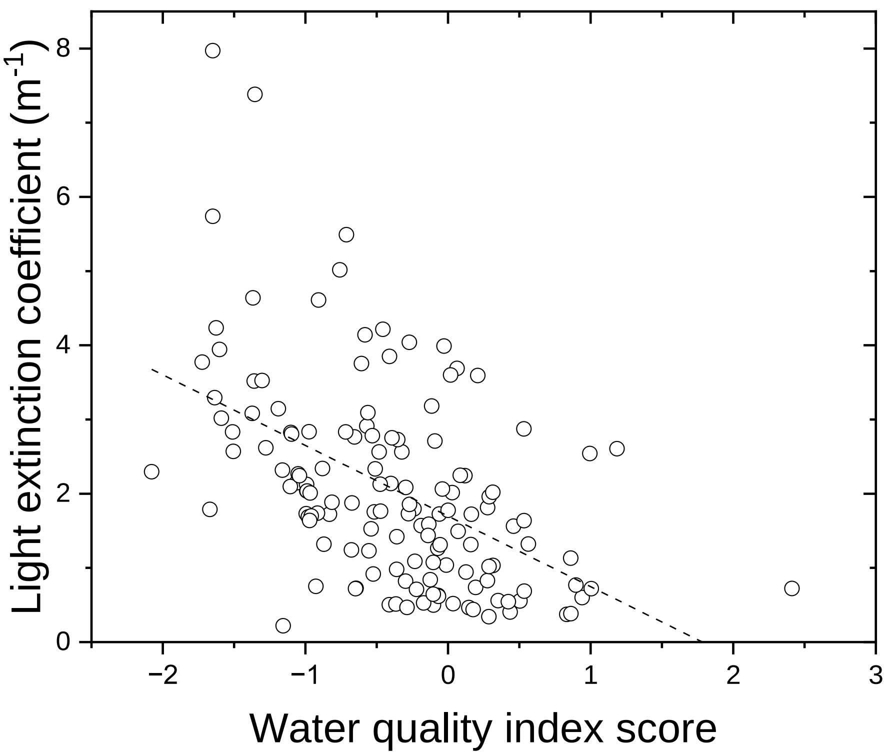

Figure 2.3. Linear regression fit of light extinction coefficient data as a function of water quality index score.

regression model generated an R^2 value of 0.33 explaining more variation than the WQI model. The multivariate PCA model is given by:

Light extinction coefficient = $1.53 \pm 0.229 \cdot PCA1_{score} + 1.345 \pm 0.510 \cdot PCA2_{score} + 2.154$; $p<0.001$; $R^2 = 0.33$

PCA1 and PCA2 scores can be generated where data on specific conductivity, chlorophyl a concentrations and turbidity area available according to:

$PCA1_{score} = 0.0439 \cdot \log SPC + 0.544 \cdot \log \text{chlorophyll a} + 0.838 \cdot \text{turbidity} - 0.983$

$PCA2_{score} = 0.046 \cdot \log SPC + 0.837 \cdot \log \text{chlorophyll a} - 0.546 \cdot \text{turbidity} + 0.576$

Figure 2.3 provides goodness of fit contrasts between predicted light extinction coefficients generated by the WQI model and multivariate PCA models against measured light extinction coefficient data.

2.3.3 High temporal resolution light extinction coefficient estimates

In situ water quality sondes were installed at 4 stations to take readings of specific conductivity, chlorophyll a, turbidity and sensor depth at 2-minute intervals. Light extinction coefficients for each site and time point were estimated according to the multivariate PCA score model as described in section 2.3.3. For simplicity, data were averaged over each 24 h period to give daily light extinction coefficient estimates.

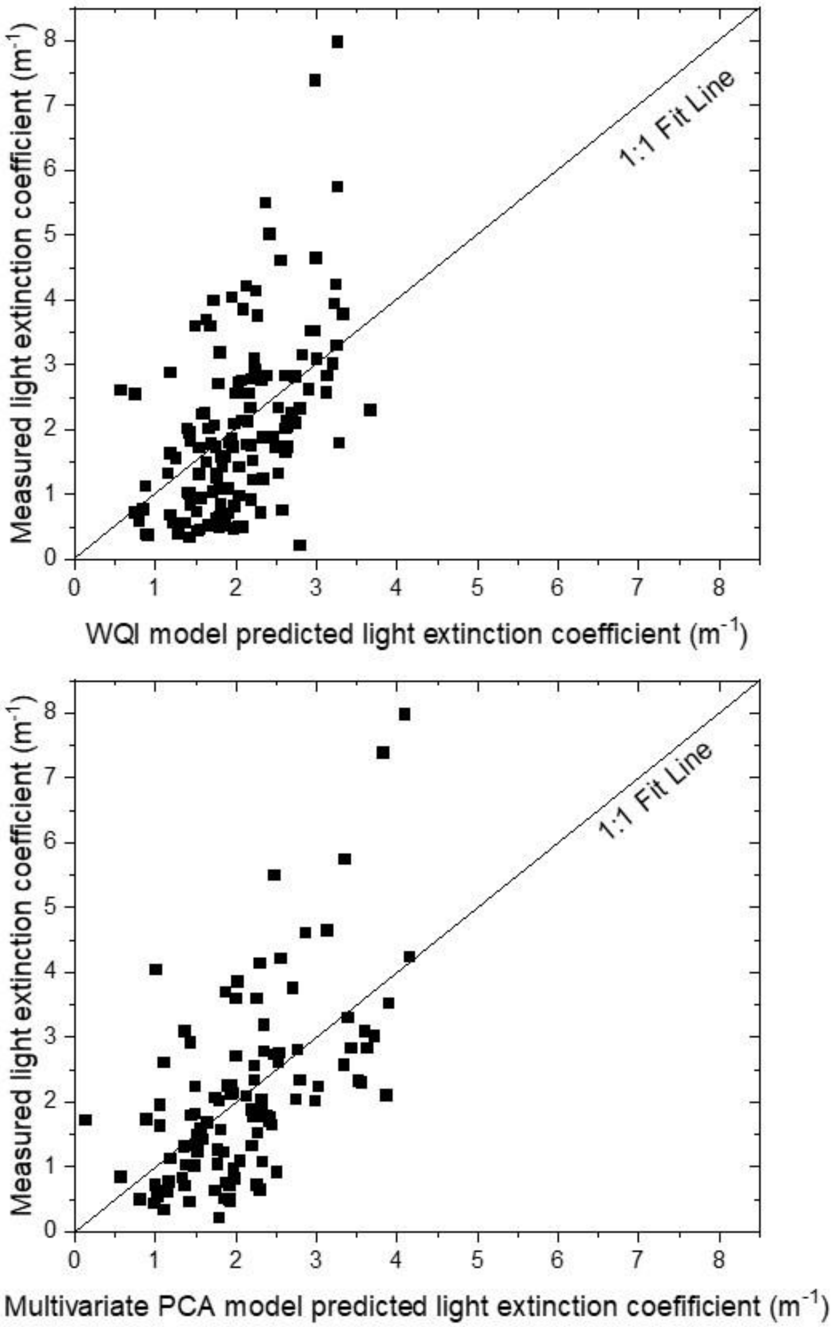

Figure 2.3. Goodness of fit of the WQI and multivariate PCA model predictions of light extinction coefficient. WQI model $R^2 = 0.24$; multivariate PCA model $R^2 = 0.33$.

Figure 2.4 presents high resolution temporal trends of light extinction estimates generated by the multivariate PCA model. Peche Island and Boblo Dock, which were the most distant sites from one another, exhibited very little deviation in their estimated light extinction coefficients across time whereas East Turkey Island and River Canard were much more variable. After aligning by day, the strongest correlations between light extinction coefficients across days was between east Turkey Island and Boblo Dock (Pearson R = 0.620; $p<0.001$) but significant temporal correlations were also observed between Peche Island and East Turkey Creek (Pearson R = 0.527; $p<0.001$); Peche Island and Boblo Dock (Pearson R = 0.447; $p<0.001$); Peche Island and River Canard (Pearson R = 0.263; $p<0.05$) and East Turkey Creek and River Canard (Pearson R = 0.311; $p<0.01$). The only sites where light extinction coefficient was not correlated across days was between River Canard and Boblo Dock (Pearson R = 0.127; $p>0.9$) which were among the closest sites in proximity to one another.

The relative contributions of specific conductivity, chlorophyll *a* and turbidity to daily averaged light extinction coefficient estimates was determined by back calculating how each parameter contributed to the PCA 1 and 2 scores. Each site demonstrated unique contributions across the three parameters to the estimated light extinction coefficient. For Peche Island, the light extinction coefficient was driven by turbidity which contributed on average of 82.5% of the coefficient followed by specific conductivity (10.6%) and chlorophyll a (6.8%). A similar signal was observed at Boblo Dock (77.9%, 9.5% and 12.6% contributions of turbidity, specific conductivity, and

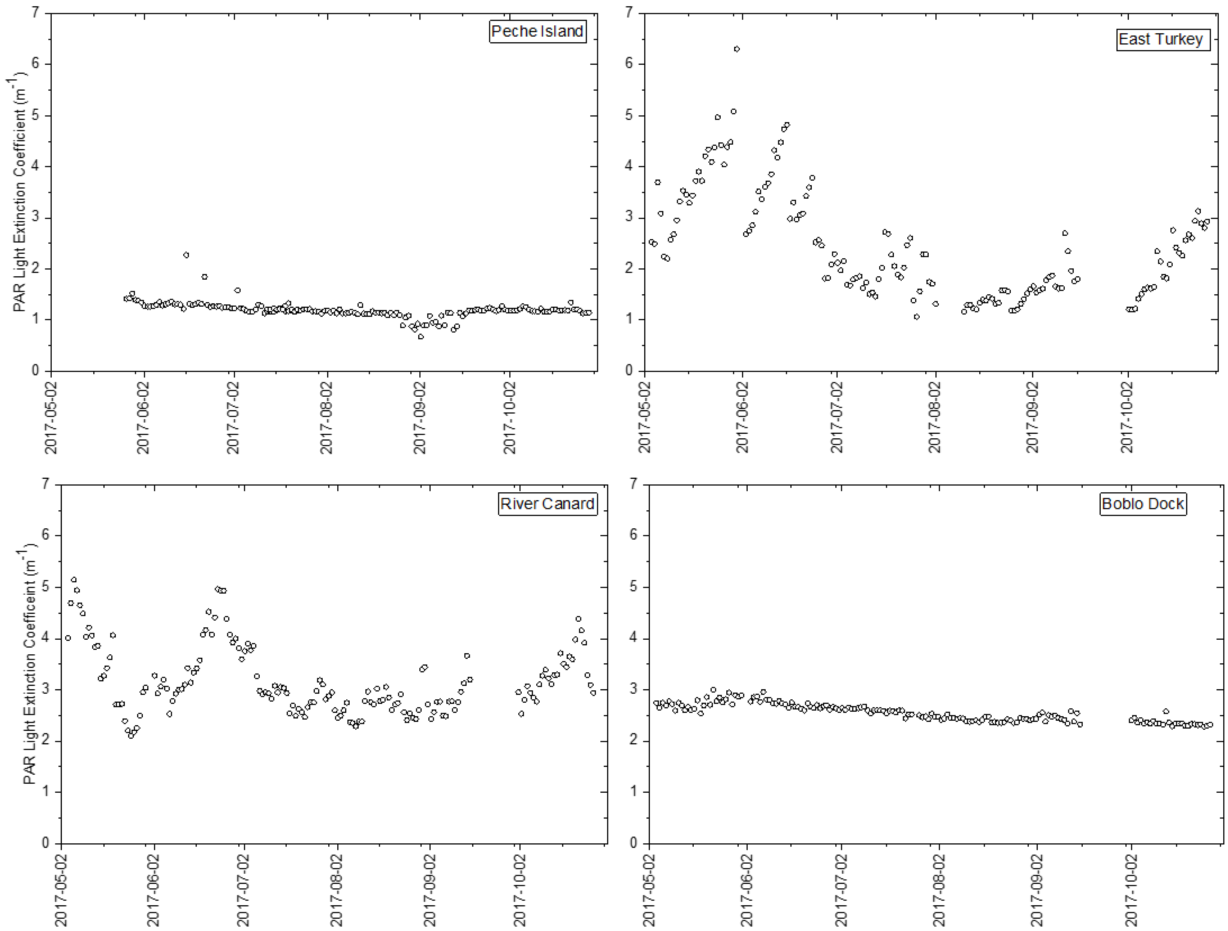

Figure 2.4. Daily changes in in situ sonde estimated PAR light extinction coefficient at four high resolution monitoring stations in the Detroit River.

turbidity, respectively). East Turkey Island and River Canard light extinction coefficient values were driven primarily by chlorophyll a concentration (66.7% and 53.2%). For River Canard, the next largest contributor to light extinction was turbidity (36.7%) while East Turkey Creek had equal contributions of turbidity and conductivity. Figure 2.5 presents the temporal patterns of parameter contributions to daily light extinction coefficient estimates at each of the sites. For River Canard, turbidity, and chlorophyll a contributed nearly equally to the coefficient throughout June and July but became dominated by chlorophyll a in the spring and fall. East Turkey Island was consistently dominated by chlorophyll a contribution except for a 1-week period in July.

Given the high frequency of in-situ sonde readings (2-minute intervals), data from the pressure sensors was further used to evaluate wave height and wave frequencies at the four selected high resolution sonde monitoring stations. Wave intensity and maximum wave height were found to be strongly correlated with one another and therefore wave intensity was selected as a potential predictive variable to explore for its association with the light extinction coefficient. Table 2.5 provides summary statistics of maximum daily wave height and wave intensity across the monitoring stations. Peche Island had the lowest mean wave height but the highest overall wave frequency. Boblo Dock, which is influenced by Lake Erie, had the highest mean wave height and second highest wave frequency. East Turkey Creek and River Canard experienced intermediate wave heights and wave frequencies.

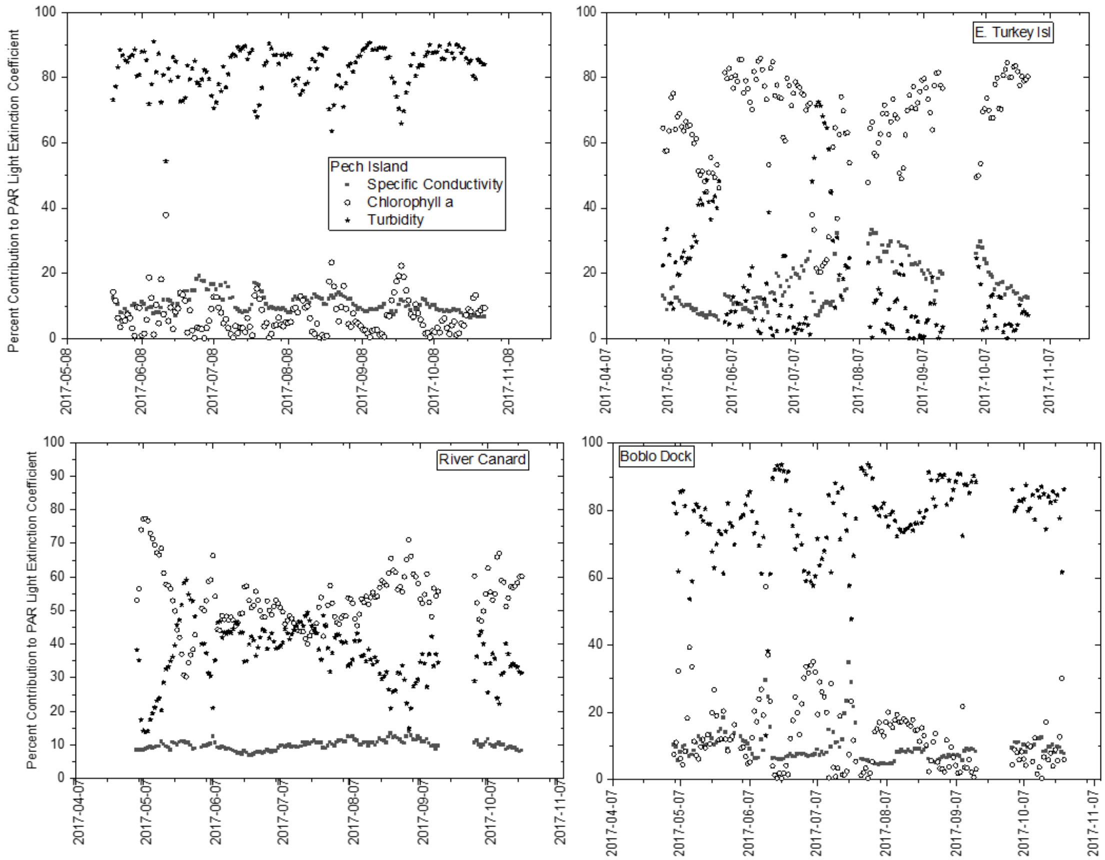

Figure 2.6. Relative contributions of specific conductivity, chlorophyll *a*nd turbidity to PCA 1 score used to estimate light extinction coefficient four locations across time.

Table 2.5. Seasonally averaged differences in maximum daily wave height (cm) and wave intensity across in situ sonde deployment stations.

Site	Mean (Range) Wave Height (cm)	Mean ± SD Wave Intensity (%CV)
Peche Island	5.2 (1.6-31.9)	28.0±199.8
East Turkey Island	8.1 (1.9-61.9)	12.9±28.6
River Canard	7.8 (2.2-23.9)	10.49±4.24
Boblo Dock	16.1 (3.5-107.2)	25.9±101.7

At Peche Island there was a highly significant relationship between wave intensity and multivariate PCA model estimate light extinction coefficient. In this case, the linear regression model explained 11.9% of the variation in daily light extinction coefficients (Figure 2.7). No significant relationships between wave intensity and predicted light extinction coefficients were observed at the other stations (Figure 2.7). Therefore, wind induced wave action appears to be important only at the Peche Island site which is strongly influenced by Lake St. Clair. Surprisingly, wind induced wave action did not appear to contribute strongly to the light regime at Boblo Dock which is also influenced by Lake Erie.

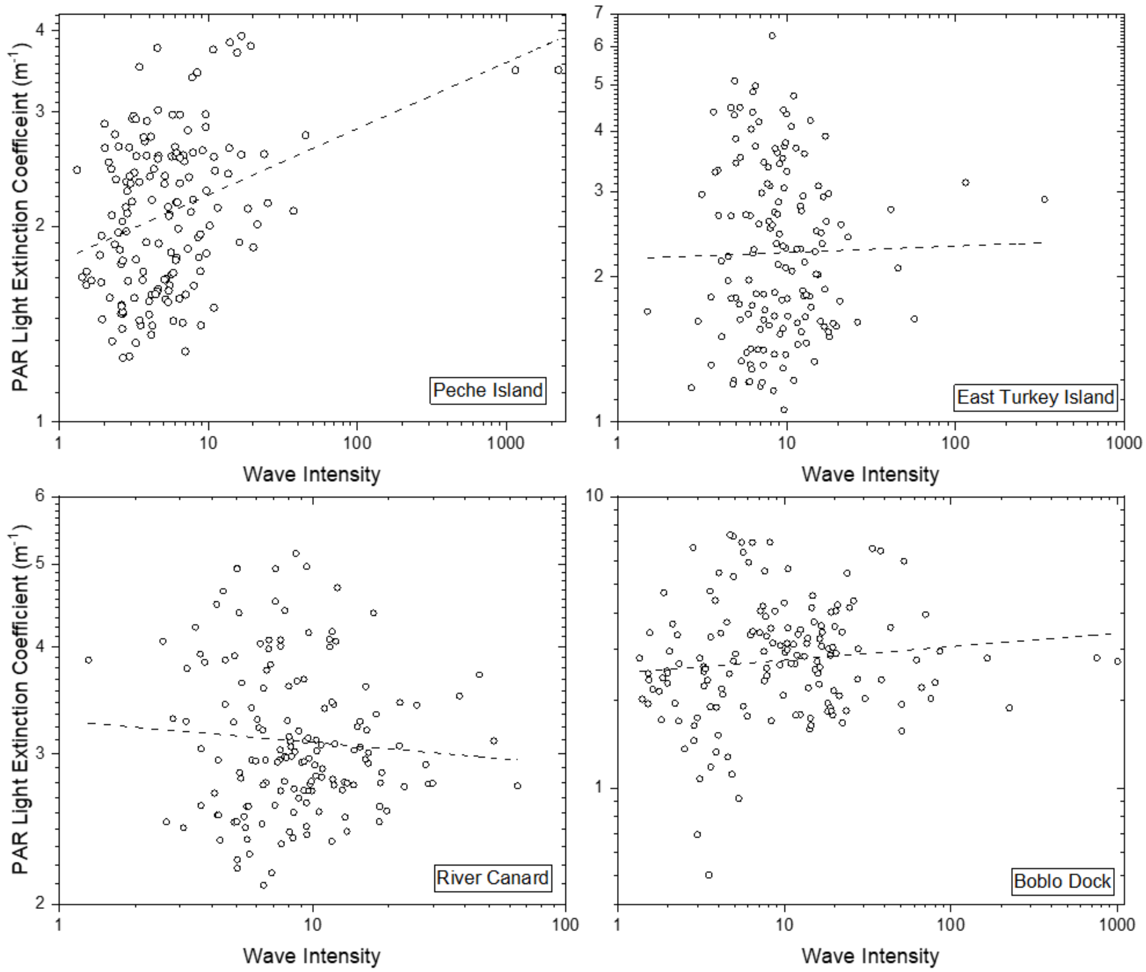

Figure 2.7: Scatter plot relationship between wave intensity and PAR light extinction coefficient for main four sites. The daily wave intensity was established as the coefficient of variation (%) in daily recorded sonde depths at a given site.

2.3.4 Relationship between macrophyte community structure, ε_{PAR} and WQI

A total of twenty species of macrophytes were identified across the sample locations over the combined macrophyte sampling time points (July 10-12, July 24-26, Aug 9-10, and Sep 16-17). Macrophyte community metrics (species richness, diversity, evenness, light sensitivity composition index and conservation score; Table 2.6) were contrasted against environmental predictors that included: Water quality index score, light extinction coefficient,, sediment organic carbon content and sediment substrate type (grain size delineation of gravel, sand, or silt). Initially, all combinations of environmental predictors were contrasted against each macrophyte community metric and then likely candidate predictor variables were explored using linear. Across all combinations, only the conservation score showed a significant relationship with measured light extinction coeffcient. However, the correlation between conservation score and light attenuation coefficient was positive, the opposite of expectations if light limitation is considered a stressor as part of the conservation index formulation. Closer examination of the conservation score vs light extinction coefficient relationship shows that the positive correlation was strongly influenced by two stations (Island View Marina and River Canard) both of which were ranked as moderately degraded according to the water quality index ranking (Figure 2.8). As such, the observed correlation was deemed spurious and none of the aquatic macrophyte community indices could be predicted with confidence based on light regime, water quality index or sediment characteristics.

Table 2.6. Macrophyte composition indices estimated for each sampling location

Site	Site ID	Richness, H, Pielou's J	Total Dry Biomass (g)	Ratio of light sensitive/tolerant species biomass	Macrophyte Conservation Score
North Peche Island	19	7, 0.19, 0.10	65.43	11.556	5.999
East Peche Island	18	9, 1.23, 0.56	211.08	0.121	5.997
South Peche Island	20	13, 2.03, 0.79	96.29	0.957	5.271
Abar's Bay	17	13, 1.85, 0.72	48.06	5.760	5.476
Chewitt Bay	21	5, 0.78, 0.48	162.24	0.238	4.415
Ojibway Shores	16	7, 0.94, 0.48	62.45	4.892	5.812
Upstream Turkey Crk	12	11, 1.51, 0.63	84.19	1.288	5.276
Turkey Creek B	13	11, 1.36, 0.47	77.33	0.052	4.079
Turkey Creek A	14	11, 1.07, 0.45	130.10	1.672	5.776
Upstream Grass Isle	2	11, 1.55, 0.65	164.87	0.148	4.319
West Grass Isle	3	14, 1.54, 0.58	169.23	0.099	4.704

Island View Bay	1	7, 1.21, 0.62	132.13	0	8.791
West Fighting Isle	4	11, 1.43, 0.60	115.34	0.135	4.371
South Fighting Isle	15	9, 1.08, 0.49	132.19	0.030	4.137
Up Turkey Isle	5	10, 1.06, 0.46	95.31	2.504	5.803
Nd Turkey Isl	7	10, 0.85, 0.37	138.78	0.217	5.667
East Turkey	6	15, 1.79, 0.66	90.17	0.145	6.600
Up Riv. Canard	8	8, 0.94, 0.45	36.74	1.953	5.930
River Canard	9	4, 0.60, 0.43	156.79	0	8.879
Boblo Island	11	10, 1.31, 0.57	86.84	0.0956	4.329
Boblo Dock	10	11, 1.23, 0.51	211.08	0.227	4.402

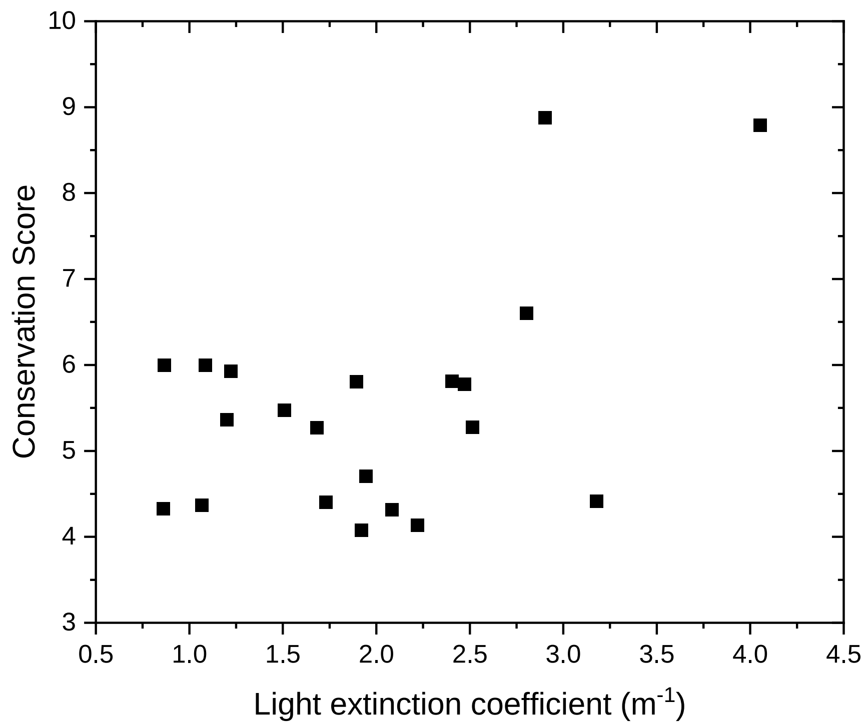

Figure 2.8. Relationship between macrophyte community conservation score and light extinction coefficient.

2.4 Discussion

Direct measures of light extinction coefficient and calculated water quality scores showed differences across sites throughout the Detroit River. The first hypothesis tested if light penetration and water quality scores were reduced at coastal wetland sites that received inflow from Canadian tributaries at Turkey Creek and River Canard. This hypothesis was supported given that light extinction coefficients were significantly elevated at tributary influenced sites and water quality index scores were significantly lower compared to other test locations in the Detroit River. These data are broadly consisted with the ECCC (2017) data set which computed lower water quality scores at River Canard and Turkey Creek compared to other established wetland sites. The much larger number of stations used in the present work and higher temporal resolution of observations compared to ECCC's limited 5 wetland x 2 week characterization study scope substantiates that differences in light and water quality at coastal wetlands subject to tributary inflow are indeed compromised throughout the open water season. These observations confirm that further clean-up efforts to increase water quality in Canadian tributaries such as Turkey Creek and River Canard would have positive benefits to coastal wetlands within the Detroit River, at least for wetlands locations immediately within the tributary/Detroit River confluence zones.

Hypothesis 2 examined if water quality and light availability at prospective wetland restoration sites designated by ERCA (2016) were similar to what is observed at established wetlands within the Detroit River. The present study found no significant differences in either light penetration or water quality index scores at prospective wetland restoration sites compared to established wetland sites within the Detroit River. These observations imply that both water quality and light availability at planned restoration sites are sufficiently good to support submerged aquatic macrophyte growth implying that restoration efforts are likely to be successful with respect to expanding macrophyte coverage within the Detroit River Area of Concern. Planned restorations at these locations include extension of breakwaters, deflection zones and/or construction of small islands coupled with amending fine grain sediments and planting of native macrophyte species (ERCA, 2016). Indeed, some of the planned restoration efforts have already been completed (Chewitt Bay) and/or initiated (Peche Island) since the completion of data collection activities for this thesis. Preliminary observations indicate that macrophytes are already established at Chewitt Bay, even though light attention was relatively low at this location.

Hypothesis 3 tested whether water quality index score is correlated to light extinction coefficient. This hypothesis was supported by the data with water quality index score explaining 24% of the variation in measured light extinction coefficient data. The parameters included in the water quality index score include temperature, specific conductivity, turbidity and pH. At least some of these parameters, e.g. turbidity and specific conductivity have theoretical connections to water transparency (Scheffer, 2004). For example, conductivity can be a marker of nearshore erosion processes or urban runoff including road salts that are expected to correlate with suspended solids concentration in the water (Rasheed & Dawood, 2019). Turbidity measures light scattering by suspended particles including living cells and is therefore considered a direct proxy of suspended solids concentration (Rügner et al., 2014; El Din, 2021). The original calibration of the water quality index was completed across a large range of Great Lakes coastal wetland sites over a gradient of macrophyte bed quality ranging from highly degraded to excellent (Chow-Fraser, 2006). Light limitation is likely one of the major stressors contributing to macrophyte bed quality (Scheffer, 2004) and this explains why the present research observed a correlation between water quality index and light penetration depth. The results from this thesis suggest that ECCC's water quality index scores generated for coastal wetlands throughout Canadian AOCs can be converted, with some notable error, to light extinction coefficient data where direct measures of PAR light attenuation are not available. This may extend the utility of existing federal government monitoring programs beyond wetland quality assessment. For example, light extinction coefficient data could be used in conjunction with productivity models to estimate plant and algal production potential provided other parameters in the productivity models are also available (Conde et al., 2002).

However, the WQI model had lower predictive power for estimating light extinction coefficients compared to the multivariate PCA model which explained up to 33% of variation in measured light extinction coefficients. The multivariate PCA model included measures of specific conductivity and turbidity both in common with the WQI model but also included chlorophyll a which is not part of the WQI model. Chlorophyll *a* is the photosynthetic pigment used by algae and macrophytes to absorb light as part of the light reaction of photosynthesis and is commonly used as a surrogate measure of algal biomass in the water column (Ortiz et al., 2020; Rajala, 2022). Although chlorophyll a is expected to be a component of turbidity measurements and was indeed correlated to turbidity as evidence by their combined high loadings onto PCA1, inclusion of the two parameters increased model predictive power. However, given that the multivariate PCA model was specifically trained on the Detroit River dataset, it is not known if the multivariate PCA model would still outperform the WQI model at other Great Lakes coastal wetland sites outside of the Detroit River. Additional research to validate the multivariate PCA model's performance as contrasted against the WQI model using independent data collected from the Detroit River and other systems would be warranted. Finally, it must be noted that even the best performing light extinction coefficient model generated by this research explained only 33% of the variation in measured data implying that other constituents in water not related to the measured water quality parameters were contributing to light attenuation in the Detroit River.

Hypothesis 4 was concerned with testing if light limitations in the Detroit River are driven by the same major water quality parameters and if such trends are consistent through space and time. The multivariate PCA model was used in conjunction with in-situ water quality sonde loggers to provide high resolution temporal estimates of light extinction coefficients at four monitoring stations. The data revealed that lake-influenced sites in the upstream and most downstream stations had relatively consistent light penetration through time whereas sites associated with River Canard outflow and upstream of River Canard exhibited more stochastic light penetration trends.

However, the major contributors to light extinction coefficient differed in both time and space. The two lake-influenced sites had light extinction coefficients most strongly driven by turbidity. Peche Island was also strongly influenced by daily wave intensity. However, this was not the case at Boblo Dock expected to be influenced by its connectivity to downstream western Lake Erie and subject to periodic storm surges and lake seiches. At Boblo Dock, daily changes in ε_{PAR} were related to turbidity but not correlated with wave intensity. Differences in bottom substrate and between site differences in susceptibility to sediment resuspension may explain such differences. East Turkey Island light penetration patterns were not related to wave intensity but were driven by chlorophyll a indicating that plankton productivity contributes to most of the light attenuation at this location. River Canard light penetration was also not predicted by wave intensity and had extinction coefficients regulated by near equal contributions of chlorophyll *a* and turbidity. Overall, the light regimes at each location were observed to respond to different combinations of water quality parameters that varied independently across time and space. Therefore, hypothesis 4 was rejected based on evidence generated from this thesis.

Given that light extinction coefficient is shown to not only vary dramatically across sample locations but be driven by different chemical constituents in water, this research suggests that some caution is warranted when extrapolating light extinction from a single water quality parameter such as chlorophyll *a* or turbidity. Other high resolution methods for water transparency measurement have been explored using remote sensing methods (Rowan and Kalacska, 2021; Rooney and Bayley, 2011). Zofaghari et al., (2017) calibrated satellite-derived light extinction coefficients for Lake Erie using Secchi disc measures of water transparency as a baseline. Their models used artificial intelligence algorithms to generate models of ε_{PAR} using irradiance reflectance across fifteen spectral bands derived from daytime MERIS images. They reported a model validation where their best model explained 78% of in situ Secchi disc depth measures, better than the PCA model generated in this research. However, Secchi depth, while widely available, may not be a good surrogate measure of ε_{PAR}. As in the case with the Pendant loggers, the Secchi depth technique is dependent on the light sensitivity of the human eye, i.e., the photopic spectrum, which is much more constrained compared to the PAR spectrum (Wetzel, 2001). Scheffer (2004) reported that the relationship between Secchi depth and light meter generated light extinction coefficient explained only 15% of ε_{PAR} and therefore the apparently accuracy of remote sensing models in explaining Secchi depth may not translate into a similar accuracy for prediction of euphotic depth.

Macrophyte community analysis was performed to compare community metrics including species richness, diversity, evenness, proportion of light sensitive species, relative light tolerant species, and species conservation scores. None of these community metrics were associated with light regime, water quality index or sediment characteristics. Overall, these results suggest that between site differences in light penetration did not necessarily translate into altered macrophyte community structure. Even sites such as River Canard, which was compromised in light regime, generated a very high species conservation score. Grabas et al. (2012) noted similar discontinuities between their macrophyte index of biotic integrity (IBI) and the WQI. Within the Detroit River, despite the poor water quality ranking of Turkey Creek and River Canard, the macrophyte IBI scores at these locations were commensurate with Peche Island considered of good quality with respect to WQI (ECCC, 2017). However, this study did not directly compare community composition between sites given the limited number of samples taken. In addition, the use of relative biomass rather than species counts per unit area may have introduced biases into the community analysis. The rake method, as utilized by others (Johnson and Newman, 2011) is likely to be selective as a sampling device, collecting larger, more dendritic species and plants that reach higher positions in the water column than reflected by actual species counts on an aerial basis.

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CHAPTER 3

Submerged Aquatic Vegetation Water Quality Interactions in the Detroit River

3.1 Introduction

Human activities pose a significant hazard to coastal ecosystems and the advantages that these ecosystems provide to society (Poff et al., 2002; Doney et al., 2011). The primary agent behind shifts in the global biogeochemical cycle of nutrients is widely considered to be human activity (Sabater et al., 2018). Multiple case studies have shown that anthropogenic stressors such as agricultural intensity can lead to deterioration of the quality of surface water to the point where it is unfit for drinking, can no longer be used in agriculture in a sustainable manner, and cannot maintain aquatic biodiversity and aquatic ecosystem services (Matthews, 2016; Niu et al., 2019; Harley et al., 2006; Mooney et al., 2009; Weiskopf et al., 2020).

Enrichment of nutrients, namely nitrogen and phosphorus, is a widespread form of pollution with strong negative impacts on many aquatic systems subject to agriculture and/or urban influences (Saunders and Kalf, 2001; Wang et al., 2021). The cumulative effects of nutrient enrichment from point sources (such as sewage effluent) and nonpoint sources (such as nutrient loss from agriculture) increases the concentration of nitrogen and phosphorus in receiving waterbodies, which in turn degrades the structure and function of aquatic ecosystems via eutrophication (Dodds & Smith, 2016; Houser & Richardson, 2010). Eutrophication is characterized by excessive primary production often induced in suspended and benthic algae in response to nutrient amendment (Scheffer, 2004). Previous studies have frequently reported threshold or breakpoint relationships between stream degradation caused by eutrophication and nutrient concentrations (Scheffer, 2004). Furthermore, alternative steady state theory predicts hysteresis in threshold values, such that returning a eutrophic waterbody back to its pre-eutrophic state can necessitate decreasing nutrients below the threshold nutrient concentration that caused the initial state to change (Scheffer, 2004).

Lake Erie is a Laurentian Great Lake that currently occupies the eutrophic state and is subject to frequent late summer harmful algal blooms (Kane et al., 2009). The Great Lakes Water Quality Agreement (GLWQA), signed in 1972 by the governments of Canada and United States, initially focussed on point source nutrient reductions to reduce the prevalence of algal blooms most commonly observed in Lake Erie. Although 1972 GLWQA benchmark phosphorus loads for Lake Erie were achieved by the mid-1980's, the lake began reverting to a regular prevalence of algal blooms post 1990's (Nicholls and Hopkins, 1993; Scavia et al. 2019). One massive algal bloom in Aug of 2014 resulted in the closure of the City of Toledo's drinking water treatment plant, forcing more than 500,000 people to find alternative water sources (Steffen et al., 2017). As a result, Annex 4 of the amended 2012 GLWQA re-focused attention on nutrient – harmful algal bloom management strategies resulting in new phosphorus loading benchmarks being developed for Lake Erie (US EPA, 2015). This new benchmark necessitates a 40% reduction in spring phosphorus load from the 2008 baseline (Scavia et al., 2019). The Detroit River, a large source of phosphorus loads to Lake Erie, was also tasked to reduce its P loads by 40%. Based on recent load assessments conducted in 2019, the Detroit River still requires a further reduction of 567 MTA total phosphorus to meet the revised GLWQA benchmarks (Scavia et al., 2019). However, much of the on-going P-reduction strategies for the Detroit River focus on point and non-point sources of nutrients. There remains little consideration of within-river processes that may retain and sequester nutrients from the water column (Colborne et al. 2019) and whether effective management of such processes including stimulating submerged aquatic macrophyte (SAV) growth could help address phosphorus reduction targets.

Macrophytes play an essential role in the structure and function of river ecosystems, since they regulate the flow of energy, the cycling of nutrients, and sedimentation processes (Ansari et al., 2020; Dubey and Dutta, 2020). The water's depth, hydrology, properties of the substrate, light availability and nutrient concentrations all have a role in determining the number and variety of macrophytes in a body of water (Fares et al., 2020). Extensive submerged aquatic vegetation (SAV) beds actively contribute to increased water transparency by a combination of processes. These include removing nutrients from the water column, release of allelopathic substances that can inhibit the growth of phytoplankton, acting as predator refuges for zooplankton grazers which feed on algae and by promoting sediment stability to reduce sediment resuspension (Scheffer 2001; Girdner et al., 2020; Cho et al., 2022; Clifton et al., 2018; Zhang et al., 2021). Macrophytes also have a significant effect on the daily fluctuations of dissolved oxygen that further promotes diversity of benthic invertebrates important as food for fish and by increasing redox conditions that favour sediment nutrient retention (Nagisetty et al., 2019; Zhang et al., 2019). Owing to the multiple mechanisms by which macrophytes facilitate water transparency described above, Scheffer et al. (2001) described SAV beds as a critical ecosystem component necessary to reinforce a clear water state in shallow waterbodies and a major contributor to ecological resistance towards the transition from a clear to a turbid, algal dominated states.

Within the Detroit River, there are several submerged aquatic vegetation (SAV) beds located along downstream coastal margins and along nearshore deposition zones surrounding islands. The quality of these wetlands varies, such that Canadian SAV beds in the receiving plume of tributaries including Canadian Turkey Creek and River Canard outflow have a compromised Water Quality Index score (WQI; ECCC, 2017). A main objective of this chapter was to evaluate if submerged aquatic vegetation of the Detroit River are capable of reducing nutrient concentrations and enhancing water quality of the system. This was tested by according to the hypothesis: nutrient concentrations in water overlying submerged aquatic macrophyte beds are lower compared to nutrient concentrations upstream of the bed margin. In addition, it is further predicted that healthy wetlands, identified as good quality via a high water quality index score, will have enhanced function with respect to nutrient retention. This prediction was tested according to a second hypothesis: nutrient drawdown over macrophyte beds are higher in wetlands designated as better quality based on WQI scores compared wetlands designated as degraded according to the water quality index.

3.2 Methods

3.2.1. Sample locations and sampling design

Samples were collected across five wetland locations designated as provincially Significant Wetlands, four of which are utilized by Environment and Climate Change

Canada as SAV monitoring sites (ECCC, 2017). The design of sampling stations is outlined as follows. The areal extent of the five wetland beds were initially mapped using the ERCA online land-use classification mapping tool (www.ercamaps.countyofessex.ca) to identify boundaries of Provincially Significant Wetlands in the Detroit River. These boundaries were then contrasted against bathymetry layers used as part of the University of Windsor Delist Areas of Concern GIS database (Grgicak-Mannion, personal communication) and the wetland boundaries were further refined to ensure that designated wetland waters did not exceed 3 m (Peche Island, Grass Island and Detroit River Marsh sites) or 1.5 m (Turkey Creek and River Canard Marshes) depth. For each wetland, five stations were designated at the upstream bed perimeter and another five at the downstream bed perimeter. Owing to limitations in the perimeter length of beds at the upstream and downstream portions of beds, the same bed perimeter coordinates were used at each sampling time point. A grid consisting of cells 100 m x 100 m was then overlayed over each wetland bed area. Each cell was assigned a unique number and a coordinate was generated corresponding to the centre of the cell. Cells that were not fully enclosed by the bed boundaries were excluded from the numbering system. At each sampling time point Microsoft excel @randbetween function was used to randomly select cells (3-6 replicates per time point) to be sampled. Figure 3.1. identifies marsh locations within the Detroit River and provides satellite images of each marsh area coupled with sample points for the upstream and downstream boundaries.

Each wetland was visited over eight sampling events between May to October of 2018. Typically, the downstream marshes (Grass Island, Detroit River Marshes and River Canard) were sampled in one day and the upstream marshes (Peche Island and Turkey

Creek) were sampled the following day. Sampling events took place May 22-23, July 11-12, July 25-26, Aug 8-9, Aug 22-23, Sep 14-15, Sep 28-29, and Oct 21, 2018. During sampling, the boat was anchored to within 60 m of the grid centre coordinate. Two 1L water samples were taken at each sampling event and site with a van Dorn water sampler at 0.5 m below the surface. The sample was stored in a pre-washed, acid-rinsed polyethylene sample bottles and labelled with the date and site information. The samples were placed in a cooler over ice and stored in the refrigerator at the lab until analysis completed within 72 h of sampling. A water quality sonde (RBR-global, Ottawa, Ont., Canada) equipped with temperature, dissolved oxygen, pH, turbidity, and conductivity probes as lowered to the 0.5 m depth to take water quality readings and data were downloaded to excel files on board the vessel after retrieving the sonde.

3.2.2 Analytical Methods

At the laboratory, one water sample was used to determine total suspended solids concentrations (mg/L). The water sample was filtered through a pre-weighed one µm glass fibre filter. The filter was dried in an oven at 90^{o}C overnight and the dry residues were weighed on a 4-digit analytical balance. The other sample was split for total phosphorus (mg/L) and nitrate + nitrite concentration (mg/L) and analysed in the GLIER Organic and Analytical Nutrient Laboratory following SOP 03-002 TDP-TP and SOP 03-003 TON using a Smartchem Discrete Analyzer. The analytical SOP's are described in brief below.

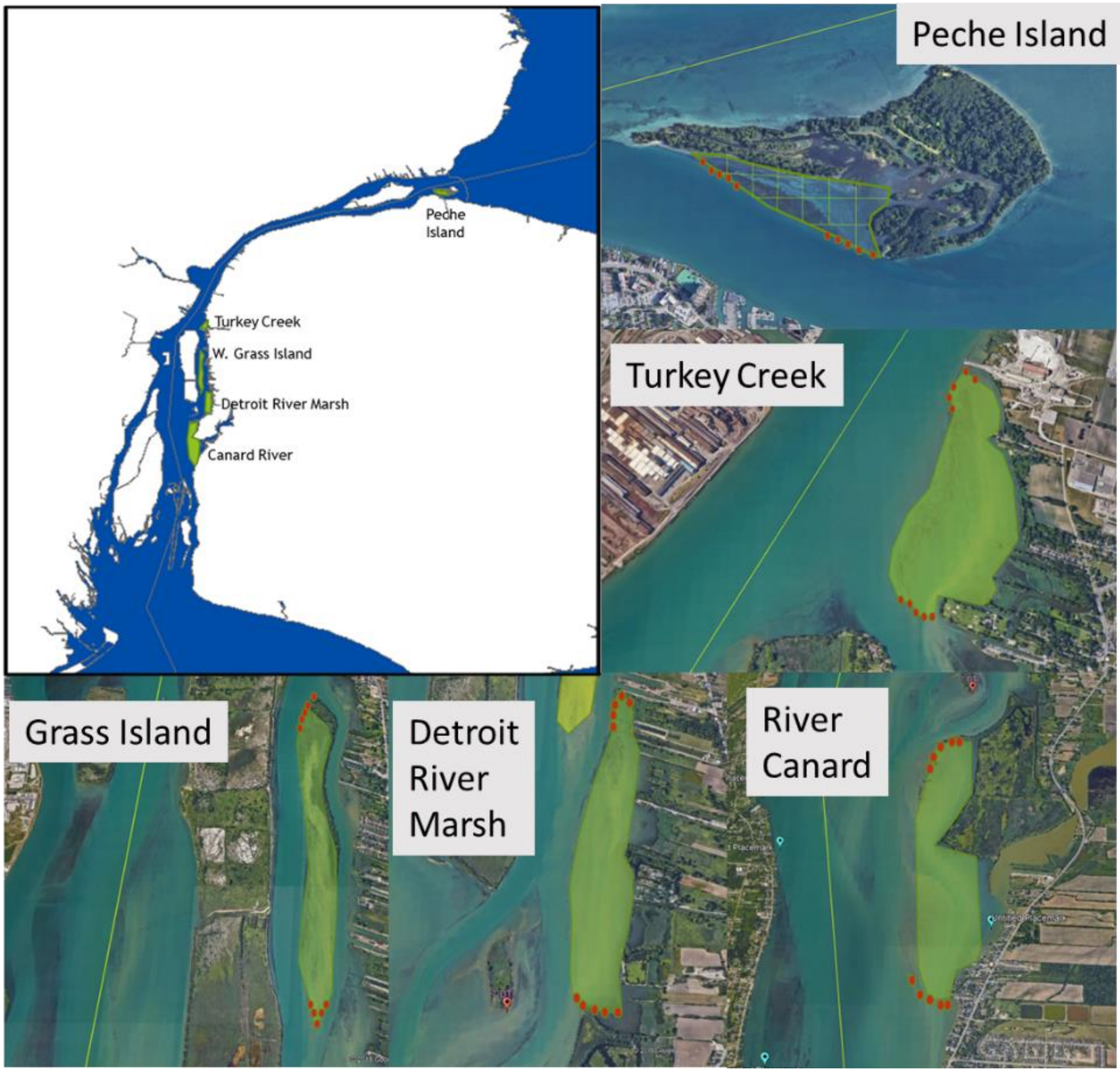

Figure 3.1 Marsh bed location map and satellite images showing extent of each bed and bed margin sites.

For total phosphorus, 50 g of unfiltered sample was added to a 125 mL Erlenmeyer flask along with 1 mL of 11N sulfuric acid and 1 mL of ammonium persulfate digestion solution (40 g $(NH_4)_2S_2O_8$ in 75 mL of purified water). The flask was placed on a hot plate (90ºC) for 2 h until the volume reduced to approximately 10 mL. The condensed sample was then filtered through a 0.45 µm nylon syringe filter and brought to a volume of 50 mL with purified water. The digestion converts inorganic and organic forms of phosphorus in the water sample into a common species of soluble orthophosphate (PO_4^{-3}). The digested sample is then analysed by SMARTCHEM 170 Discrete Analyzer which automates the colorimetric reaction with (PO_4^{-3}). This involves reacting the digesta with ammonium molybdate and antimony potassium tartrate to form a 1,2-phosphorus molybdenum acid complex. Subsequent reaction with ascorbic acid reduces the complex to molybdenum blue that is detected by the instrument's spectrometer at 880 nm. Sample blanks (purified water) and calibration standards are run as part of the first twelve autosampler positions and additional calibration standards are run after every 10the field sample and in the last autosampler position to check for calibration drift. An eight-point calibration curve generated from standards (KH_2PO_4 in purified water with concentrations from 0-1 mg $PO_{4\text{-}3}$/L) is used to convert absorbance signals in blanks and field samples into concentration estimates. Calibration curves must achieve a an R^2 of 0.99 or better as a quality control check and blank TP concentration must be non-detected.

Nitrate + nitrite concentrations, or total oxidized nitrogen (TON), was determined according to GLIER SOP 03-003 NO_3-NO_2 in water. The pH of sample is first checked with a pH meter and adjusted to between 5-9 with concentrated HCl or NaOH if required.

pH adjusted water samples are then filtered through a 0.45 µm nylon syringe filter and added to autosampler vials for loading onto the SMARTCHEM Discrete Analyzer. The automated procedure involves the following steps. The sample is first passed over a copperized cadmium nitrate reductor column which converts any nitrate in the sample into nitrite. Nitrite is then reacted with sulphanilamide followed by reaction with N-(1-naphthl)-ethylenediamine dihydrochloide to form a coloured azo dye that is detected by spectrometer at 550 nm. Similar to the phosphorus method, the absorbance signal is converted into concentration units of mg TON/L comparing the signal from samples to those produced from an 8-point calibration curve ranging in concentration from 0 to 2 mg TON/L. Blanks and calibration standards are loaded onto the first twelve autosampler positions followed by field samples. Calibration standards are interspersed every 10-field sample and in the final autosampler position to check for calibration drift. To achieve quality control checks, the calibration curve must achieve an R^2 better than 0.99 and blanks should be non-detected for TON.

3.2.3 Data Interpreation and Statistical Analysis

The Environment and Climate Change Canada Water Quality Index (WQI) was calculated for individual sample points according to the model reported by Chow-Fraser (2006):

$$WQI = -1.37 \cdot \log Turbidity - 1.58 \cdot \log Conductivity - 1.63 \cdot \log Temperature - 2.37 \cdot \log pH + 9.27 \qquad \text{(Equation 1)}$$

Where turbidity is given in units of NTU, conductivity in µsiemens/cm^2, temperature in ^oC and pH as generated from the water quality sonde. Since samples were collected across the open water season where temperatures varied widely, the wetland-specific mean temperature across all sample time points was substituted into Equation 1 to limit drift in water quality category assignment resulting from seasonal temperature changes. All other parameters in Equation 1 used the site and time-specific measured value. WQI scores were converted into wetland status quality categories according to the scoring matrix reported by Chow-Fraser (2006). Scores in the range of +2 to +3 are classified as excellent, +2 to +1 very good, +1 to 0 good, 0 to -1 moderately degraded, -1 to -2 degraded and -2 to -3 very degraded. Water Quality Index scores were statistically compared between wetlands by non-parametric Kruskal-Wallis test coupled with Conover-Inman's pairwise comparisons using Systat Version 12 statistical software. Non-parametric tests were used because raw and log transformed WQI scores failed normality tests during pre-data analysis screening (Lillefor's test, $p<0.05$).

Principle components analysis (PCA) was performed as a data reduction technique across water quality parameters (temperature, dissolved oxygen, pH, turbidity, conductivity, total suspended solids, total phosphorus, and nitrate + nitrite concentrations). Raw data were first log transformed prior to PCA analysis. Samples with missing or non-detected values for any of the water quality parameters were excluded to generate a complete matrix for all parameters. This reduced the total samples from 574 to 324 samples used in the PCA analysis. The PCA analysis used a correlation matrix. Only PCA axes with eigen values greater than one were considered for interpretation while lesser PCA axes were ignored. Water quality parameters with loadings exceeding

0.6 onto a given PCA axis were considered significantly associated with that axis. The PCA analysis was used to screen co-variate water quality parameters in the sample. Where multiple water quality parameters loaded strongly onto a PCA axis, a single parameter from the group was chosen as representative of spatial trends for analysis by univariate statistics.

Nutrient stoichiometric ratios were calculated by converting Nitrate + Nitrate expressed on a mass basis (mg/L) to total nitrogen in molar equivalents according to:

$$N_{\left(\frac{Moles}{L}\right)} = C_{NO3\left(\frac{mg}{L}\right)} \cdot \frac{0.2259_{\left(\frac{N}{NO3}\right)}}{1000_{\left(\frac{mg}{g}\right)} \cdot 14.007_{\left(\frac{g}{mol}\right)}}$$

The constant 0.2259 refers to mass fraction of Nitrogen present in Nitrate (NO_3-). The conversion assumes that nitrate dominates the nitrate + nitrite concentration measurement and will slightly underestimate total Nitrogen dependent on the fraction of nitrite present in the sample. Total Phosphorus in phosphate equivalents were converted to P-molar equivalents according to:

$$P_{\left(\frac{Moles}{L}\right)} = C_{PO4\left(\frac{mg}{L}\right)} \cdot \frac{0.3261_{\left(\frac{P}{PO4}\right)}}{1000_{\left(\frac{mg}{g}\right)} \cdot 30.974_{\left(\frac{g}{mol}\right)}}$$

The constant 0.3261 refers to the mass fraction of phosphorus present in inorganic phosphate (PO_4^{3-}). Stoichiometric ratios of N:P were derived by dividing the molar equivalent of Nitrogen measured in water samples by the molar equivalent of Phosphorus.

3.3 Results

3.3.1 Water Quality Index (WQI)

A total of 458 data points on water quality parameters were taken across sample locations and time points (Figure 3.1). Table 3.1 summarizes seasonal mean water quality index score calculations at the five monitored wetlands along with summary statistics for equivalent coastal monitoring stations identified in Chapter 2 and Environment and Climate Change Canada's Detroit River BUI Assessment Report (ECCC, 2017) generated for the 2008-2016 time period.

There were differences among WQI scores for individual wetland areas across years. However, the wetland qualitative descriptor based on WQI score categories were similar for 3/4 wetlands monitored across studies. Peche Island was categorized as 'good quality' in all years, Detroit River Marshes (DRM) and Turkey Creek were classified as moderately degraded. River Canard ranged from Moderately Degraded (2018, 2019) to very degraded (2008-2016). Grass Island stations were monitored only in 2017 and 2018, but both studies categorized this wetland as moderately degraded.

Statistical comparisons of WQI scores between studies were not performed due to differences in the sampling design and number and position of sample locations allocated to each wetland between different studies. However, the 2018 survey generated notably better WQI scores for all wetland locations except for Peche Island compared to the 2017 and 2008-2016 ECCC studies. For example, in the 2018 survey, the two tributary influenced wetlands (Turkey Creek and River Canard) had WQI scores that were commensurate with downstream Detroit River Marsh and west of Grass Island, yet in

Table 3.1. Water Quality Index (mean standard error, count) across the monitored wetlands from the present study and previous research.

Wetland	2018	2017	2008-2016 Mean Across Year ECCC BUI Assessment
Peche Island	0.20±0.07, n=77 Good	0.28±0.13, n=24 Good	0.36±0.19, n=7 Good
Turkey Creek	-0.18±0.06, n=83 Moderately Degraded	-0.76±0.15, n=21 Moderately Degraded	-0.77±0.16, n=7 Moderately Degraded
Grass Island	-0.14±0.022, n=100 Moderately Degraded	-0.58±0.20, n=8 Moderately Degraded	Not Available
Detroit River Marshes	-0.14±0.04, n=100 Moderately Degraded	-0.28±0.22, n=21 Moderately Degraded	-0.16±0.22, n=5 Moderately Degraded
River Canard	-0.16±0.06, n=86 Moderately Degraded	-0.65±0.08, n=33 Moderately Degraded	-1.80±0.07, n=7 Very Degraded

2017 and 2008-2016 these designated wetlands achieved the lowest values of WQI leading ECCC to conclude that the tributary influenced SAV beds were stressed from a water quality perspective (ECCC, 2017).

When data were restricted to the 2018 survey results, Kruskal-Wallis Test indicated highly significant differences ($p<0.001$) in the seasonally averaged WQI scores between monitored wetland areas. Peche Island had a WQI score that was significantly ($P>0.001$; Conover-Inman's pairwise comparisons) higher than all other sites. The remaining stations were statistically similar to one another ($p>0.05$; Conover Inman's tests) except for Turkey Creek which had a significantly lower score than River Canard ($p<0.05$; Conover Inman's Test). Despite the lowest 2018 WQI score being observed in Turkey Creek, this tributary did not differ from Detroit River Marshes nor Grass Island wetland areas. Thus, based on WQI, only the Peche Island wetland is considered different with respect to the water quality index from the other monitored wetlands.

3.3.2 Intervariable correlations between measured water quality parameters.

There were 459 measurements of turbidity, 550 detectable measures of total suspended solids, 454 samples with detected total phosphorus and 572 samples with detected nitrate/nitrate concentrations across the 2018 sample data set. After censoring missing data, a complete matrix of 323 observations was generated comprised of detectable readings for temperature, dissolved oxygen, pH, specific conductivity, turbidity, total suspended solids, nitrate/nitrites, and total phosphorus. The PCA analysis generated two component axes with eigenvalues greater than one that cumulatively explained 62.4% of the variance of the data (Table 3.2). The first PCA axis was strongly loaded by temperature (-0.94), specific conductivity (0.85), nitrate + nitrites (0.82), turbidity (0.81) and total suspended solids (0.750). The second axis showed strong loadings only for total phosphorus (loading coefficient = 0.83). Dissolved oxygen and pH did not exhibit strong loadings to any of the significant PCA axes.

Based on the PCA results, total phosphorus was found to be the only parameter that loaded onto the second PCA axis and therefore this parameter was not considered a co-variate with other measured water quality parameters. As a result, univariate tests were used to deduce spatial and temporal patterns of this parameter separately. In contrast, intervariable correlations between nitrite + nitrates, total suspended solids, specific conductivity, turbidity and temperature were observed indicating that it would be inappropriate to perform univariate tests on each of these parameters independently. To limit the problem of covariance of PCA axis 1 loaded water quality parameters, only nitrate + nitrite concentrations were used to deduce spatial and temporal trends as a representative of how other parameters in this group behave.

3.3.3. Spatial patterns of total phosphorus concentrations within and between wetland sites

Across the 454 detectable total phosphorus concentration measurements, the median (5-95 percentile) of river wide TP concentration was 0.011 (0.002 – 0.045) mg PO_4^{-3}/L. Given the PCA results from section 3.3.2, univariate tests were used to examine differences in total phosphorus concentrations at upstream, downstream bed margins and overlying bed sites. When data were combined across wetlands there were no significant differences ($p>0.5$; Kruskal-Wallis Test Statistics 0.571; $df=2$, $n=454$ samples) between

Table 3.2 Principal component loadings of water quality variables across the combined data set.

Parameter	Loading onto PCA1	Loading onto PCA2
Temperature	**-0.953**	-0.010
Dissolved Oxygen	0.382	0.308
pH	-0.123	0.097
Turbidity	0.544	0.410
Total Suspended Solids	**0.617**	0.502
Specific Conductivity	**0.868**	-0.352
Total Phosphorus	-0.080	**0.700**
Nitrate/Nitrite	**0.847**	-0.338

** loadings in bold are meet the criteria of being strongly associated with a given PCA axis.

total phosphorus concentrations across bed margins compared to water samples taken over the beds.

The analysis was also repeated for each wetland separately. Similar observations showing non-significant differences in the seasonally median total phosphorus concentrations over SAV bed stations versus their respective bed margins were observed for each of the tested wetlands: Peche Island ($p>0.1$; Kruskall-Wallis Test, n=64 samples), Turkey Creek (($p>0.2$; Kruskall-Wallis Test, n=99 samples), Grass Island ($p>0.9$; Kruskall-Wallis Test, n=98 samples), Detroit River Marshes ($p>0.8$; Kruskall-Wallis, n=100 samples) and River Canard ($p>0.6$; Kruskall-Wallis Test, n=93 samples). Figure 3.1 provides box and whisker plots of total phosphorus concentrations at upstream margins, downstream bed margins and bed stations for each of the monitored wetlands. Although patterns were non-significant across statistical tests, it is noted that the overall pattern at Peche Island and Turkey Creek was broadly consistent with expectations but not at other sites.

Between wetland differences in total phosphorus concentrations were subsequently examined to identify potential phosphorus sources within the Detroit River based on geographic location. For this analysis, sample sites at bed margins and over the SAV bed were combined given the lack of difference in nutrient concentrations between bed margins and beds themselves. There were significant differences ($p<0.05$; Kruskall-Wallis Test Statistic = 11.273; df = 4; n=454 measurements) in total phosphorus concentrations across the wetland locations. Figure 3.2 presents a box and whisker plots comparing total phosphorus concentration distributions across wetland locations. The most upstream wetland, Peche Island, had the lowest, but also most variable, median total

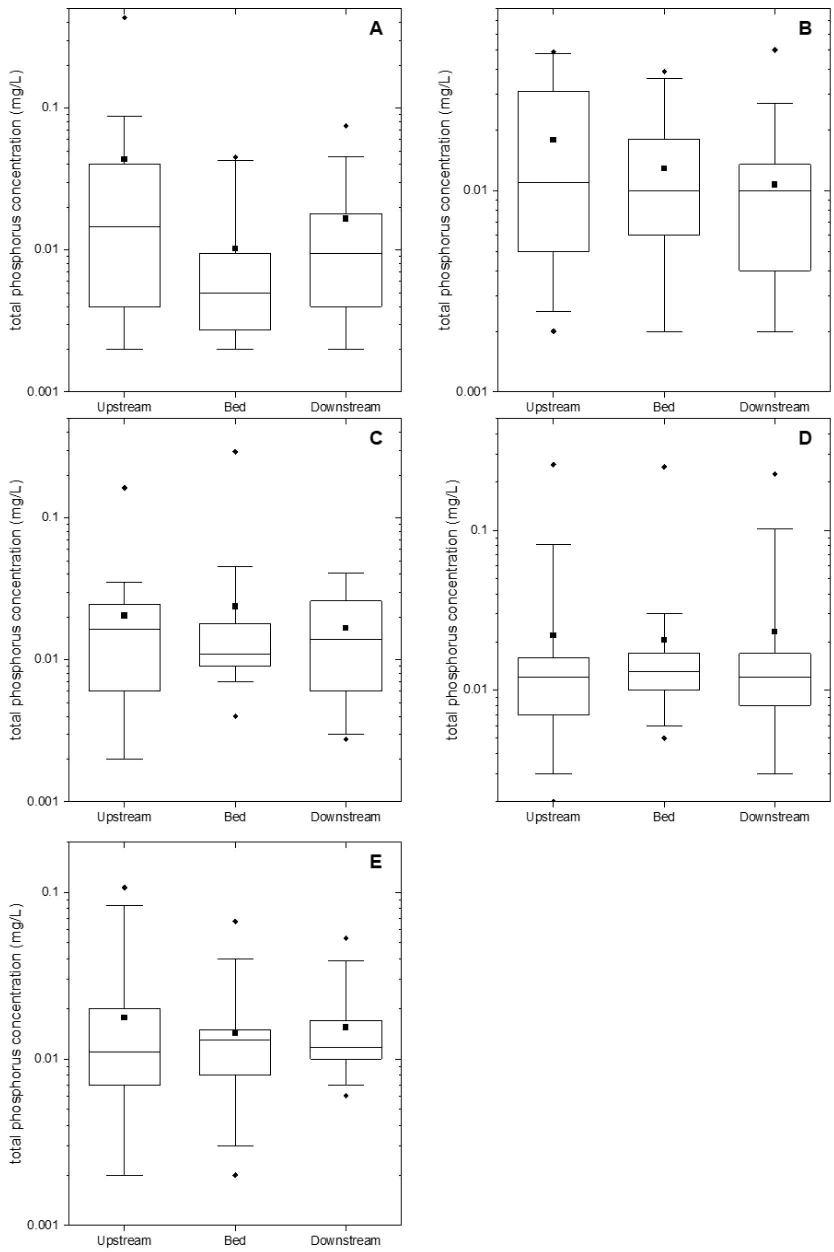

Figure 3.1. Total phosphorus concentrations in water samples at upstream margin, overlying SAV bed and downstream of the wetland margin. Box denotes median and 25-75 percentiles, whiskers are 5-95 percentiles, square is the mean and diamonds are outliers. Graphics A = Peche Island, B = Turkey Creek, C = Grass Island, D = Detroit River Marshes and E = River Canard.

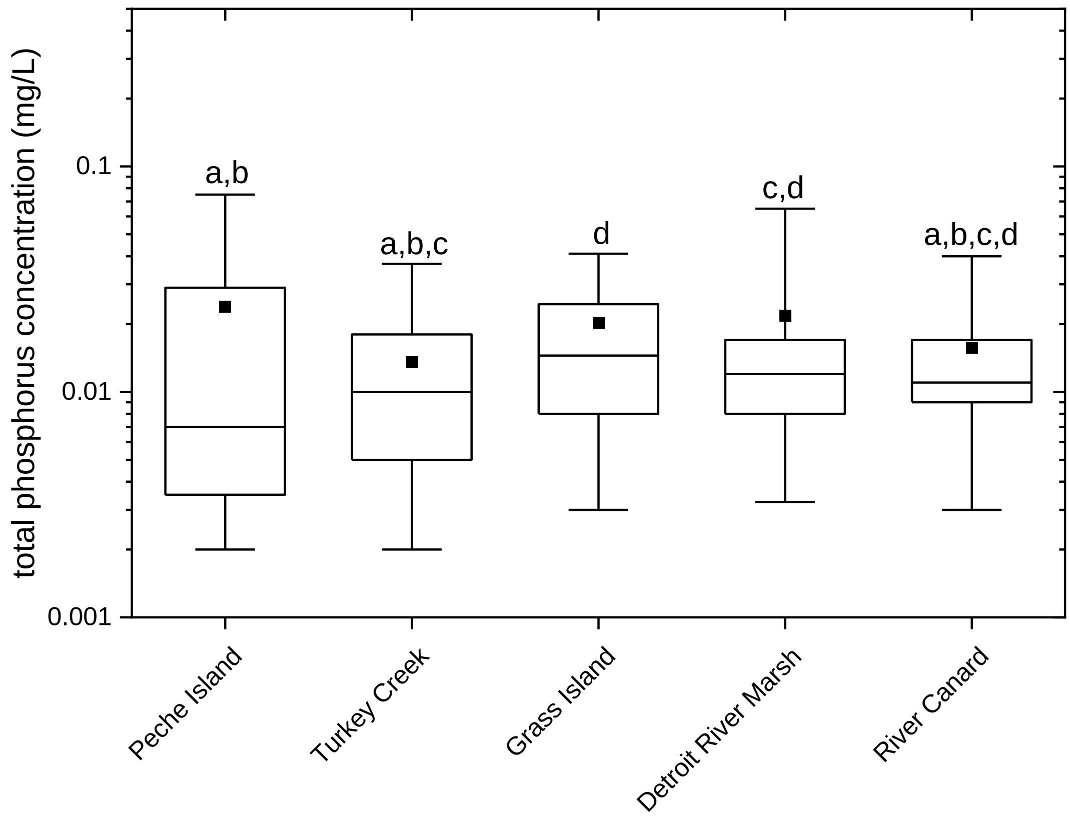

Figure 3.2. Total phosphorus concentrations across Detroit River wetland locations. Box denotes median and 25-75 percentiles, whiskers are 5-95 percentiles, square is the mean. Boxes with different letters are significantly different from one another ($p<0.05$; Conover Pairwise comparison test).

phosphorus levels that were statistically comparable to the two tributary influenced wetlands Turkey Creek and River Canard. Grass Island had the highest median phosphorus concentration that was statistically similar to the Detroit River Marsh and River Canard wetlands.

3.3.4 Temporal patterns of total phosphorus at individual wetland sites

Data were analysed for temporal trends of total Phosphorus at each wetland area separately. Figure 3.3 presents box and whisker plots of total phosphorus concentrations across sample dates for the five wetlands. At all locations, there were highly significant differences ($p<0.001$ Kruskall Wallis test completed for each wetland independently) in total phosphorus concentration between sample dates. Turkey Creek Marshes showed a common temporal pattern with lowest phosphorus concentration measured in early July and highest concentrations measured on Aug 9 followed by Oct 11. The temporal pattern at Peche Island was obscured by a lack of detection of total phosphorus during May 21 and July 12 sampling dates, but this site also exhibited an increase in phosphorus concentration at the Oct 21 sampling. River Canard had the most consistent phosphorus concentration with time.

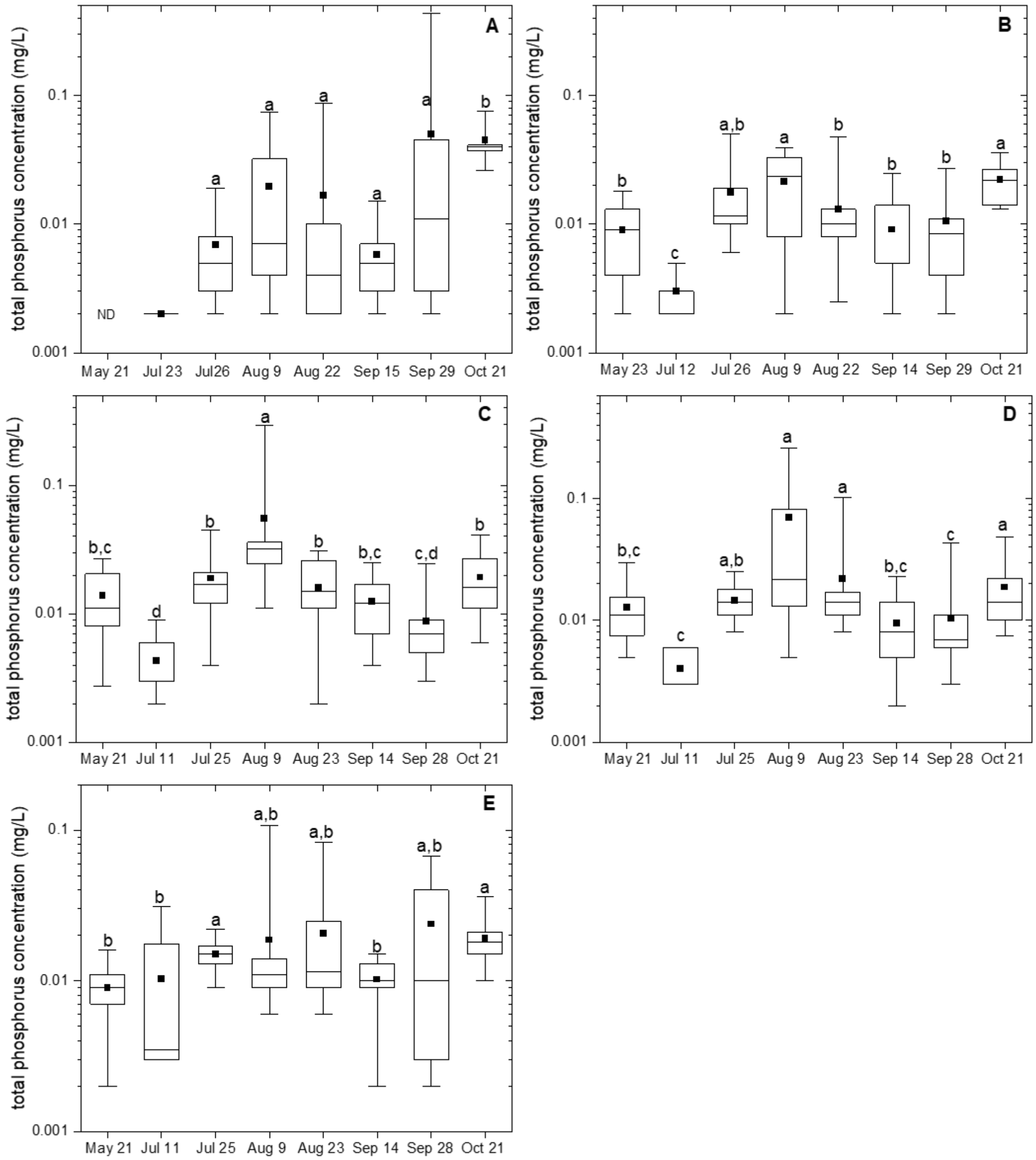

Figure 3.3. Total phosphorus concentrations in water samples from each wetland across different sample time points. Box denotes median and 25-75 percentiles, whiskers are 5-95 percentiles, square is the mean concentration. Boxes with different letters are significantly different ($p<0.05$; Conover-Inman's pairwise test). Graphics A = Peche Island, B = Turkey Creek, C = Grass Island, D = Detroit River Marshes and E = River Canard.Grass Island and Detroit River

3.3.5. Spatial patterns of nitrate + nitrite concentrations within and between wetland sites

There were 572 detectable measurements of nitrate + nitrite concentrations generated by the study with a river wide median (5-95 percentile) concentration of 0.229 (0.126 – 0.972) mg TON/L. There were non-significant differences ($p>0.05$; Kruskal-Wallis; test statistic = 5.435; df = 2; n = 572 samples) in nitrate+nitrites between bed perimeters and bed sites across the combined dataset. However, the above test statistic approached significance with an absolute p-value of 0.07. Sample stations overlying bed sites tended to be lower (non-significantly), intermediate at the downstream perimeter and highest at the upstream site consistent with expectations of a nitrogen drawdown arising from macrophyte beds.

Spatial analyses were subsequently re-evaluated at each wetland individually. Most of the wetlands demonstrated non-significant differences (p ranging from >0.1 to > 0.8; Kruskal-Wallis tests) for nitrate+nitrate concentrations between the perimeters and overlying bed locations. The exception was Detroit River Marshes where there was a significant difference ($p<0.05$; Kruskal-Wallis; test statistic = 8.929; df = 2; n = 105 samples). For this wetland, nitrate + nitrate concentrations were significantly ($p<0.05$; Conover-Inman's tests) elevated at the upstream perimeter compared to both bed sites and the downstream perimeter. Figure 3.4 presents spatial patterns in nitrate + nitrite sites separated by perimeters and water samples overlying the beds. Given the differences observed at Detroit River Marshes, between wetland comparisons for nitrate + nitrates were restricted to water samples taken over SAV bed locations and the perimeter data were excluded. There were significant differences ($p<0.05$; Kruskal Wallis Test Statistic

= 12.319; d.f. = 4; n =191 samples) among nitrate+nitrate concentrations between the wetland locations. The highest median nitrate+nitrite concentration was observed at Turkey Creek and concentrations were statistically elevated ($p<0.05$; Conover-Inman's tests) relative to Grass Island, Peche Island and Detroit River Marshes but similar to River Canard bed sites. There were no other significant differences between the other wetland sites examined (Figure 3.5).

3.3.6 Temporal patterns of nitrate + nitrite concentrations at individual wetland sites

Figure 3.5 presents box and whisker plots of nitrate + nitrite concentrations across sample dates for the 5 wetlands. All wetlands exhibited spikes in nitrate + nitrate concentrations during May 23 and Oct 21 sample dates consistent with the negative correlation between nitrogen concentration and temperature described in section 3.3.2. Except for Peche Island, all other wetland locations demonstrated a nitrogen minimum on Aug 22nd with intermediate nitrogen concentrations at the other sample time points. In contrast, Peche Island did not show the Aug 22 minima and temporal trends were dampened at this site compared to the others. River Canard also showed a somewhat dampened temporal pattern of nitrogen with an overall consistency to the other locations.

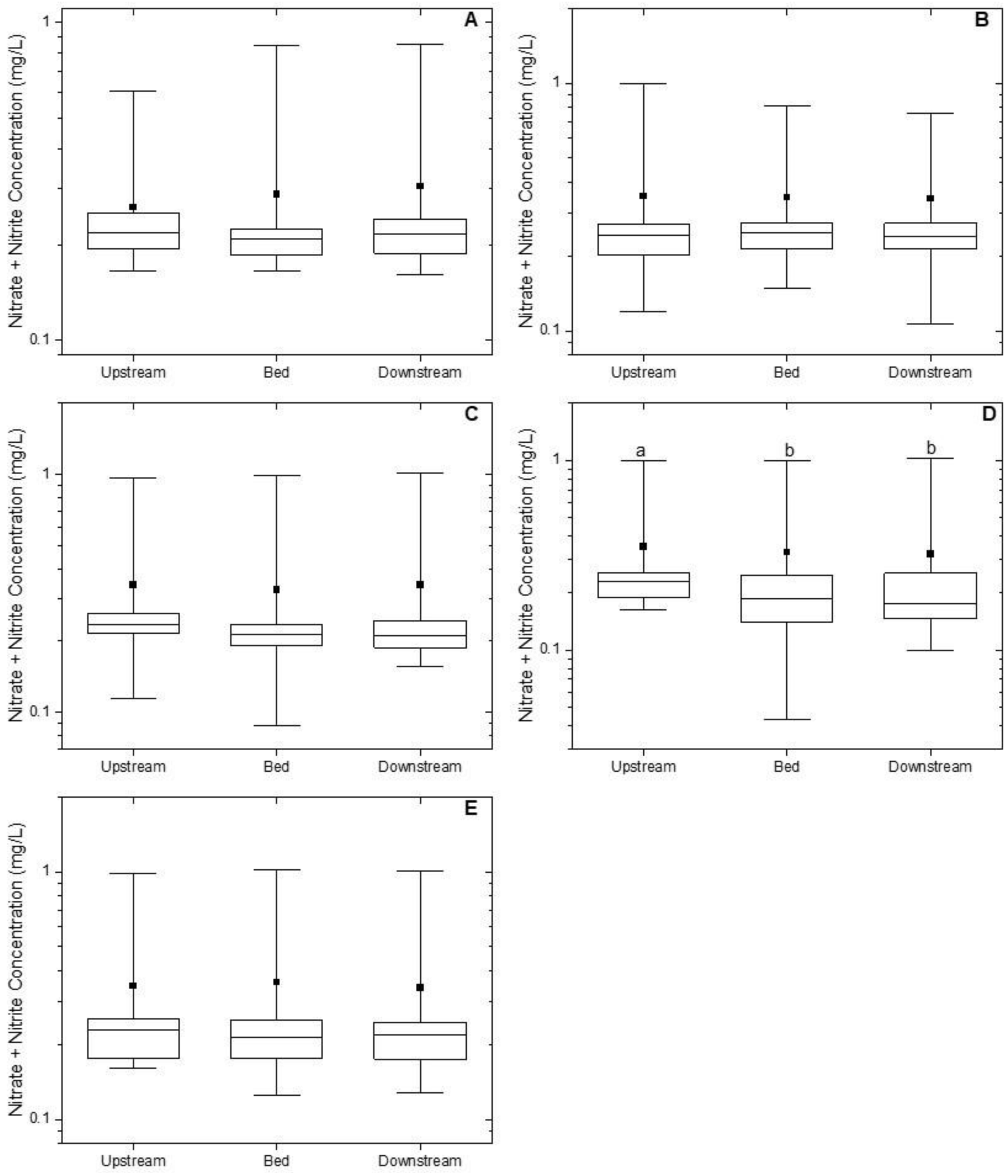

Figure 3.4. Nitrate + nitrite concentrations in water samples at upstream margin, overlying SAV bed and downstream of the wetland margin. Boxes denote median and 25-75 percentiles, whiskers are 5-95 percentiles, square is the mean and diamonds are outliers. Boxes with different letters are significantly different ($p<0.05$; Conover-Inman's test). Graphics A = Peche Island, B = Turkey Creek, C = Grass Island, D = Detroit River Marshes and E = River Canard.

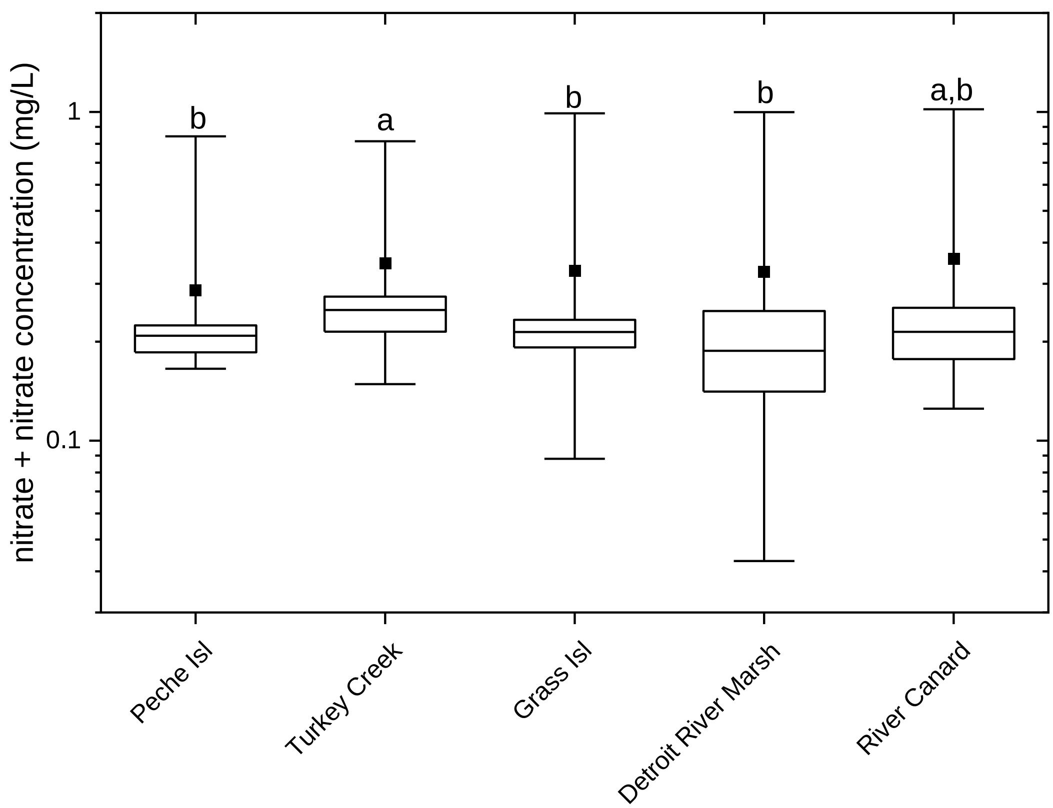

Figure 3.5. Nitrate + nitrite concentrations across Detroit River wetland locations. Box denotes median and 25-75 percentiles, whiskers are 5-95 percentiles, square is the mean. Boxes with different letters are significantly different from one another ($p<0.05$; Conover Pairwise comparison test).

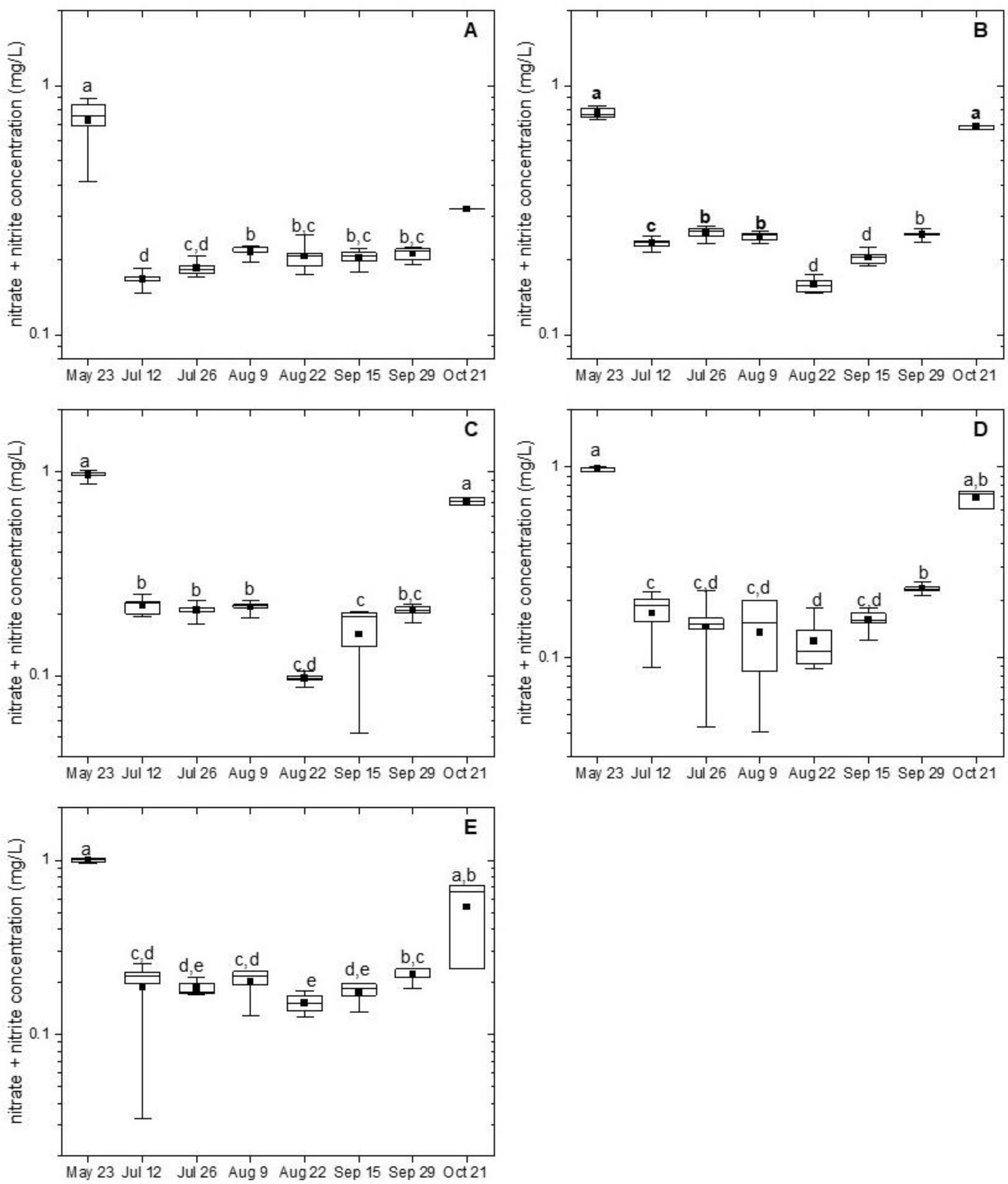

Figure 3.6. Nitrate + nitrite concentrations in water samples from each wetland across different sample time points. Box denotes median and 25-75 percentiles, whiskers are 5-95 percentiles, square is the mean concentration. Boxes with different letters are significantly different (p<0.05; Conover-Inman’s pairwise evaluate). Graphics A = Peche Island, B = Turkey Creek, C = Grass Island, D = Detroit River Marshes and E = River Canard.

3.3.7. Stoichiometric ratios of nitrogen and phosphorus

Nutrient stoichiometry was be used to evaluate nutrient limitations by comparing N:P ratios relative to the Redfield Ratio (N:P = 16:1). Across the 453 measurements where N (as nitrate plus nitrite) and P (as total P-phosphate) were detected in the same water samples, the median (5 – 95 percentile) N:P molar ratio was 33.8 (7.1 – 187.0). There were 100 (22.1%) measurements) where N:P ratios were less than fifteen and 335 (74.0%) observations with ratios greater than seventeen indicating that phosphorus limiting conditions predominate at most sites in the Detroit River.

When comparing proportions of N:P ratios > 17 (P-limiting conditions) across wetlands, the two tributary impacted sites had the largest proportion of ratios exceeding 17 at 81.8 and 79.6% for Turkey Creek and River Canard, respectively. The other wetlands had between 63.2-72.0% of their N:P ratios greater than 17. Figure 3.7 presents temporal trends of N:P ratios in water at each wetland location. Temporal trends at Peche Island were obscured due to lack of detection of total phosphorus during May and the earliest July sampling points. However, given the elevated nitrate + nitrite concentration at Peche in May (Figure 3.5), it can be inferred that the N:P ratio would have been in the high category for water samples at this location in the spring. Peche Island did not show a distinct summer minimum in N:P ratios as were evident at other wetland locations. N:P ratios at the remaining sites were consistent in their temporal pattern. N:P ratios were typically minimized at the July 29 or Aug 12 sampling points corresponding with lower

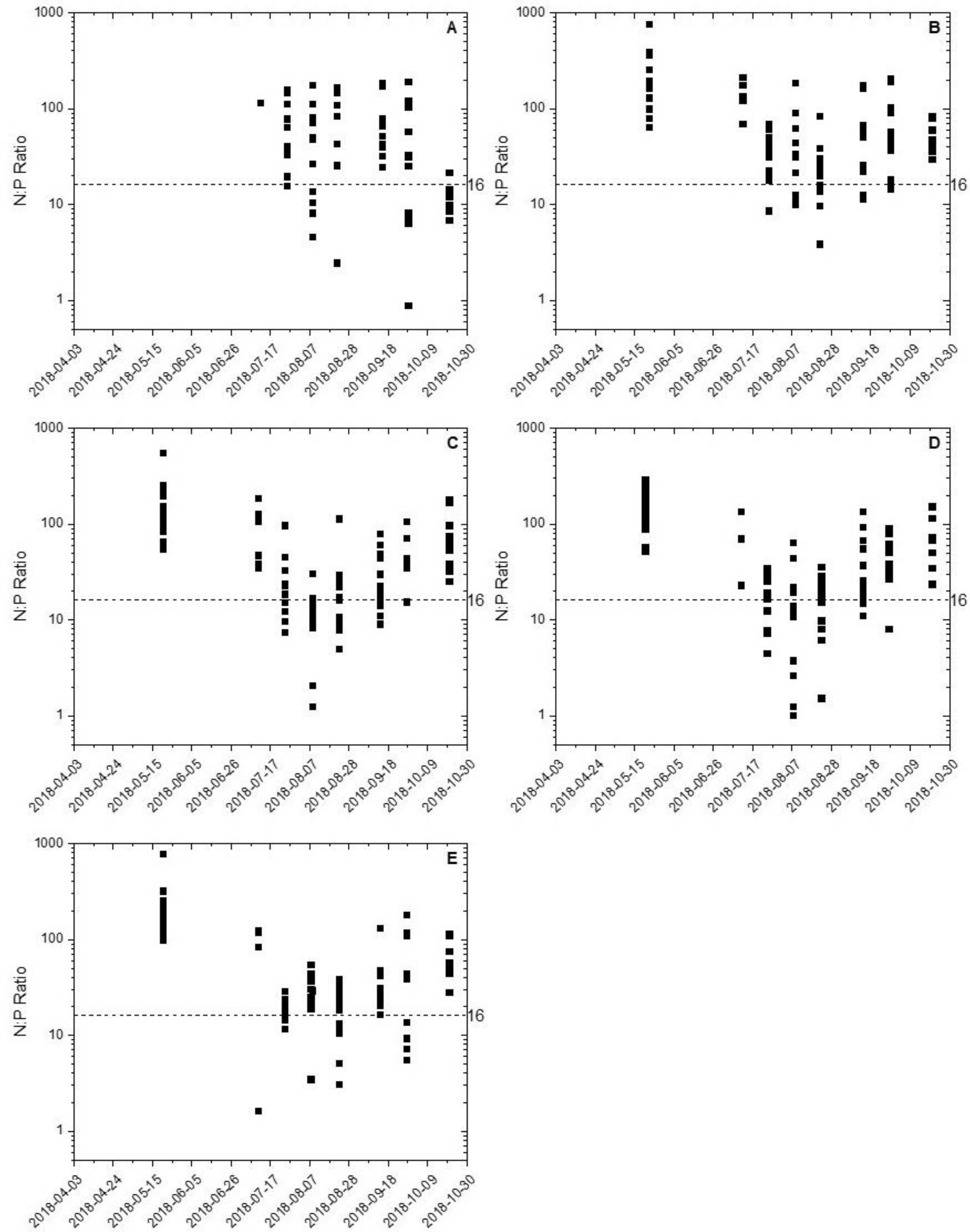

Figure 3.7 N:P ratios across sample time points at Detroit River wetland sites. Horizontal line presents the N:P ratio value of 16 indicative of water nutrient availability equivalent to Redfield Ratio. Graphics A = Peche Island, B = Turkey Creek, C = Grass Island, D = Detroit River Marsh and E = River Canard.

oxidized nitrogen concentrations (Fig 3.5) and generally variable total phosphorus concentrations (Figure 3.1). At Grass Island and Detroit River Marsh, a majority of wetland N:P ratios were <17 between July and mid-August. However, the summer minima in N:P ratio was less evident at Turkey Creek, River Canard and Peche Island.

3.4 Discussion

The river wide TP concentration of 0.011 (0.002 – 0.045) mg/L measured in the present study was similar to the median TP concentrations of 0.01 mg/L and 0.015 mg/L reported by Burnisten et al. (2018) for downstream mid-river and Amherstburg Channel transects collected in 2014 and 2015 but lower than median TP concentrations measured along the U.S. Trenton Channel (0.02 mg/L). Colborne et al. (2019) reported a 2016 mean±standard deviation (range) dissolved phosphate concentration (expected to be lower than TP) across 23 sampling stations of the Detroit River equal to 0.0081±0.0024 mg/L (0.0049 – 0.0155 mg/L), that was consistent with the present TP findings. The difference in phosphorus concentrations along the US and Canadian shorelines is well recognized in Detroit River phosphorus load models. The Great Lakes Water Authority WWTP which empties into the middle reach along the U.S. side of the Detroit River discharges effluents with an average TP concentration of 0.38 mg/L (Scavia et al., 2019) and is the major point source contributor to Detroit River phosphorus loads from within the river's watershed (Hu et al., 2019). Loadings from City of Windsor's two wastewater treatment plants are considered minor despite Windsor being the third largest urban area in the St. Clair – Detroit River watershed. The City of Windsor was estimated to contribute less than 2% of the Detroit River phosphorus load (Hu et al., 2019). In their

SAV monitoring program, ECCC reported mean 2016 TP concentrations of 0.026, 0.040, 0.027 and 0.156 mg/L for Peche Island, Turkey Creek, Detroit River Marshes, and River Canard, respectively (ECCC, 2017). Except for River Canard, the ranges are equivalent to the present study that ranged from 0.014 to 0.024 mg/L. However, our mean TP concentration at River Canard was among the lowest at 0.016 mg/L and an order of magnitude less than ECCC's reporting. This difference is related to the different sample design and positioning of water samples within wetland beds described in more detailed below. In addition, total phosphorus can be highly influenced by inclusion of suspended particulate matter at any given sampling event.

Burniston et al. (2018) noted more pronounced spatial variability in nitrogen concentrations within the Detroit River compared to phosphorus. Nitrate + Nitrate concentrations were highest at near shoreline sampling locations of the Amherstburg transect in 2014-2015 and more variable across the Amherstburg transect compared to variation observed at the mid-river and Trenton Channel downstream transects. However, the above authors did not report actual concentrations of nitrate + nitrate but reported nitrogen loads. Colborne et al. (2019) reported mean±standard deviation (range) nitrate concentration of 1.26±034 mg NO_{3-}/L (0.9-2.30 mg NO_3^-/L) across 23 Detroit River sample locations in 2016 that were higher compared to the present results (median of 0.229 mg TON/L and 5-95 percentiles of 0.126 to 0.972 mg TON/L). However, these differences may be due to different analytical techniques given that the methods of Colborne et al. were specific to nitrate and optimized to detect nitrogen isotopes in the dissolved nitrogen phase. Colborne et al. (2019) described Canadian nitrate patterns as being heightened in the upstream nearshore waters and declining along the river length in

Canadian stations. Similar spatial pattern for nitrate + nitrates were not observed here. The upstream Peche Island wetland is located offshore contrasting against the nearshore upstream station used by Colborne which would be more likely affected by the City of Windsor's Little River wastewater treatment plant. However, the present research did implicate the two tributaries as nitrogen sources, consistent with Colborne's assessment of Little River, an upstream Detroit River tributary.

Similar to the present research, Colborne et al. (2019) reported that TP and Nitrate concentrations were not correlated to one another. The above authors found that nitrate was correlated to dissolved calcium, chloride, potassium, magnesium, and sodium ions which is consistent with the present observations showing correlation between nitrate+nitrite and specific conductivity, a measure of total dissolved salts. Colborne et al. (2019) concluded that nitrogen and phosphorus had different sources from one another in the Detroit River and that nitrogen isotopes suggest a combination of agricultural fertilizer and wastewater effluent sources. ECCC's SAV wetland study (ECCC 2017) reported 2016 nitrate + nitrate concentrations of 0.133, 0.110, 0.021 and 0.006 mg/L at Peche Island, Turkey Creek, Detroit River Marshes, and River Canard showing a considerable difference between nitrogen in the upper and middle reach wetlands compared to the lower wetlands. However, this pattern was not evidence in other monitoring years (2008-2015) and the magnitude of nitrogen varied widely between the monitored years across ECCC's study. For example, in 2015 nitrate+nitrite concentrations across the four wetlands were 0.354, 0.592, 0.195 and 1.610 mg/L and in the present 2018 study mean values were f 0.284, 0.346, 0.332 and 0.348 mg TON/L. Thus, year to year variability in nitrate+nitrate concentrations are quite high as are within year variation described in Figure 3.7 which exceed well over an order of magnitude in difference.

Considerable differences were observed between the present research wetland WQI scores and to a lesser extent the wetland quality categories than those reported by ECCC (ECCC, 2017). The differences in WQI scores between surveys are attributed to differences in sampling designs. In the present study, wetland areas were defined as continuous beds within distinct regions of Canadian waters of the Detroit River. Wetland bed maps were generated based on polygons defined by ERCA's on-line habitat mapping tool coupled with depth limitations derived from Chapter 2 and distributed samples randomly across the entire bed. In contrast, the ECCC surveys perform sampling at a smaller subset of total wetland bed area. The exception was Peche Island where most of the wetland is constrained to the southern portion of the Island. Because of its smaller size, there would be greater overlap between sampling stations from the present research and ECCC's program. In contrast, the ECCC surveys of Turkey Creek and River Canard were restricted to locations that either fell in the lower portion/outfall of the tributary itself or were found within the direct confluence of the tributary/Detroit River mixing zone. Yet the SAV bed boundaries in this area are much broader than the tributary plume itself. Given our random sampling protocol, some stations would be distributed outside of the tributary plumes whereas all ECCC sampling stations were designed to be located directly within the plume. Therefore, ECCC's survey generates a 'worst case' estimate of tributary plume influenced conditions over a portion of the wetland bed whereas the present study provides a more holistic assessment of the overall wetland water quality. Here, we show that the two tributary influenced wetlands do not substantially differ from other Detroit River wetland sites in their overall WQI score or quality rating. The only exception is Peche Island which both the present research and ECCC's interpretation designated as better quality.

A main objective of this research was to determine if Detroit River wetlands were causing improvements to water quality parameters, nutrient concentrations, as a result of nutrient drawdown by macrophytes and their associated periphyton and biofilm communities. For phosphorus, there were no statistical differences in total phosphorus concentrations at bed margins compared to waters overlying the beds at any of the wetlands examined. However, general patterns of total phosphorus concentrations at Peche Island and Turkey Creek were consistent with an expected draw down pattern, albeit non-significant. Phosphorus uptake by SAV occurs from both sediments and water but in general most of the phosphorus taken up directly by macrophytes occurs from the sediment (Cargnan and Kalff, 1980). However, wetlands indirectly can retain P by SAV supported biofilms and epiphytes which can absorb P directly from water and by augmenting particulate settling coupled with increasing surface sediment oxygenation that favours sediment retention of phosphates (Dierberg et al., 2002).

In their systematic review of wetland removal of nitrogen and phosphorus utilizing 203 North American and European case studies, Land et al. (2016) concluded on average natural and restored wetlands significantly reduce transport of TN and TP from treated wastewater, urban and agricultural runoff. However, there was high heterogeneity in computed nutrient removal efficiencies across studies and wetland sites distributed throughout Europe and North America. For total phosphorus, 29 of 51 wetlands showed significant nutrient removal, thirteen were non-significant and nine studies showed the wetland to be a source of net phosphorus release. For total Nitrogen, 21/38 studies showed significant removal rates of nitrogen by wetlands and seventeen cases were non-significant. Nitrogen removal efficiency was strongly related to hydraulic loading rate and temperature while phosphorus removal was driven by inlet total phosphorus concentration, hydraulic loading rate, wetland area and temperature. Many of the case studies reviewed by Land et al. (2016) pertained to wetlands constructed in much smaller streams compared to the Detroit River. In addition, most of the wetland studies were examined soon after they were constructed and/or restored compared to established natural wetlands evaluated in the present study. The Detroit River has much higher flows compared to most small tributaries studied by Land et al. (2016) and its wetland beds are discontinuous across the river width being confined to nearshore regions and the margins of open water islands. The high flow rates of this system therefore make detection of absorbed nutrients difficult given the scale of phosphorus assimilation efficiencies presented in the literature. Furthermore, low phosphorus concentrations, as observed in the Detroit River, correspond to reduced wetland phosphorus removal efficiencies (Land et al., 2016). Overall, the evidence indicates that the initial hypothesis that Detroit River wetlands are effective at improving water quality with respective to phosphorus is considered falsified. Therefore, additional use of wetland restoration in the Detroit River as a P-load mitigation tool is not likely to have strong impacts on water quality and phosphorus loadings to Lake Erie.

There was some support for Detroit River wetlands having a positive effect on nitrogen loss. Nitrate + Nitrite concentrations showed a significant decrease in concentration from the upstream bed margin compared to bed sites and the downstream bed margins at 1/5 wetlands - Detroit River Marshes. Although non-significant, similar overall spatial patterns for nitrate+nitrite decline from the upstream bed margin were also observed at Peche, Grass Island and River Canard sites. Furthermore, shifts in nitrate+nitrate concentrations and water column N:P ratios over some wetlands (Grass Island and Detroit River Marshes in particular) were negatively correlated with water temperature and minimized during late summer consistent with Land et al.'s (2016) models for wetland nitrogen removal efficiency. For Grass Island and Detroit River Marshes, the summer minimums in nitrate+nitrites potentially contributed to nitrogen limiting conditions for phytoplankton helping to reinforce antagonistic feedback loops between macrophyte presence and phytoplankton production. However, some caution in the interpretation of N:P ratios from the present research is warranted. Total nitrogen was estimated from oxidized nitrogen (measured concentration on NO_3 and NO_2) and assuming that NO_3 dominated these two nitrogen species. Other forms of bioavailable nitrogen in water may have not been included in the analysis leading to underestimates in N:P ratios. Similarly, samples where nitrite concentrations were relatively higher would cause slight underestimates of the N:P ratio. Overall, the hypothesis that Detroit River wetlands improve water quality with respect to nitrogen is partially supported.

As a secondary objective, it was hypothesized that healthy wetlands would demonstrate better nutrient drawdown compared to disturbed ones. The water quality index scores and quality rankings were used as a means of defining wetland health. The results from the present study did not support the second hypothesis. However, wetland quality rankings from this work differed from previous assessments. In this research, overall wetland quality was only distinguished between Peche Island and the remaining

Detroit River wetland sites. Based on this, it was expected that Peche Island would show enhanced nutrient drawdown compared to the other sites. There was no evidence to support this for either phosphorus or nitrogen. Other studies suggest that downstream Detroit River wetlands, despite having compromised WQI score, contained commensurate macrophyte communities. ECCC (2017) did not show differences in SAV-IBI's between Peche Island and the tributary influenced wetlands. Similarly, Chapter 2 did not show any differences in SAV quality indices across the wetlands that could be linked to WQI or light attention. Thus, WQI may not be a proper surrogate measure of wetland functioning nor relate to nutrient drawdown as hypothesized in this work.

Water quality in the Detroit River appears to be a function of hydrological regime and local meteorological events such as storms and winds, as indicated in the strong temporal patterns observed among the sites, and similarity in timing of temporal patterns for individual variables reinforced from the data generated by Chapter 2. Restoration of Detroit River wetlands may not be an effective phosphorus mitigation tool to achieve required load reductions specified for this river by the Lake Erie action plan. However, given the many other positive benefits associated with submerged vegetation to ecosystem function and health and supporting evidence that they do facilitate nitrogen drawdown at some locations in summer months, I recommend continuation of on-going efforts to restore and protect wetlands within the Detroit River

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CHAPTER 4

General Discussion

The main objective of this thesis was to explore water quality – submerged aquatic macrophyte (SAV) interactions across wetlands sites within Canadian waters of the Detroit River. Chapter 2 examined differences in water quality index (WQI) scores and light attenuation across several wetland sites including those previously identified as wetlands of significant provincial interest and at sites designated as prospective wetland restoration areas. In chapter 2, I was interested in light as a limiting factor for SAV distributions in the Detroit River and the major water quality parameters that contribute to light limitation in this system.

Water quality parameters and light attenuation was measured at 21 locations in the Detroit River every two weeks to determine location specific WQI's and euphotic depth. At selected sites, continuous monitoring loggers were installed to generate high resolution sampling of specific conductivity, turbidity and chlorophyll a to determine temporal variation in water quality parameters used in WQI formulation and euphotic depth estimation at twenty-one stations. The data from Chapter 2 was used to evaluate four hypotheses:

H1: Wetland sites adjacent or downstream of tributary inputs have lower seasonally averaged WQI scores and greater light limitation than wetland sites not associated with tributary inputs in the Detroit River.

H2: Water quality scores and light limitation at proposed wetland restoration sites are similar to water quality and light limitation at established wetland locations in the Detroit River.

H3: The ECCC water quality index is strongly correlated to light attenuation and light extinction coefficients and therefore predictive of light constraints of submerged aquatic macrophyte growth.

H4: Light limitation through time in the Detroit River is driven by a subset of water quality parameters and the major drivers of light limitation are similar across locations.

Hypothesis 1 was supported by the findings of Chapter 2. There were highly significant ($p<0.001$; Kruskal-Wallis test) differences between light extinction coefficient measurements at tributary influences wetlands compared to wetland sites without tributary influence. These differences translated into macrophyte euphotic depth ($Z_{EU(SAV)}$) estimates of 1.34 m at wetland sites without tributary influence compared to euphotic depth of 0.83 m at sites receiving tributary input. These results were mirrored by significant differences in water quality score between the two groups, showing higher water quality index scores at non-tributary influenced sites compared to tributary influenced sites. These data support an interpretation that watershed sources of particulate and dissolved materials entering from Turkey Creek and River Canard contribute to light limitation and lower overall water quality scores within in receiving waters of the Detroit River. Thus, restoration activities that generate improvements to water quality in Turkey

Creek and River Canard would have a positive influence on water quality in some wetlands of the Detroit River.

Hypothesis 2 was also supported by data generated from this thesis. There were no differences in either light extinction coefficient or water quality index scores at stations designated as established wetland sites compared to sites designated for future (or on-going) restoration. This provides supporting evidence that planned restoration activities are likely to succeed with respect to promoting the expansion of macrophyte bed area in the Detroit River Area of Concern. Some of the restoration activities have been completed since the collection of this data. For example, restoration activities at Chewitt Bay have been completed since the time when data from Chapter 2 was generated. Even though this site had low overall light penetration, macrophyte beds have indeed established at this location. As such, the data from this thesis provide support for the continuation of wetland restoration activities planned for the Detroit River.

Hypothesis 3 was also supported by Chapter 2 results. Water quality index score was found to be a highly significant predictor of light extinction coefficient. This implies that Environment and Climate Change Canada monitoring datasets computing water quality index scores across Great Lakes Areas of Concerns can be extended to estimate light extinction coefficients. Such information may have utility to extend the interpretative value of Environment and Climate Change Canada's monitoring dataset across applications different from wetland quality assessment. For example, light extinction coefficient data may be of use for estimating primary production potentials when coupled with dedicated production models. However, in the present research, the water quality index score was not found to be the best predictor of light attention. A multivariate PCA model that included specific conductivity, turbidity and chlorophyll a concentrations explained more variation in light extinction coefficient data then the WQI model. This may be due to the fact that the multivariate PCA model was trained using Detroit River data whereas the WQI model was trained over a much broader geographic range. Further research to verify the multivariate PCA model and WQI performance using independent data on water quality parameters would be useful for future studies.

Hypothesis 4 was rejected by the results from Chapter 2. Despite apparent correlation of light extinction coefficients across sites, the high resolution monitoring data provided evidence to indicate that each station had different contributors to light attenuation. Even within a given station, drivers of light attenuation were observed to change as a function of time. The implications of this finding are that care must be taken when using single-parameter proxies to estimate light extinction coefficient. Where possible, use of PAR based light meters are preferred as a direct measure of light extinction coefficient.

Chapter 3 took a different perspective, moving from characterization light constraints on macrophyte habitat towards understanding wetland function in relation to nutrient drawdown. Data from Chapter 3 were used to test 2 hypotheses:

H1: Nutrient concentrations in water overlying submerged aquatic macrophyte beds are lower than nutrient concentrations at the upstream bed margin.

H2: Nutrient drawdown over the macrophyte bed is higher in wetlands designated as better quality based on WQI scores compared wetlands designated as degraded according to the water quality index.

There was partial but limited support for Hypothesis 1. Total oxidized nitrogen was significantly enriched at the upstream bed perimeter compared to bed sites and the downstream bed margin for the Detroit River Marshes site but not at any of the other four monitored wetlands. There were no statistical differences in total phosphorus concentration at upstream bed margins compared to bed sites for any of the monitored wetlands although overall trends (non-statistically significant) were consistent for this nutrient at Peche Island and Turkey Creek. Based on the weight of evidence from Chapter 3, monitored wetlands were not generating significant improvements in seasonally averaged water quality over the beds when compared to the Detroit River water quality as a whole. Therefore, increasing the total area of SAV beds is unlikely to be a significant management approach to reduce phosphorus loadings generated by the Detroit River Area of Concern.

The second hypothesis from Chapter 3 was not supported. However, it should be noted that wetland quality rankings from this work differed from previous assessments. In this research, overall wetland quality was only distinguished between Peche Island and the remaining Detroit River wetland sites. Based on this, I expected that Peche Island would demonstrate greater nutrient drawdown compared to other monitored wetlands. There was no evidence to support nutrient drawdown for any of the water quality parameters measured at Peche Island.

Overall, water quality in the Detroit River appears to be a function of hydrological regime, local meteorological events such as storms, winds, and temperature as indicated in the strong temporal patterns observed among the sites, and similarity in timing of temporal patterns for individual variables reinforced from the data generated by Chapters 2 and 3. Restoration of Detroit River wetlands may not be an effective phosphorus mitigation tool to achieve required load reductions specified for this river by the Lake Erie Action Plan. However, given the many other positive ecosystem service benefits associated with submerged vegetation, the lack of support for hypotheses 2 and 3 of Chapter 3 should not be considered reasons for halting planned wetland restorations.

For future directions of research related to Chapter 3, additional track down studies of nitrogen removal in wetlands during the summer when water temperatures are highest should be explored. My study was limited in the number of summertime points in which the bed margin/bed comparisons were made which may have confounded the nutrient drawdown inferences based on combined seasonal data. By focussing on summertime periods and increasing spatial sampling resolution at bed margins vs bed sites one would likely be able to better substantiate nitrogen drawdown as an important nutrient process operating in Detroit River wetlands. This work should be coupled with additional measures of nutrient cycling including microbial communities known to be responsible for nitrogen transformations. This thesis suggests that nitrogen drawdown in some Detroit River wetlands may be in important process that can potentially alter nitrogen delivery from this system and further work to quantify SAV-nitrogen interactions and its linkage to Detroit River nitrogen loadings should be conducted.

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