FACTORS INFLUENCING COASTAL MARSH WATER QUALITY

FACTORS INFLUENCING COASTAL MARSH WATER QUALITY IN GEORGIAN BAY, ONTARIO

By

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PREFACE

The following M.Sc. thesis is comprised of two chapters that form separate manuscripts for publication in peer-reviewed journals, and which are put into context with a General Introduction. *Chapter 1* has been published in *Environmental Management*, and the complete reference is provided below. *Chapter 2* has been submitted to *Limnology and Oceanography*. As first author, I analysed the data and wrote both manuscripts, under the supervision of Pat Chow-Fraser. However, water chemistry data from the synoptic database for the sites used in *Chapter 1* were initially compiled by Maja Cvetkovic for her M.Sc. thesis, and she appears as a co-author on the resulting publication. All landscape analyses, field work and laboratory analyses for *Chapter 2* were done by me, with assistance from technicians.

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DeCatanzaro, R., and Chow-Fraser, P. Effects of landscape variables and season on water chemistry of coastal marshes in eastern Georgian Bay.

GENERAL ABSTRACT

Human-induced degradation of coastal marshes has been relatively limited in Georgian Bay. This part of the Great Lakes is sparsely populated, with human activity in most areas occurring primarily in the form of diffuse recreational and cottage development. Despite this, water chemistry varies considerably within the Bay. The overall objective of this thesis was to gain an understanding of factors currently controlling water quality conditions in marshes of Georgian Bay, so that this information may be used to assess the potential impacts of continued human development.

Coastal marsh water quality variation among sub-basins of the eastern and northern coasts of Georgian Bay was assessed with data from 105 marshes in 28 quaternary watersheds visited during synoptic surveys. Road density, wetland cover, watershed size and bedrock type were determined for each sub-watershed. Analyses revealed that road density (used as an indicator of human disturbance) is currently a significant predictor of marsh water quality, showing positive relationships with nutrients and suspended solids concentrations, and a strong negative relationship with a published index of wetland water quality, the Water Quality Index (WQI). Watershed size and wetland cover also had significant (but usually weaker) relationships to some water quality variables.

To identify factors governing the chemistry of reference marshes in eastern Georgian Bay, 34 relatively pristine marshes were sampled in spring and summer of 2009, and a GIS was used to quantify catchment features. While

watershed variables such as drainage slope and amount of upstream wetland influenced some water chemistry variables, drainage basin size and order were the most important factors controlling water chemistry; marshes with large, high-order watersheds contained higher concentrations of catchment-derived constituents (e.g., phosphorus, sediments, colour), suggesting that they may be more sensitive to land development that adds nutrients or promotes soil erosion in their watershed. This would be particularly apparent in spring, when watershed runoff has a larger influence on marsh water chemistry.

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I would also like to thank my family and friends for giving me a rich life outside of school. In particular I thank my parents, Jennifer and Denys, for instilling in me an interest in ecology and the outdoors during my childhood, and for encouraging my academic endeavours. Finally, I owe a special thank you to Dan for his support and encouragement both at work and at home.

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General Introduction

Wetlands

Wetlands cover approximately 14% of the land surface in Canada, and are defined as "*areas with the water table at, near or above the land surface for long enough to promote hydric soils, hydrophytic vegetation and biological activities adapted to wet environments*" (NWWG 1997). As integral parts of many ecosystems, they perform a variety of biological and biogeochemical functions. Various species of fish, birds and other wildlife rely on wetlands for foraging, breeding, spawning, nesting or nursery habitat (Maynard and Wilcox 1997; Mitsch and Gosselink 2000). Wetlands also function in water storage, sediment control, primary production and decomposition (Richardson 1994; Maynard and Wilcox 1997), and play a key role in the cycling of nitrogen, sulphur, carbon and phosphorus, by behaving as sinks, sources and transformers of nutrients (e.g., Devito et al 1989; Richardson 1994; Bridgham et al 2006).

Wetlands can be classified as bogs, fens, swamps, marshes or shallow waters, based on hydrologic, chemical and vegetative characteristics. Bogs receive water and nutrients only through direct precipitation (ombrotrophic); they tend to be acidic and nutrient-poor, and are dominated by *Sphagnum* mosses. Other wetland classes receive water and nutrient inputs from the atmosphere and from ground and surface waters (mineratrophic). Fens have a water table near the ground surface, are dominated by mosses and emergent vegetation, and have chemistry that is influenced by the surrounding mineral deposits. Both swamps and marshes experience large seasonal water-level fluctuations and have limited moss growth. Swamps are generally less wet than marshes and have over 30% tree and shrub cover, while marshes are characterized by non-woody emergent vegetation and eutrophic conditions. Finally, shallow water wetlands form where water levels are sufficient to support submergent and floating vegetation; they are often located at the transition between permanently inundated waterbodies and other wetland classes (Zoltai and Vitt 1995; NWWG 1997).

The Laurentian Great Lakes and their coastal wetlands

The Laurentian Great Lakes basin consists of five hydrologically-connected large lakes (Superior, Michigan, Huron, Erie and Ontario) that lie within two countries (Canada and the United States) and three physiographic provinces (Canadian Shield, Central Lowlands and St. Lawrence Lowlands). The lakes formed late in the Pleistocene Epoch, when ice scour from the advance and retreat of glaciers deepened pre-glacial river valleys (Mayer et al 2002). Together, the Great Lakes have a surface area of 244,160 km^2 and a volume of 22,684 km^3, representing the largest freshwater system on earth (Herdendorf 2004). Consequently, they hold enormous ecological and economic value. By volume, Lake Superior is the largest (12,100 km^3), followed by Lake Michigan (4,920 km^3), Lake Huron (3,540 km^3), Lake Ontario (1,640 km^3) and Lake Erie (484 km^3). The lakes drain a watershed of 521,830 km^2 and have an expansive shoreline (17,017 km) harbouring over 216,000 ha of coastal wetland (Herdendorf 2004; Ingram et al 2007).

Great Lakes coastal wetlands, of which marshes are the most common (Maynard and Wilcox 1997), are distinguished from inland wetlands in having direct hydrological connection to Great Lakes waters (Keough et al 1999). In addition to landward influences, coastal wetlands are shaped by a number of large-lake processes, including wave action, seiches, and seasonal and long-term water-level fluctuations (Keough et al 1999; Mayer et al 2004). Most coastal wetlands form where some natural or artificial protection from wave action, erosion and ice scour exists (Herdendorf 2004; Albert et al 2005). They are known to be areas of high biological diversity and productivity compared to the open lake (Jude and Pappas 1992; Cardinale et al 1998), in part due to the flux of energy and nutrients that enter from the watershed. Coastal wetlands of the Great Lakes provide critical spawning and nursery habitat for many fish species (Jude and Pappas 1992; Wei et al 2004), and are used by more than 30 species of waterfowl each year (Prince et al 1992). They are also used by a variety of other aquatic and terrestrial wildlife, including many mammals, reptiles and amphibians (Maynard and Wilcox 1997).

Hydrogeomorphic classification of coastal wetlands

Great Lakes coastal wetlands are configured along a continuum of hydrogeomorphic types, which help shape ecosystem properties. A number of classification schemes exist for coastal wetlands (e.g., Keough et al 1999; Herdendorf 2004; Albert et al 2005), but three broad hydrologic classes are generally recognized. Albert et al (2005) referred to these classes as (*a*) lacustrine, (*b*) riverine and (*c*) barrier-enclosed wetlands, and further divided each of them into a number of geomorphic types (Table i.1). Lacustrine wetlands form in shoreline embayments or along stretches of open coast and are affected by coastal processes such as waves, seiches and ice scour. Their chemistry may be strongly influenced by constituents of the lake water, with varying amounts of influence from the watershed. Riverine wetlands include a broad variety of types (see Table i.1). Generally, they experience both coastal and riverine processes, and have chemistry that is determined by the mixing of lake water and river water. Finally, barrier-enclosed wetlands often occur landward of a barrier feature (such as a sand barrier) and are therefore subject to a lesser degree to lake-generated currents; many of these wetlands have thick organic substrates and their chemistry tends to be largely influenced by groundwater and precipitation inputs (Keough et al 1999; Albert et al 2005).

Hydrogeomorphic type can greatly influence the biotic community of a coastal wetland. The degree of protection or exposure to waves and currents is known to affect vegetative characteristics such as plant cover (Randall et al 1996; Johnston et al 2007), as well as the types of invertebrates (Burton et al 2004) and fish (Wei et al 2004; Trebitz et al 2009) that inhabit a wetland. Additionally, lacustrine wetlands tend to be more homogeneous with respect to their water chemistry, vegetation and fish composition compared to riverine and barrier-enclosed wetlands; this is likely due to the relatively strong, uniform hydrologic connection to the adjoining lake and the absence of channelized and back-bay segments (Trebitz et al 2005; Trebitz et al 2009).

Anthropogenic impacts on coastal wetland ecosystems

The Great Lakes watershed is home to over 40 million people, including about one tenth of the population of the United States and one quarter of the population of Canada (Larson and Schaetzl 2001). Since humans first settled the area in 1850, wetland destruction, infilling and conversion to other landuses such as agriculture, has resulted in a loss of over 60% of wetland cover in southern Ontario (Snell 1987). In recent years, a disproportionately large area of wetland losses to development has occurred within 10 km of the Great Lakes coast, with most occurring within the nearest kilometre (Wolter et al 2006). To date, over two thirds of Great Lakes coastal wetlands have been destroyed (GLIN 2009).

Of the coastal wetlands that remain, many have been degraded by nutrient and sediment inputs resulting from deforestation, urbanization, industry and agriculture in their watersheds (Crosbie and Chow-Fraser 1999; Trebitz et al 2007a; Morrice et al 2008). Some of this pollution originates from point sources (enter at discrete locations) such as sewage treatment plants or other facilities with wastewater discharge. Non-point source pollution (occurs diffusely throughout a watershed) can include nutrients and sediments in runoff from fertilized agricultural lands and paved or deforested surfaces, as well as atmospheric deposition, and is often the major source of pollution to surface waters (Bhaduri et al 2000). Water quality degradation has been most severe in parts of Lakes Erie, Ontario and Michigan that are heavily populated or intensively farmed (Chow-Fraser 2006; Danz 2007; Cvetkovic 2008). Studies have demonstrated that across the Great Lakes basin, anthropogenic activity now explains a large portion of variation in coastal wetland water quality (Chow-Fraser 2006; Danz et al 2007; Trebitz et al 2007a; Morrice et al 2008).

Degradation of coastal marsh water quality has major implications for productivity and species assemblages. In P- or N- limited systems, high natural or anthropogenic loadings of these nutrients can lead to elevated primary productivity in the form of increased macrophyte and algae growth (Harlin 1995). Nutrient and sediment enrichment also results in loss of submergent macrophytes due to increased water turbidity (Chow-Fraser 1998; Lougheed et al 2001), and a distinct shift in the resident flora and fauna (Jude and Pappas 1992; McNair and Chow-Fraser 2003; Seilheimer and Chow-Fraser 2006; Trebitz et al 2007b). Species of zooplankton, aquatic insects and fish that are intolerant of water quality degradation or which require submergent vegetation for shelter or spawning are generally replaced by more tolerant taxa as wetlands become degraded, resulting in marked changes in food-web dynamics (Chow-Fraser 1998; Chow-Fraser et al 1998; Jude and Pappas 1992; Lougheed and Chow-Fraser 2002; Trebitz et al 2007b).

In Canada, wetlands protection and conservation is carried out through a variety of means. This includes policies such as the *Federal Policy on Wetlands*

Conservation, and agreements and treaties such as the *Convention on Wetlands of International Importance especially as Waterfowl Habitat* (RAMSAR Convention), the *North American Waterfowl Management Plan* and the *Canada-United States Great Lakes Water Quality Agreement.* In addition, federal legislation such as the *Fisheries Act*, the *Species at Risk Act*, the *Migratory Birds Convention Act*, the *Canada Wildlife Act*, the *National Parks Act* and the *Canadian Environmental Assessment Act* often afford indirect protection of wetland habitats.

Lake Huron and Georgian Bay context

With a surface area of 59,600 km^2 and a shoreline length of 6,157 km, Lake Huron supports a disproportionately large area (over 61,000 ha) of Great Lakes coastal wetlands (Ingram et al 2007). Wetlands of this lake are characterized as having low levels of phosphorus, nitrogen, chlorophyll and suspended solids relative to those of the other Great Lakes (Trebitz et al 2007a). A large portion of these wetlands are located in eastern Georgian Bay and the North Channel, where the expansive, convoluted shoreline and abundant nearshore islands are conducive to wetland formation. Due to the geologic setting in eastern and northern Georgian Bay (hard igneous and metamorphic rock), riverine and barrier-enclosed wetlands are proportionately less common than they are in the lower lakes, and wetlands occur most often in lacustrine protected embayments (GLCWC 2004) with moderate exposure to seiches, waves and ice scour (Albert et al 2005).

The land surrounding Georgian Bay has undergone limited human development relative to other areas of the Great Lakes (particularly Lakes Erie, Ontario, and Michigan). Along much of the coast, the majority of development is for recreational and cottage use, with little agriculture and few permanent residents. The eastern and northern coasts are dominated by extensive forested uplands and wetland complexes, with outcrops of Precambrian Shield bedrock. The littoral zone of the eastern coast of Georgian Bay has been recently appointed a UNESCO World Biosphere Reserve due to the unique landscape and habitats it supports. In the south of Bay, the Bruce Peninsula and on Manitoulin Island, softer sedimentary rock underlies thicker, more fertile soils. Cottage, residential and agricultural development is most prominent south of the Severn River. Cvetkovic (2008) showed that there is considerable variation in coastal marsh water chemistry across Georgian Bay, with marshes located in southern Georgian Bay currently showing the most signs of water quality degradation (highest nutrients and turbidity).

Landscape ecology

The term "landscape ecology", generally referring to the study of spatial patterns and ecological processes operating across broad spatial scales (Turner 1989; Opdam et al 2001), has become increasingly popular in recent years. This integrative science deals with the study of spatial heterogeneity, and the organismal and material exchanges, as well as biotic and abiotic processes operating across heterogeneous landscapes (Turner 1989). The approach has been developed primarily in response to environmental problems related to human exploitation of resources (Weins 2002); a common goal of landscape ecology studies is to understand how landscape patterns relate to sustaining ecological processes, so that the resulting knowledge can be integrated into landuse planning and management (Opdam et al 2001). The approach is frequently undertaken to address problems pertaining to wildlife conservation, by studying habitat patch sizes and shapes, ecosystem interactions, landscape resistance (barriers to migration or material flow) and metapopulation dynamics (Forman 1995).

The principles of landscape ecology have also been extended to freshwater systems, based on the premise that patterns and processes in a landscape, and human alterations thereof, will affect the hydrology and chemistry of rivers, streams, and downstream waterbodies (Roth et al 1996; O'Neill et al 1997; Weins 2002). Because watersheds are hydrologically defined, they often provide the most ecologically-meaningful landscape units within which terrestrial stressors or features can be quantified and related to downstream conditions (e.g., Danz et al 2007; Hollenhorst et al 2007). The utility of this approach has been highlighted by the large amount of literature that has emerged in recent years which focuses on relating variation in freshwater quality to variation in watershed characteristics across a number of landscapes (e.g., Crosbie and Chow-Fraser 1999; Gergel et al 1999; Carignan et al 2000; Prepas et al 2001).

Thesis objectives

In order to set appropriate water quality standards for coastal wetlands and aid in development planning for different areas of Georgian Bay, it is essential to gain an understanding of the current conditions and processes that are controlling water quality variation. The first objective of this thesis (addressed in Chapter 1) is to tease apart the relative importance of human disturbance (using road density as an indicator) and physical landscape features (watershed size, wetland cover, bedrock type) in determining marsh water quality in eastern and northern Georgian Bay, an area with a low human population density. In doing this, I illustrate the potential for low-level diffuse human development to negatively impact coastal habitats, while demonstrating the importance of accounting for sources of natural variation.

The second objective of this thesis (addressed in Chapter 2), is to explore in greater depth the factors controlling water chemistry of reference marshes in a region of eastern Georgian Bay that has undergone little development for cottage and residential use. In particular, I examine the influence of (1) characteristics of the marsh and its individual drainage basin, and (2) season. The results of this study will advance our understanding of factors governing the reference conditions of coastal marshes, while establishing a baseline for this area and allowing us to better gauge the potential for these systems to be negatively impacted by changes to watershed dynamics.

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Table i.1: Descriptions of the major hydrogeomorphic classes of Great Lakes coastal wetlands, as proposed by Albert et al (2005).

Hydrologic system	Geomorphic type	General features
Lacustrine	Open shoreline	High exposure to wave action, with little or no protection by offshore features; typically has a substrate of rock or clay; narrow fringes of emergent vegetation
	Open embayment	Large (generally > 3-4 km wide) embayments exposed to moderate-high wave energy; gravel, sand, or clay substrates; generally only emergent vegetation
	Protected embayment	Small (generally < 3-4 km wide), protected bays in shorelines of bedrock or till; moderate accumulation of organic matter (10-60 cm); diverse vegetation (emergent and submergent)
	Sand-spit embayment	Shallow embayments protected by sand spits extending along the coast; moderate accumulation of organic matter (10-60 cm); diverse vegetation (emergent and submergent)
Riverine	Connecting channel	Includes wetlands of a variety of hydrogeomorphic classes located along channels connecting the Great Lakes; exposed to strong currents; variable substrates and vegetative characteristics
	Delta	Often extensive wetland areas formed on deltas of fine or coarse alluvial materials; influenced by fluvial processes and wave action; thick organic sediment
	Drowned river-mouth, barred	Located behind a barrier at a river mouth; lagoon formation common, but river flow maintains the connection with the lake; thick organic sediment; vegetation is concentrated at the river mouth
	Drowned river-mouth, open	Form along river banks in the absence of a barrier at the river mouth; thick organic soils; diverse emergent zones; submergent vegetation where river flow is slow
Barrier-enclosed	Barrier beach lagoon	Form behind a sand barrier that limits mixing with lake water and exposure to coastal processes; affected by ground water and surface drainage inputs; thick organic soils; submergent and emergent vegetation zones; peatland vegetation may dominate
	Swale complex	Form either between recurved fingers of sand spits or between relict beach ridges; sand substrate with variable organic matter; some portions may develop into shrub swamps with shallow organic soils; some embayments may remain connected to the lake and maintain herbaceous vegetation

Chapter 1:

The relative importance of road density and physical watershed features in determining coastal marsh water quality in Georgian Bay

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Abstract

We used a GIS-based approach to examine the influence of road density and physical watershed features (watershed size, wetland cover and bedrock type) on water quality in coastal marshes of Georgian Bay, Ontario. We created a GIS that included landscape information and water quality data from a 9-year synoptic survey of 105 coastal marshes spanning 28 quaternary watersheds. Multiple regressions and partial correlations were used to discern confounding effects of human-induced (road density) versus natural physical watershed determinants of water quality. Road density was the dominant factor influencing many water quality variables, showing positive correlations with specific conductivity (COND), total suspended solids (TSS) and inorganic suspended solids (ISS) and a negative correlation with overall Water Quality Index scores. Road density also showed positive correlations with total nitrate nitrogen (TNN) and total phosphorus (TP). By comparison, larger watershed area was most closely related to elevated TP concentrations. The proportion of the watershed occupied by wetlands explained the largest amount of variation in TNN concentrations (negative correlation) and was also negatively correlated with COND and positively correlated with TSS and ISS when we controlled for road density. Bedrock type did not have a significant effect in any of the models. Our findings suggest that road density is currently the overriding factor governing water quality of coastal marshes in Georgian Bay during the summer low-flow period. We recommend that natural variation in physical watershed characteristics be

considered when developing water quality standards and management practices for freshwater coastal areas.

Key words: wetland; watershed; water quality; anthropogenic stress; geographic information system; road density

Introduction

Within the Laurentian Great Lakes basin, coastal wetland water quality has been closely linked to the magnitude of anthropogenic stress (i.e., the degree of urban and agricultural development) on these systems (Crosbie and Chow-Fraser 1999; Chow-Fraser 2006; Trebitz et al 2007; Morrice et al 2008). It has been demonstrated that suspended solid, nutrient and ionic concentrations in wetlands are strongly related to a gradient of agricultural and/or urban intensity in the watershed (Chow-Fraser 2006; Trebitz et al 2007). Further, Morrice et al (2008) have found that human population is the strongest independent predictor of total phosphorus levels, and a significant factor affecting several other water quality variables. These studies have occurred across basin-wide scales within the United States (Trebitz et al 2007; Morrice et al 2008) or both the United States and Canada (Chow-Fraser 2006) and have therefore captured conditions across broad gradients of human disturbance.

Currently, little information is available on water quality impacts in relatively remote areas of the Great Lakes with low levels of human development; in such areas, hydrological and geological factors can be expected to play a significant role in determining near-shore water quality and have the potential to confound effects of human activities. Eastern and northern Georgian Bay, Lake Huron, has had limited human development in comparison with the lower Great Lakes (Lake Erie and Lake Ontario) because shallow soils and underlying granitic bedrock in all but the most southern portion of the eastern coast render it poor for agriculture (Weiler 1988). Human activity in the area occurs mainly in the form of recreational and cottage development. The lack of more land- and resource-intensive development projects has allowed coastal wetlands in the Bay to remain among Ontario's most pristine (Chow-Fraser 2006; Cvetkovic 2008).

Determining an appropriate measure of anthropogenic stress for sparsely populated regions such as Georgian Bay can be a challenging task. Common metrics for quantifying stress within the Great Lakes basin include measures of agricultural intensity, atmospheric deposition, human population density, road density, landcover and density of point sources within watersheds (Houlahan and Findlay 2004; Host et al 2005; Danz et al 2007; Trebitz et al 2007; Morrice et al 2008). Many of these metrics are inappropriate for use in eastern and northern Georgian Bay due to the minimal amounts of industry and agriculture. Road density is an attractive metric because road data are widely available in Canada and relatively simple to interpret. The creation of road networks provides access to previously remote areas; consequently, an increase in road density is often associated with an increase in housing density and population density and a decrease in forested area on lakeshores in North America (Hawbaker et al 2005; Wolter et al 2006; Danz et al 2007). Further, Danz et al (2007) have shown that road density and other measures of human population are strongly correlated with an overall stress index for the Great Lakes basin that incorporated multiple types of anthropogenic impacts on coastal wetland water quality.

Accounting for natural variation in water chemistry among regions that results from variation in physical watershed features is important in conservation of aquatic ecosystems since water quality standards and regulations are best established when there is knowledge of the natural (reference) state (Keough et al 1999). Research on small inland lakes and rivers elsewhere in North America has provided some insight into the capacity for physical processes in watersheds to affect water quality dynamics (e.g., Johnston et al 1990; D'Arcy and Carignan 1997; Dillon and Molot 1997; Devito et al 2000; Eimers et al 2008). The size of watersheds can play a crucial role in determining the chemistry of tributary outflow. Larger watersheds can produce higher nutrient loads to receiving waters because they generate larger volumes of runoff with greater opportunity for physical and chemical alteration of water as it flows over and through the land toward the outlet. Landscape features such as bedrock and upstream wetlands may also play a role. Runoff in temperate Precambrian Shield regions is topographically controlled (D'Arcy and Carignan 1997), with wetlands positioned in low-lying areas (Devito and Hill 1997). As a result, much of the generated runoff passes through wetlands as it moves toward the outlet. These inundated upstream areas often have a high efficiency for denitrification (Whigham et al 1988; Seitzinger 1994) and collection of organic matter and sediments that can store phosphorus and sulphur (Richardson et al 1997; Mandernack et al 2000). Therefore, areal extent of wetlands within a watershed may be related to nutrient and ionic concentrations in runoff (Johnston et al 1990; Dillon and Molot 1997).

While previous work in Georgian Bay has shown significant variation in coastal marsh water quality in relation to varying levels of human disturbance throughout the Bay (Cvetkovic 2008), there is also considerable natural variation in drainage basin characteristics, and the relative importance of each factor in determining coastal water quality has not yet been ascertained. The goal of this paper is to separate the effects that road density, watershed size, wetland cover and bedrock type have on water quality. Based on the well-documented potential for human development to impact coastal freshwater ecosystems by increasing nutrient and sediment loadings (Chow-Fraser 2006; Trebitz et al 2007; Morrice et al 2008), we expect road density to explain a significant amount of variation in water chemistry variables such as phosphorus, conductivity and suspended solids, even at the low end of the human disturbance gradient. The influence of physical watershed characteristics such as size of the watershed, extent of wetlands and bedrock type is likely to play a secondary role for most water quality parameters, although wetland cover may show a stronger relationship to nitrate concentrations due to processes of nitrogen uptake and transformation.

Methods

Study area

Georgian Bay is a naturally oligotrophic waterbody on the eastern arm of Lake Huron (Figure 1.1). The eastern and northern shores of the Bay as far south as the Severn River are underlain by Precambrian Shield rock, covered by approximately 30 cm of sandy, infertile soil (Weiler 1988) (Figure 1.2); 21 of the

28 watersheds in our study are located within this landscape. The remainder of the watersheds examined in this study were located on the Silurian and Ordovician rocks of the southern portion of the eastern shoreline, the tip of the Bruce Peninsula and Manitoulin Island; there, rocks are covered by a layer of more fertile clay, silt and sandy loam soils. The Shield rock is associated with ground water of low alkalinity, while Silurian/Ordovician rock is associated with hard, highly mineralized groundwater (Weiler 1988).

Historically, natural geological and hydrological factors in the drainage basin and water exchange with Lake Huron and the North Channel have been dominant controls over water chemistry in the Bay. Atmospheric inputs are a significant source of nitrogen, phosphorus and chloride (Weiler 1988). There are extensive areas of wetland extending back from the shore, which have been largely influenced by beaver (*Castor canadensis*) activity. While the age of the beaver ponds is difficult to estimate without a complete inventory of historical aerial photos, these systems are known to be both temporally and spatially dynamic, and can strongly influence hydrology and runoff chemistry (Johnston and Naimen 1990; Collen and Gibson 2001). In addition to beaver ponds, several other types of wetlands exist in the watersheds, including conifer swamps, bogs and fens.

Georgian Bay has maintained a low human population density relative to other parts of the Great Lakes, but the presence of humans in the area has introduced a new watershed dynamic. Beginning in the late 1800s, resorts and cottages were being developed on the shores, along with septic beds and marinas (Sly and Munawar 1988). Until the early part of the 1900s, deforestation occurred along much of the coast to feed a thriving lumber industry. As a result, much of the forest that now surrounds the shores of Georgian Bay is second-growth.

Today, timber extraction occurs at a slower pace in areas where soils are most productive (Sly and Munawar 1988). Within our study area, the southeast portion of the Bay (south of Severn River) has been most heavily populated with seasonal cottagers and year-round residents (>20 persons km^{-2} in the Township of Severn). There, agriculture creates additional impacts, particularly in the Sturgeon Bay-Hog Bay and Matchedash Bay watersheds (Sherman 2002). With the exception of Manitoulin Island, other portions of the bay examined in this study have had minimal agricultural impacts. In the late 1980s, eastern hardwood forests still covered about 95% the land area north of the Severn River, but only about 63% south of it (Weiler 1988). The southeast corner of the bay also shows more signs of water quality degradation than any other section of the east or north coasts (Cvetkovic 2008).

Watershed data

We obtained the most recent version of road network and wetland shapefiles from the National Topographic Database (NTDB; Natural Resources Canada) and imported them into ArcMap 9.0 (ESRI, Redlands, CA, USA). These data were produced at the 1:50,000 scale from scanned topographic maps that originated in the late 1980s and were updated as data became available. The files have been recently (post 2000) planimetrically enhanced with Landsat 7 orthoimages. Road networks were obtained in two separate files. The first contained non-limited-access (non-limited-use) roads; in the Georgian Bay area, these included a sparse network of highways and primary (numbered) roads and a more widespread network of secondary local or rural roads and streets. The second file contained limited-access (limited-use) roads, which in the study area consisted of car tracks and dry-weather use roads; these roads generally extended out a short distance from non-limited-access roads. The wetland and road network shapefiles were overlaid onto quaternary watersheds draining into Georgian Bay that were obtained from the Ontario Ministry of Natural Resources (OMNR). Names were assigned to the watersheds according to major rivers, bays, islands or other dominant features (modified from Cvetkovic 2008). NTDB files were clipped for each watershed. Wetland area was expressed as the proportion of the quaternary watershed that it occupied (PROPWET), while road density was calculated as length per unit area for the entire watershed.

We used only the 28 quaternary watersheds for which water quality data were available (Figure 1.1). This included all but four watersheds located along a continuous stretch of the east and north coasts of Georgian Bay and eastern North Channel, as well as two watersheds in the Tobermory area on the northwest coast of the Bay at the tip of the Bruce Peninsula (Figure 1.1). Two of the watersheds from the eastern coastline of Georgian Bay for which no water quality data were collected are located near the town of Parry Sound. This area was not sampled during surveys because it contains relatively few coastal wetlands compared to the rest of the eastern Georgian Bay coast. The other two watersheds for which no data were available are located in the more northern portion of the Bay, where accessibility poses an additional constraint on sampling efforts. In watersheds for which water quality was assessed, the number of sampling stations at marshes along the stretch of watershed outflow ranged from 1 to 22.

Water quality sampling

Water quality data for this study were obtained over a 9-year period of synoptic sampling along eastern and northern Georgian Bay. During this time, 105 coastal marshes (126 site-years) were sampled. Most of these data have been used in previously published studies (e.g., Chow-Fraser 2006; Cvetkovic 2008). Although sampling each year took place between late May and early September, wetlands were sampled primarily in June, July and August. This sampling period excluded any influence of snowmelt, which can elevate concentrations of nutrients and dissolved minerals in coastal zones each spring (Weiler 1988). The time of day at which sampling occurred varied among sites but fell between 09:00 and 20:00 h.

Field sampling and analytical procedures for determining specific conductivity (COND), pH, temperature (TEMP), turbidity (TURB), total phosphorus (TP), soluble reactive phosphorus (SRP), total nitrogen (TN), total ammonia nitrogen (TAN), total nitrate-nitrite nitrogen (TNN), total suspended solids (TSS) and inorganic suspended solids (ISS) followed procedures outlined in detail by Chow-Fraser (2006); for TN analysis, however, we used Hach Test 'N Tube reagents and protocols beginning in 2005. The samples were processed on the day of collection for TAN and TNN. At that time, water was filtered for suspended solids (TSS and ISS) and chlorophyll (CHL) *a*, and filtered water was frozen for SRP analysis. Raw water samples were frozen and brought to the lab for TN and TP analyses. All frozen samples were processed in the lab within roughly 4 months of collection.

Use of the Water Quality Index

We have chosen to use the Water Quality Index (WQI) developed by Chow-Fraser (2006) to provide an overall measure of the condition of Georgian Bay coastal marshes with which to compare across watersheds. Unlike other water quality indices available in Canada, many of which were designed for use on inland lakes and rivers (e.g., Rocchini and Swain 1995; CCME 2001), the WQI used here is specific to assessing Great Lakes coastal marshes and was developed using water quality data from 110 marshes spanning all five Great Lakes, including 18 in Georgian Bay.

The index was derived using principal components analysis of 12 water quality variables (TSS, TURB, ISS, TP, SRP, TAN, TNN, TN, COND, TEMP, pH, CHL *a*) that were $\log_{10}$-transformed (Chow-Fraser 2006). The WQI score for each site was formed by the weighted sum of all 12 principal component site scores. A predictive equation that can be used to generate WQI scores from a given dataset containing the required water quality parameters was then created using stepwise multiple regression to give:

$$\begin{aligned} WQI = {} & 10.0239684 - (0.3154965 * \log TURB) - (0.3656606 * \log TSS) \\ & - (0.3554498 * \log ISS) - (0.3760789 * \log TP) - (0.1876029 * \log SRP) \\ & - (0.0732574 * \log TAN) - (0.2016657 * \log TNN) - (0.2276255 * \log TN) \\ & - (0.5711395 * \log COND) - (1.1659027 * \log TEMP) - (4.3562126 * \log pH) \\ & - (0.2287166 * \log CHL\mathit{a}) \end{aligned}$$

The WQI has been found to be significantly negatively correlated with the proportion of altered land in the associated watershed, assessed as the sum of urban and agricultural landuse types, and can be used to indicate the degree of anthropogenic impairment of coastal marsh water quality (Chow-Fraser 2006).

Data analysis

Because we were interested in a landscape approach to water quality modeling, we chose to focus on water quality variables that can be linked directly to watershed processes, including nutrients (TP, SRP, TN, TAN, TNN), COND, TSS and ISS. These variables, along with TURB, TEMP, pH and CHL *a*, were combined to give a WQI score for each wetland. Means of water quality variables were computed for each watershed. Water quality variables that were noticeably right-skewed were $\log_e$- or square root (sqrt)- transformed prior to further analysis to approach normality.

Statistical analyses were performed in SAS JMP 4.0. We used a significance level of 0.05 for all statistical tests. ANOVAs were used to look for potential effects of bedrock type on landscape and water quality variables. Two classes were used: (1) sedimentary rock (Silurian/Ordovician) and (2) Precambrian Shield rock (Southern/Grenville provinces). A Pearson's correlation matrix was used to explore relationships among water chemistry and landscape variables, and to examine the degree of collinearity among the landscape variables. The density of limited-access roads (RDLA) was initially included; however, because it showed only weak relationships to some water quality variables, we opted to focus on non-limited-access road density (RDNL) rather than limited-access or total road density in further analyses. We also believe the density of non-limited-access roads to be a superior indicator of the degree of human activity in the watershed, since these roads are easily accessed year-round and provide the primary access routes into most areas, whereas most limited-access roads extend only short distances out from non-limited-access roads.

We used a forward stepwise multiple regression procedure to derive explanatory equations and to determine the relative power of each watershed variable for explaining variation in water quality parameters. Bedrock type was included as a dummy variable along with continuous watershed variables. Only watershed variables with significant effects were retained in the models. When forming models, we also tested for significance of interactive effects of two variables. Partial correlation plots were used to illustrate relationships between individual watershed variables and water quality variables when more than one watershed variable had a significant effect in the multiple regression models (Draper and Smith 1981; Findlay and Houlahan 1997; Houlahan and Findlay

2004). Partial correlation statistically controls both the independent and the dependent variables for the effects of another variable, thereby removing spurious correlations and unmasking relationships hidden by the effects of other variables.

Results

Watershed landscape characteristics

Landscape variables were tabulated at the level of quaternary watersheds for eastern and northern Georgian Bay (Table 1.1). Watersheds ranged in size from 1,372 to 555,653 ha, with a mean area of 46,377 ha. The largest was Spanish River watershed, located at the east end of the North Channel; it was more than four times the size of the next largest watershed. Several of the watersheds consisted of a group of islands or island and mainland contributors rather than a single landmass. Many island watersheds were only accessible by boat and contained no roads. The highest density of non-limited-access roads was 16.13 m ha^{-1} in the Matchedash Bay watershed in the most southerly portion of eastern Georgian Bay. The adjacent Sturgeon Bay-Hog Bay watershed also had an exceptionally high density, at 14.00 m ha^{-1}. Great La Cloche Island had the highest density of limited-access roads, at 6.71 m ha^{-1}, despite having a relatively low density of non-limited-access roads. Wetlands constituted between 0.16% (in the Beausoleil-Bone watershed) and 23.29% (in the Shebeshekong River watershed) of the land area, with an average coverage of 7.01%.

There was minimal collinearity observed among landscape variables

(Table 1.2). The density of non-limited-access roads was not significantly correlated with proportion wetland or $\log_e$-transformed watershed area, though it was noted that the watersheds with very high road densities had low values for proportion of wetlands in the watersheds. There was also no significant relationship between watershed size and proportion wetland. With respect to bedrock class, we found that the density of non-limited-access roads was higher (r^2=0.284, P=0.0035) and the proportion wetland lower (r^2=0.151, P=0.0407) in sedimentary watersheds than in watersheds located on the Precambrian Shield.

Water quality

Water quality characteristics varied considerably among the 28 watersheds (Table 1.3). Mean WQI score was lowest in the Matchedash Bay watershed (–0.059), indicating moderately degraded water quality conditions. This watershed also had the highest levels of TP (43.06 $\mu g\ L^{-1}$), TNN (0.427 $mg\ L^{-1}$), COND (331 $\mu S\ cm^{-1}$) and TSS (13.29 $mg\ L^{-1}$). Mean WQI score for all other watersheds was >0.000, indicating that these watersheds are among the least human-disturbed in the context of the entire Great Lakes Basin (Chow-Fraser 2006). Mean WQI score was highest in the Shawanaga River watershed (2.150); this watershed also had the lowest mean COND measurement (26 $\mu S\ cm^{-1}$). The Fathom Five, Giroux River, Great La Cloche Island and Moon River-Musquash River watersheds also contained marshes with exceptionally good water quality.

Several of the water quality variables were significantly correlated with each other (Table 1.2). WQI score showed highly significant negative correlations with log TP, log COND, log TN, sqrt TNN, log TAN, log TSS, and sqrt ISS. We found log TP to be positively correlated with log SRP, log TAN, log TSS, and sqrt ISS, while sqrt TNN was positively correlated with log COND. There was also a strong positive relationship between sqrt ISS and log TSS.

Relating water quality to watershed variables

COND was the only water quality variable for which bedrock type was a significant ANOVA predictor; log COND levels were higher in watersheds with sedimentary bedrock than in watersheds underlain by Precambrian Shield rock (r^2=0.196, P=0.0182). The initial bivariate analyses involving continuous landscape variables (Table 1.2) revealed a highly significant negative relationship between the density of non-limited-access roads and WQI scores and significant positive relationships between road density and all other water quality variables except log TN, log TAN and log SRP. Watershed area ($\log_e$-transformed) showed a positive relationship with log TP but was not significantly related to other water quality variables. Sqrt TNN and log COND both had a significant negative relationship to proportion wetland. All of these relationships remained significant when partial correlations were used to control for the confounding effects of other watershed variables identified in the stepwise regression procedure (Table 1.4, Figure 1.3). Correlation of proportion wetland with both log TSS and sqrt ISS also became significant once we controlled for road density (Figure1.3).

Explanatory models

We present explanatory models built from forward stepwise multiple regressions for all water quality variables that showed a significant relationship with at least one watershed variable (Tables 1.4, 1.5). The density of non-limited-access roads was the only watershed variable to have a significant effect on WQI, alone explaining 58.2% of the variation (Figure 1.4). Road density also contributed significantly to all other models, explaining the largest percentage of variation in log COND (31.4%), log TSS (26.1%) and sqrt ISS (20.6%) of all watershed variables. Watershed area (log_e-transformed) contributed strongly to the model for log TP, accounting for 32.6% of the variation, with road density explaining an additional 14.8%. Proportion wetland contributed significantly to models for log COND, sqrt TNN, log TSS and sqrt ISS, accounting for 15.5%, 20.3%, 11.3% and 15.3% of the variation, respectively. Bedrock class did not have a significant effect in any of the models. Accounting for interactive effects between two watershed variables never resulted in a significant improvement to the models and interaction terms were therefore omitted.

Discussion

Road density showed the strongest relationship to water quality conditions in Georgian Bay coastal wetlands. It accounted for a large amount of variation in several water quality parameters, including COND, TSS, ISS and overall WQI score, and was a secondary factor influencing TP and TNN levels. Increased nutrients and suspended solids have been observed across increasing anthropogenic stress gradients at the scale of the entire Great Lakes basin, including one stress gradient that was partially based on and highly correlated with road density (Chow-Fraser 2006; Danz et al 2007). The positive relationships between road density and phosphorus and nitrates have also been reported for wetlands in southeastern Ontario (Houlahan and Findlay 2004). Phosphorus is naturally limiting in coastal zones of Georgian Bay (Weiler 1988), and the anthropogenic contribution to loadings of P and other nutrients can therefore potentially have large impacts on the productivity of these systems. The degree to which road density changed over the 9-year period of our study and the extent to which this may have influenced our results are unknown. However, despite this data limitation, our findings strongly support the idea that expansion of road networks has the ability to impair coastal wetland water quality through increasing nutrient and sediment loadings from the watershed. Furthermore, this effect often overpowers the influence of natural variation in physical watershed characteristics.

The relationship with the largest percentage of variation explained (both with and without controlling for confounding variables) was that between road density and WQI score. This reflects the strong ability of this index to detect anthropogenic degradation of coastal marsh water quality even within the lower end of the disturbance gradient, and suggests that it is an appropriate measure for assessing human-induced degradation of coastal marshes. Based on the regression model, an increase in road density of 11.6 m ha^{-1} would be expected to decrease WQI scores by 1.00 unit, representing a considerable decline in water quality. This water quality impairment in turn has the potential to alter trophic dynamics and cause a shift toward more degradation-tolerant flora and fauna (Lougheed et al 2001; McNair and Chow-Fraser 2003; Seilheimer and Chow-Fraser 2006; Danz et al 2007).

Watershed area explained the greatest percentage of variation in TP levels in coastal wetlands within Georgian Bay. Johnston et al (1990) also found that watershed area influenced concentrations of P in relatively undisturbed watersheds of Minnesota. In these areas, thin soils and impermeable bedrock tend to direct runoff through organically rich surface layers with high levels of biologically available soil nutrients (Schiff et al 1998). Larger watersheds provide a greater land surface over which hydrologic flushing of nutrients can occur, leading to higher TP loads to downstream environments. While not evident in our study, watershed area can also be positively related to concentrations of other nutrients, including several forms of nitrogen (Johnston et al 1990).

Bedrock type can be an important determinant of water chemistry. Weathering of carbonate minerals occurs at a much faster rate in sedimentary bedrock than in the metamorphic bedrock found in the Precambrian Shield and is a major source of dissolved ions such as calcium and bicarbonate (Gorham et al 1983; Weiler 1988; Keough et al 1999); therefore, we expected to see naturally higher specific conductivity levels in marshes at the base of sedimentary watersheds. Likewise, weathering of sedimentary bedrock is known to promote increased nutrient enrichment of lakewaters (Conroy and Keller 1976). Our results did not identify bedrock type as a significant factor governing COND or other water quality variables once the effects of other watershed features were accounted for. Specific conductivity is also known to be a reliable indicator of anthropogenic impact on freshwater systems (Lott et al 1994; Chow-Fraser 2006), and our data suggest that it is variation in road density, rather than bedrock type, that has the dominant influence on specific conductivity values in Georgian Bay.

Understanding the relationship between wetland cover in the watershed and coastal marsh water quality is important not only for the purpose of predicting natural variation in water quality, but also for understanding the implications of wetland loss that often occurs as a result of human development (Wolter et al 2006). Like Johnston et al (1990), we found wetland cover to be a significant factor determining COND levels. Wetlands have the ability to filter dissolved ions and nutrients in surface runoff (Hemond and Benoit 1988; Johnston et al 1990) and can therefore help reduce ionic concentrations. As expected, we also found that greater wetland cover is related to lower levels of TNN in marshes at the watershed outflow. This is consistent with a large body of literature that outlines the importance of wetlands in the nitrogen cycle. Wetlands produce anoxic conditions which promote denitrification and permanent removal of nitrates from runoff (e.g., Whigham et al 1988; Seitzinger 1994). While other studies have confirmed that Precambrian Shield wetlands are important in the retention of nitrates (Devito et al 1989; Devito and Dillon 1993), other factors could have influenced the relationship observed in this study. Road density was the sole measure of human development examined, and it is possible that within Georgian Bay an inverse relationship exists between wetland cover and other measures of development such as the proportion of human-altered land; if this were the case, an increase in TNN loadings as a result of human activities could result in a negative relationship between wetland cover and TNN.

Previous studies have found conflicting results regarding the relationship between wetland cover and TP export; some researchers have shown a negative relationship (Johnston et al 1990; Houlahan and Findlay 2004), while others have found a positive relationship between the two variables (Dillon and Molot 1997; Devito et al 2000). We did not find wetland cover to be a significant factor affecting TP in Georgian Bay coastal marshes. This may be due to overriding factors not accounted for in our study, including the hydrological setting of wetlands within the landscape; wetlands connected directly to each other and to the lake tend to export P and other nutrients more readily than those that are separated by a large upland area (D'Arcy and Carignan 1997; Devito et al 2000). Additionally, wetland type can play a large role in determining whether they behave as sources or sinks of P (Devito et al 1989); our inability to distinguish among wetland types in the database means that we are uncertain as to whether they differed among watersheds or different bedrock types. Our finding of higher TSS and ISS levels in marshes with a larger proportion of the watershed covered by wetlands is somewhat consistent with the findings of Johnston et al (1990);

they found that while wetlands tend to retain ISS, wetland extent was positively related to suspended solids export when wetlands drained directly into streams. This suggests that where wetlands are hydrologically well connected to the lake, as is often observed in beaver-influenced coastal areas of Georgian Bay, the drainage of wetlands can lead to higher concentrations of suspended solids in coastal zones.

The seasonality of our sampling likely influenced the observed associations between wetland cover and water quality dynamics. The efficiency of wetlands at removing or exporting suspended solids, phosphorus, ammonia and nitrates may depend on flow conditions (Johnston et al 1990). Our sampling was conducted only during late spring and summer months and, therefore, represents water quality conditions during low flow. Since export of sediment, nutrients and dissolved ions tend to vary considerably with season due to changes in biotic uptake and the amount of precipitation and runoff (Devito et al 1989; Johnston et al 1990; Schiff et al 1998; Eimers et al 2008), sampling during peak spring runoff may lead to very different conclusions regarding the importance of wetlands in influencing water quality variation within Georgian Bay.

Our study was based on the premise that water quality conditions in coastal wetlands are influenced by characteristics of associated watersheds. We have shown this to be true for several water quality variables within Georgian Bay. Furthermore, we have shown that within this sparsely populated region, road density has a stronger influence on water quality than do physical watershed features such as size, wetland cover and bedrock type. Due to the high potential for nutrient and sediment loading during spring snowmelt, future work should focus on quantifying watershed impacts during both low and high flow to capture variation in nutrient pulses. The insight provided by this study, however, gives a solid basis for further investigations into watershed-water quality interactions in Georgian Bay coastal marshes and other freshwater coastal systems. These investigations should lead to establishment of appropriate site-specific water quality standards and permit proper assessment of anthropogenic contributions to changes in water quality.

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Table 1.1: List of the 28 watersheds, along with their assigned names and codes, and a summary of landscape characteristics for each. This includes watershed area, proportion of the watershed occupied by wetland (PROPWET), non-limited-access road density (RDNL), limited-access road density (RDLA) and bedrock type (classified as Precambrian Shield [PS] or sedimentary [SED]).

OMNR Code	Assigned Name	Assigned Code	Area (ha)	PROP WET	RDNL ($m\ ha^{-1}$)	RDLA ($m\ ha^{-1}$)	Bedrock Type
2CE-01	La Cloche	LCL	27,269	0.0321	1.973	1.918	PS
2CE-02	Spanish River	SPR	555,653	0.0412	1.367	1.166	PS
2CF-02	Philip Edward Island	PEI	4,909	0.0868	--	--	PS
2CF-18	McGregor Islands	MGI	2,179	0.0699	--	--	PS
2CG-06	Great La Cloche Island	GLC	9,643	0.0132	1.402	6.711	SED
2CG-07	Northeast Manitoulin	NEM	13,847	0.0520	7.418	3.618	SED
2CG-33	Strawberry Island	STI	1,625	0.0486	--	--	SED
2CH-01	Beaverstone River	BVR	12,957	0.1081	0.061	0.033	PS
2CH-04	Whitefish River	WFR	26,527	0.0408	1.582	0.864	PS
2DD-01	French River 1	FR1	126,103	0.0588	2.170	1.315	PS
2DD-03	French River 2	FR2	105,176	0.0533	0.937	1.746	PS
2EA-01	Key River	KYR	19,669	0.1071	0.335	1.387	PS
2EA-04	Giroux River	GIR	10,949	0.2246	1.226	0.143	PS
2EA-05	Pointe au Baril	PAB	11,554	0.1263	2.555	0.732	PS
2EA-06	Shebeshekong River	SBR	19,720	0.2329	5.167	0.809	PS
2EA-07	Parry Island	PYI	7,666	0.1129	4.476	1.161	PS
2EA-08	Spider Bay	SPB	8,816	0.0523	0.600	0.123	PS
2EA-10	Naiscoot River	NAR	92,622	0.0791	2.388	1.275	PS
2EA-13	Shawanaga River	SHR	30,979	0.1035	2.333	1.019	PS
2EA-24	East Coast Islands	ECI	11,151	0.0332	--	--	PS
2EB-01	Moon-Musquash Islands	MMI	4,392	0.0102	--	--	PS
2EB-02	Moon River-Musquash River	MMR	71,731	0.0660	3.075	1.490	PS
2EC-17	Severn River	SER	70,445	0.0902	6.221	3.713	PS
2EC-18	Beausoleil-Bone Islands	BBI	1,683	0.0016	0.027	3.112	PS
2ED-04	Sturgeon Bay-Hog Bay	SHB	18,887	0.0438	14.002	1.098	SED
2ED-05	Matchedash Bay	MTB	21,727	0.0258	16.134	1.340	SED
2FA-05	Tobermory	TOB	9,307	0.0295	8.042	3.707	SED
2FA-13	Fathom Five	FAF	1,372	0.0183	--	--	SED

Table 1.2: Correlation matrix for water quality and watershed variables. $P<0.05$ when /r/ ≥0.38 (also shown in boldface).

	PROPWET	$\log_e$ area	RDLA	RDNL	WQI	$\log_e$ TP	$\log_e$ SRP	$\log_e$ TN	sqrt TNN	$\log_e$ TAN	$\log_e$ COND	$\log_e$ TSS	sqrt ISS
PROPWET	1.00												
$\log_e$ area	0.11	1.00											
RDLA	-0.28	0.16	1.00										
RDNL	-0.04	0.20	0.26	1.00									
WQI	0.02	-0.34	-0.11	**-0.76**	1.00								
$\log_e$ TP	0.01	**0.57**	0.21	**0.49**	**-0.60**	1.00							
$\log_e$ SRP	-0.32	0.32	0.21	0.08	-0.16	**0.45**	1.00						
$\log_e$ TN	-0.23	-0.01	-0.08	0.22	**-0.48**	0.07	0.14	1.00					
sqrt TNN	**-0.45**	0.06	0.12	**0.38**	**-0.39**	0.06	0.14	0.06	1.00				
$\log_e$ TAN	-0.18	0.17	0.31	0.34	**-0.57**	**0.44**	0.37	0.33	0.32	1.00			
$\log_e$ COND	**-0.42**	-0.05	0.13	**0.56**	**-0.66**	0.11	0.17	0.29	**0.59**	0.37	1.00		
$\log_e$ TSS	0.32	0.25	-0.01	**0.51**	**-0.67**	**0.46**	-0.30	0.01	0.11	0.22	0.30	1.00	
sqrt ISS	0.37	0.09	0.02	**0.45**	**-0.60**	**0.46**	-0.30	0.12	-0.07	0.29	0.19	**0.81**	1.00

Table 1.3: Summary of water quality data from the 28 quaternary watersheds. See text for explanation of abbreviations of water quality variables.

CODE	*n*	WQI score	TP (μgL^{-1})	SRP (μgL^{-1})	TN (mgL^{-1})	TNN (mgL^{-1})	TAN (mgL^{-1})	COND (μScm^{-1})	TSS (mgL^{-1})	ISS (mgL^{-1})
LCL	2	1.522	21.36	10.76	0.950	0.205	0.015	83	0.92	0.49
SPR	4	0.621	27.80	5.80	1.334	0.317	0.056	123	4.78	3.10
PEI	3	1.420	11.15	2.45	1.500	0.038	0.012	123	4.26	2.32
MGI	2	1.555	12.54	5.44	0.520	0.420	0.030	102	0.92	0.01
GLC	3	1.812	16.03	6.11	0.387	0.137	0.017	100	1.13	0.69
NEM	1	0.848	18.81	2.37	0.834	0.327	0.037	101	7.78	3.55
STI	1	1.778	9.22	2.37	2.400	0.060	0.001	67	1.21	0.54
BVR	3	1.254	12.91	3.87	5.467	0.040	0.011	64	2.32	1.62
WFR	6	1.538	17.58	9.68	0.882	0.307	0.039	104	1.00	0.20
FR1	2	1.577	28.61	6.30	0.450	0.075	0.001	74	1.77	0.05
FR2	2	1.377	29.30	7.27	0.400	0.020	0.030	82	1.85	0.79
KYR	3	1.477	30.94	7.33	0.181	0.118	0.004	54	6.25	4.39
GIR	4	1.857	9.91	3.70	0.100	0.031	0.003	51	2.43	0.97
PAB	5	1.351	22.84	4.60	0.444	0.088	0.018	101	4.18	3.40
SBR	3	0.939	23.83	1.59	0.334	0.090	0.011	94	11.88	7.81
PYI	4	1.195	26.70	5.70	2.375	0.084	0.036	53	3.21	3.78
SPB	3	1.658	9.43	3.36	0.333	0.233	0.001	133	3.04	0.62
NAR	2	1.361	20.34	6.91	0.520	0.320	0.010	81	3.80	0.01
SHR	3	2.150	23.56	2.55	0.162	0.043	0.004	26	2.20	1.76
ECI	12	1.531	14.26	4.48	0.367	0.169	0.014	121	3.47	2.50
MMI	5	1.627	19.45	3.40	0.377	0.243	0.015	87	4.23	1.01
MMR	22	1.805	11.93	2.65	0.431	0.184	0.006	65	2.84	0.71

Table 1.3: (Continued).

CODE	n	WQI score	TP (μgL^{-1})	SRP (μgL^{-1})	TN (mgL^{-1})	TNN (mgL^{-1})	TAN (mgL^{-1})	COND (μScm^{-1})	TSS (mgL^{-1})	ISS (mgL^{-1})
SER	13	0.991	22.37	5.88	0.893	0.270	0.022	160	5.78	2.48
BBI	3	1.620	16.87	6.76	0.480	0.063	0.028	105	2.46	0.71
SHB	3	0.651	26.29	11.07	1.460	0.210	0.027	216	3.51	1.71
MTB	3	-0.059	43.06	4.62	1.377	0.427	0.037	331	13.29	6.74
TOB	5	1.277	12.95	3.00	0.350	0.312	0.012	129	2.56	1.11
FAF	4	1.937	9.34	2.69	0.350	0.337	0.003	138	1.34	0.70

Table 1.4: Watershed parameters retained in stepwise multiple regression models to predict water quality variables. Watershed variables are listed in the order they were entered into the model.

WQ variable	Watershed variable	r^2	P	Regression Coefficient (±SE)
$\log_e$ TP	$\log_e$ area	0.33	0.0027	+0.1462 (±0.0438)
	RDNL	0.15	0.0136	+0.0401 (±0.0151)
sqrt TNN	Prop. wetland	0.20	0.0132	-1.2188 (±0.4569)
	RDNL	0.13	0.0358	+0.0138 (±0.0062)
$\log_e$ COND	RDNL	0.31	0.0010	+0.0639 (±0.0171)
	Prop. wetland	0.16	0.0122	-3.4028 (±1.2589)
$\log_e$ TSS	RDNL	0.26	0.0028	+0.0912 (±0.0275)
	Prop. wetland	0.11	0.0432	+4.3085 (±2.0225)
sqrt ISS	RDNL	0.21	0.0072	+0.0783 (±0.0267)
	prop wetland	0.15	0.0219	+4.8075 (±1.9660)
WQI	RDNL	0.58	<0.0001	-0.0864 (±0.0144)

Table 1.5: Overall equations modeling relationships between water quality variables and watershed variables, generated using stepwise multiple regressions.

WQ variable	r^2	r^2_{adj}	P	Equation
$\log_e$ TP	0.47	0.43	0.0003	+1.3604 + 0.1462($\log_e$ area) + 0.0401(RDNL)
sqrt TNN	0.33	0.28	0.0062	+0.4455 - 1.2188(PROPWET) + 0.0138(RDNL)
$\log_e$ COND	0.47	0.43	0.0004	+4.5978 + 0.0639(RDNL) – 3.4028(PROPWET)
$\log_e$ TSS	0.37	0.32	0.0028	+0.4883 + 0.0912(RDNL) + 4.3085(PROPWET)
sqrt ISS	0.36	0.31	0.0038	+0.6408 + 0.0783(RDNL) + 4.8075(PROPWET)
WQI	0.58	0.57	<0.0001	+1.6388 - 0.0864(RDNL)

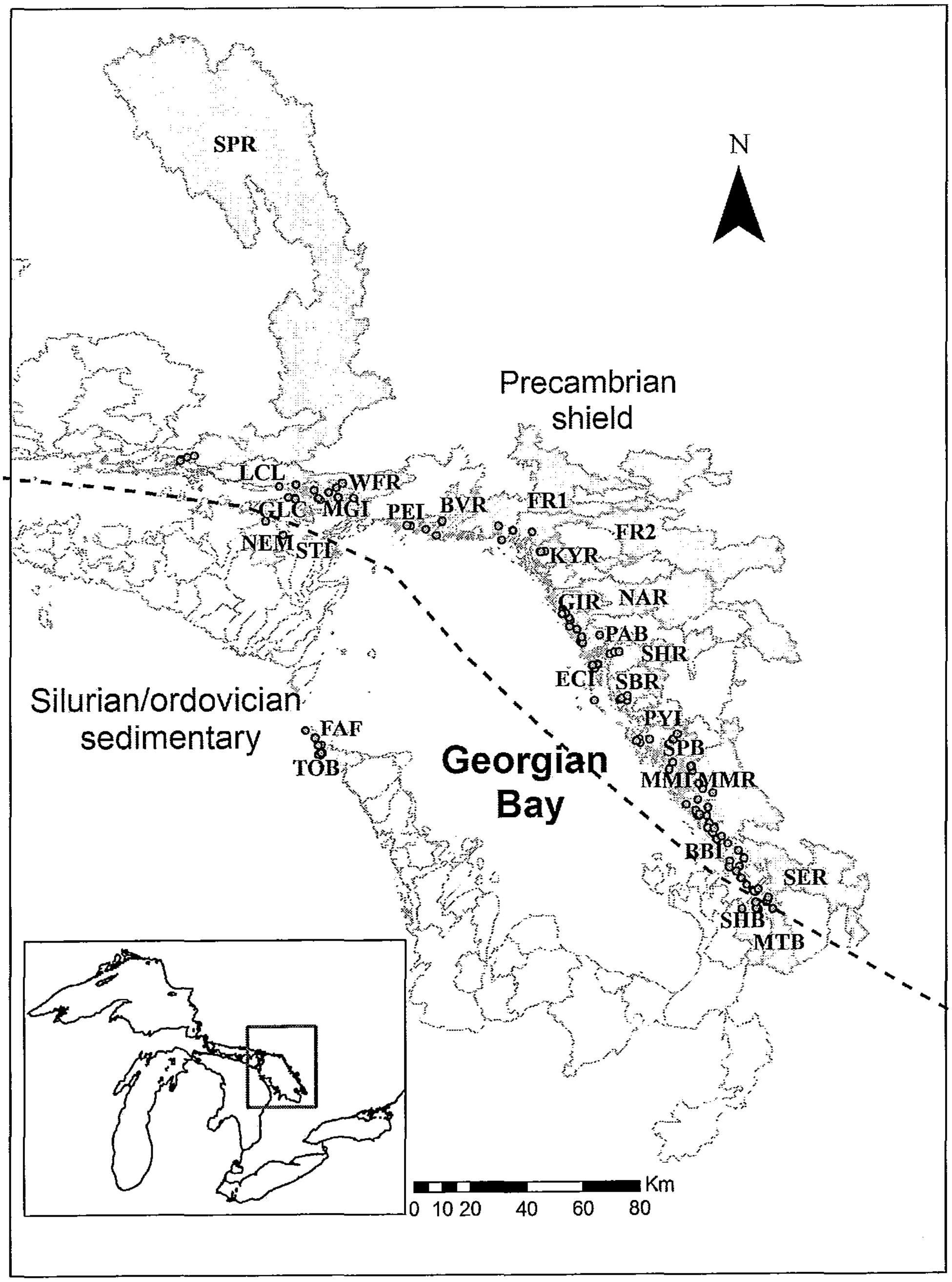

Figure 1.1: Map of water quality testing sites at outflows of quaternary watersheds in Georgian Bay. The dashed line separates watersheds underlain by Precambrian Shield bedrock and sedimentary bedrock.

Figure 1.2: Photo of a typical Precambrian Shield landscape that characterizes much of eastern and northern Georgian Bay. Thin soils and vegetation overlie hard, metamorphic rock.

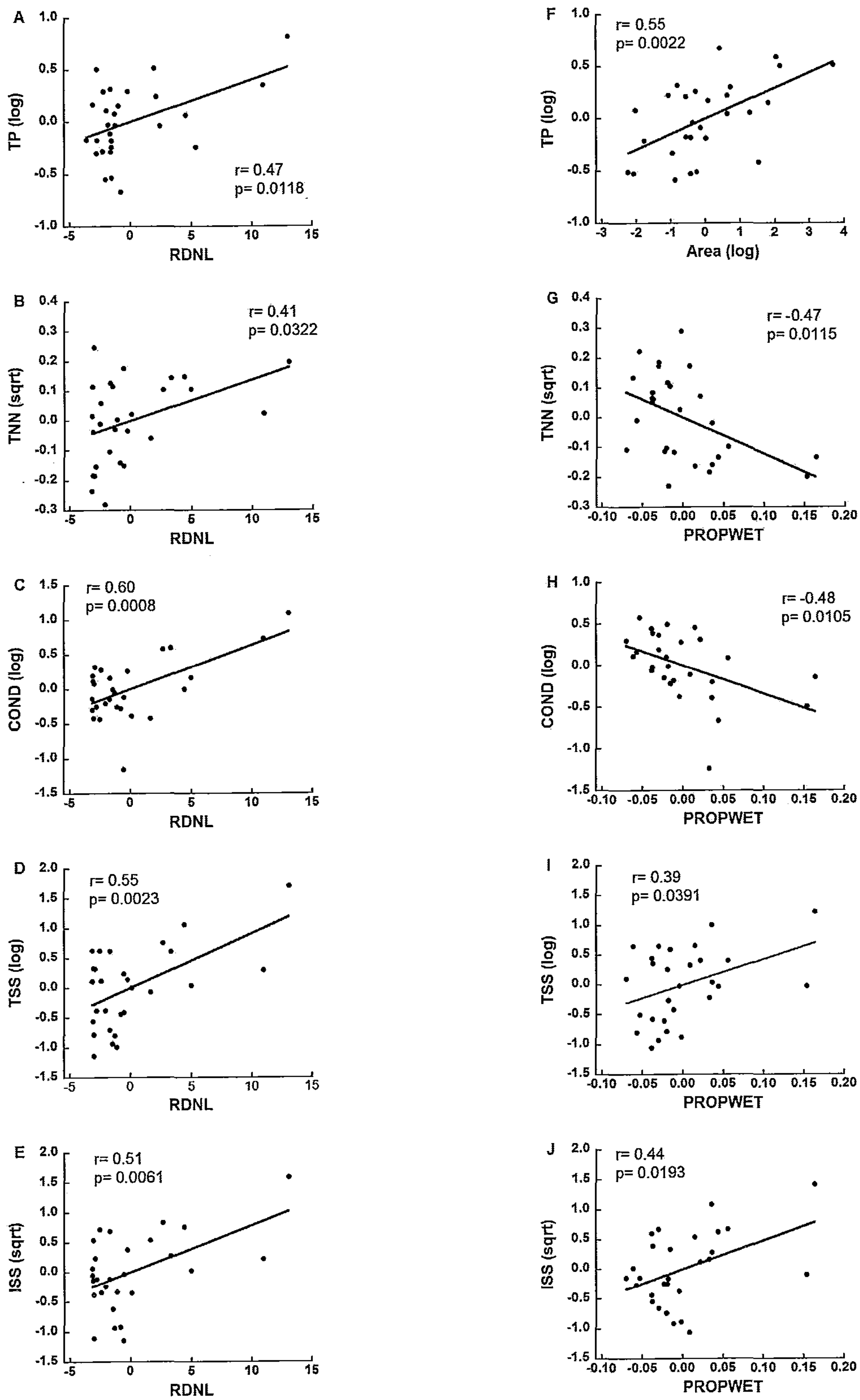
A
TP (log)
RDNL
r= 0.47
p= 0.0118
B
TNN (sqrt)
RDNL
r= 0.41
p= 0.0322
C
COND (log)
RDNL
r= 0.60
p= 0.0008
D
TSS (log)
RDNL
r= 0.55
p= 0.0023
E
ISS (sqrt)
RDNL
r= 0.51
p= 0.0061
F
TP (log)
Area (log)
r= 0.55
p= 0.0022
G
TNN (sqrt)
PROPWET
r= -0.47
p= 0.0115
H
COND (log)
PROPWET
r= -0.48
p= 0.0105
I
TSS (log)
PROPWET
r= 0.39
p= 0.0391
J
ISS (sqrt)
PROPWET
r= 0.44
p= 0.0193

Figure 1.3: Partial plots of watershed variables by water quality variables, controlling for other variables in their respective multiple regression models: (A) $\log_e$ area, (B-E) PROPWET and (F-J) RDNL.

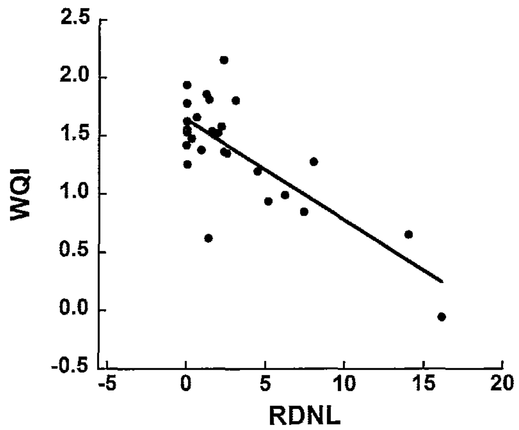

Figure 1.4: Regression of WQI on road density (non-limited-access roads). Road density alone explained 58.2% of variation in WQI scores among quaternary watersheds.

Chapter 2:

Effects of landscape variables and season on water chemistry of coastal marshes in eastern Georgian Bay

DeCatanzaro, R., and Chow-Fraser, P. Submitted 2010 to Limnology and Oceanography.

Abstract

We surveyed 34 marshes in relatively pristine catchments in Precambrian Shield eastern Georgian Bay in spring and summer of 2009. Discrete water samples were analysed for nutrient and physical parameters and related to a suite of landscape-level variables, including characteristics of the marsh and its drainage basin. The first landscape principal component explained 48% of variation in landscape variables and ordered marshes along a gradient with high values corresponding to large, high-order watersheds containing extensive upstream wetland. This axis was negatively related to specific conductivity, pH, nitrate nitrogen and SO_4^{2-} concentrations and positively related to total phosphorus, colour, suspended solids and summer dissolved organic carbon. Stepwise regression models built using watershed and marsh variables explained up to 64% of the variation in some water chemistry variables, with drainage basin area or order alone explaining up to 44%. Changes in marsh water chemistry parameters between spring and summer sampling periods were consistent for marshes draining high- and low-order catchments. Continuous monitoring at a second-order marsh indicated an increase in specific conductivity and a decrease in colour throughout spring and summer, while total phosphorus also declined in late summer and early fall. Overall, watershed influence was most evident in marshes draining large, high-order watersheds and during spring snowmelt. These results highlight the critical role of catchment morphology and season in influencing reference water chemistry of coastal marshes.

Key words: conductivity; drainage basin; freshwater marsh; hydrology; nutrients; slope

Introduction

Great Lakes coastal marshes are highly productive (Jude and Pappas 1992) and dynamic (Keough et al 1999) ecosystems with hydrologic connections to both their watershed and the adjoining lake. Human activities such as water-level manipulation and land development have had major impacts on coastal marsh dynamics in many parts of the Great Lakes (Mayer et al 2004). Urban and agricultural development can be particularly detrimental, causing increases in nutrient loadings and turbidity of coastal marshes (Crosbie and Chow-Fraser 1999; Morrice et al 2008) that result in shifts in trophic status and species assemblages (Jude and Pappas 1992; Lougheed et al 2001; Seilheimer and Chow-Fraser 2006). Wetlands vary in their sensitivity to altered hydrology and watershed dynamics, and it is widely recognized that in order to ensure proper management of these ecosystems, a better understanding of the natural hydrologic and geologic factors controlling the conditions of coastal wetlands is critical (Keough et al 1999; Mayer et al 2004; Morrice et al 2004).

Within forested landscapes, catchment morphology can exert a strong influence on the natural chemistry of surface waters. Landscape-level studies undertaken on inland lakes of the Boreal Plains of Alberta (Devito et al 2000; Prepas et al 2001) and the Precambrian Shield region of southern Quebec (D'Arcy and Carignan 1997) and south-central Ontario (e.g., Dillon et al 1991; Dillon and Molot 1997; Eimers et al 2008) have provided some insight into the general relationships between catchment features and lake chemistry. A number of these studies have found that wetland cover, drainage slope, and catchment or drainage area are among the strongest predictors of nutrient and ion concentrations and lake productivity (e.g., Dillon and Molot 1997; D'Arcy and Carignan 1997; Prepas et al 2001).

Great Lakes coastal wetlands are distinct from other freshwater inland systems in that their hydrology and chemistry are further influenced by large-lake processes through a direct hydrological connection (Mayer et al 2004). Recent studies by Trebitz et al (2002) and Morrice et al (2004) have demonstrated that watershed discharge and seiche-driven flow interact to determine residence times and nutrient loadings to coastal wetlands. Strength of hydrologic connections to watershed and lake, and thus nutrient fluxes, vary seasonally and with site morphology; under scenarios of high watershed discharge relative to seiche-driven flow, lake-water inflow and mixing in the wetland is reduced (Trebitz et al 2002; Morrice et al 2004). This is similar to the interaction of river flow and tides in coastal estuaries and salt marshes (e.g., Duxbury 1979).

Coastal marshes in the Precambrian Shield portion of eastern Georgian Bay are currently among the least human disturbed in the Great Lakes Basin (Chow-Fraser 2006; Cvetkovic et al 2009) and afford a unique opportunity to study water chemistry dynamics in the absence of major anthropogenic perturbations. Expansion of road networks, increases in cottage and residential development and a drop in lake level are expected to occur, making the establishment of reference conditions of critical importance for this area (see

DeCatanzaro et al 2009). The majority of these marshes form in lacustrine protected embayments (see Albert et al 2005) that have strong, direct surface-water connections with the lake. In contrast to dry conditions that occur throughout much of the summer, climatic conditions in eastern Georgian Bay promote snow accumulation during winter, resulting in high hydrologic flow from watersheds during spring snowmelt; this could have important consequences for upland-wetland hydrologic connectivity (Devito et al 1996) and the relative influences of watershed versus lake on the hydrology and chemistry of coastal marshes (Morrice et al 2004).

Here we examine the role of watershed and marsh morphology in determining reference water chemistry of coastal marshes in eastern Georgian Bay, where potential for mixing with surface water of a large lake creates a dynamic not present in studies of small inland waters. We expect that marshes with larger watersheds and greater hydrologic connectivity to upstream areas would have water chemistry that more closely reflects processes in watersheds of the Precambrian Shield with respect to sediment and nutrient retention and export. By comparison, chemistry of marshes with weak hydrologic connections to uplands would be influenced to a greater extent by the chemistry of Georgian Bay. Secondly, we examine seasonal changes in marsh water chemistry by (*i*) comparing survey data from spring and summer for 19 high-order and 14 low-order catchments, and (*ii*) monitoring changes in marsh water chemistry at a second-order catchment from ice-out to early autumn. We expect higher concentrations of catchment-derived constituents in the marshes during spring, when snowmelt increases discharge and potential for nutrient export, whereas we expect summer chemistry to reflect an increase in lake-water intrusion and mixing under baseflow conditions.

Methods

Study area

We selected 34 coastal marshes in protected embayments with predominantly forested watersheds and minimal human disturbance (no roads in the watershed and no cottages directly bordering the marsh). The marshes are situated between northern Musquash Channel and Woods Bay on the eastern shore of Georgian Bay (Figure 2.1). The landscape is characterized by thin (about 30 cm), sandy, acidic, patchy soils, where Precambrian Shield bedrock is exposed between areas of vegetated till deposits and wetlands (Weiler 1988). Landward vegetation is predominantly a mix of second-growth deciduous and coniferous forests of the Great Lakes-St. Lawrence Forest region, characterized by species such as white pine (*Pinus strolobus*), red pine (*Pinus resinosa*), hemlock (*Tsuga canadensis*), white spruce (*Picea glauca*), sugar maple (*Acer saccharum*), red oak (*Quercus rubra*) and beech (*Fagus grandifolia*). Extensive wetland complexes form in topographic depressions and along beaver (*Castor canadensis*)- altered streams and tributaries.

Within this area, the offshore Bay water is alkaline and has high specific conductivity (COND; 162-198 μS cm^{-1}) due to the influence of dissolved ions from easily-eroded Palaeozoic limestones that surround the south and the west of Georgian Bay (i.e. Bruce Peninsula of the Niagara Escarpment; Weiler 1988). Offshore total phosphorus (TP) concentrations range from 7.0 μg L^{-1} in spring to 3.9 μg L^{-1} in summer, while sulphate (SO_4^{2-}) is over 10 mg L^{-1} and nitrate nitrogen (TNN) over 200 μg L^{-1} during the ice-free season. Concentrations of ammonia nitrogen (TAN; 6-10 μg L^{-1}), dissolved organic carbon (DOC; 2.3-2.7 mg L^{-1}), colour (COL; 3-7 mg L^{-1} Pt) and total suspended solids (TSS; 0.6-0.9 mg L^{-1}) are all low in the open-water areas (MOE unpubl.; Table 2.1). The climate is characterized by extremes of cold and dry or hot and humid weather. Winter temperatures are below freezing for up to four months of the year, while summers have a mean July temperature of 18°C. Average annual precipitation is around 1000 mm. Snowmelt and the majority of high runoff occur in March and April (Weiler 1988).

Landscape analyses

Analyses for all landscape variables (Table 2.2) were performed in ArcGIS 9.2 (ESRI™, Redlands, CA, USA). We delineated marsh drainage basins by using digitized contours and spot elevations of Ontario Base Maps (OBM; 1:10,000; Ontario Ministry of Natural Resources) and applying traditional cartographic procedures. Delineations were made with contours overlain on 2002 1-m resolution IKONOS satellite images to facilitate identification of surface drainage networks. Drainage basin area (DBA) was calculated from watershed polygons. We determined average slope (SLOPE) for each watershed by using the Provincial Digital Elevation Model (10 m resolution; Ontario Ministry of Natural Resources) and the Spatial Analyst extension of ArcGIS 9.2.

To calculate catchment/marsh order (ORDER), we used Strahler stream order (Strahler 1952), in a manner similar to that which Riera et al (2000) used to determine lake order. ORDER was based solely on surface drainage networks (OBM stream layer) as follows: a zero (0) order marsh receives only diffuse runoff from the watershed (no channelized inputs), a first (1) order marsh is fed by a first-order stream, a second (2) order marsh is fed either by inlets of second order and below or by two or more first-order streams, and a third (3) order marsh is fed either by streams of third order and below or by two or more second-order streams.

To identify and quantify wetland areas within each catchment, we used the McMaster Coastal Wetland Inventory (Chow-Fraser, unpubl.). This inventory was created from the same 2002 IKONOS imagery used to examine surface-water connections. Wetlands upstream of the marsh (WET) that fell within the watershed (also expressed as a proportion of the total watershed area; PROPWET) consisted of a combination of newly formed beaver ponds, fens, marshes, swamps and bogs. Meadow marsh (MED) occurred landward of the shoreline boundary and consisted predominantly of sedges and shrubs, with saturated soils near the surface but without standing water for most of the year. The aquatic marsh (AQUAT) was defined as the fully inundated area occurring at the transition between the meadow and the open water, and is characterized by a mixture of floating, submergent and emergent vegetation. Because the marshes were situated in well-defined embayments, the lakeward boundary of the marsh was drawn across the mouth of the embayment. We used this to calculate drainage ratio (DBA/AQUAT), and the ratio of upstream wetland to aquatic marsh (WET/AQUAT). We also determined the width of the opening that connects the marsh to Georgian Bay (OPEN), through which surface water can flow.

Field sampling

Marsh surveying

Sampling surveys were conducted twice in 2009. The first sampling period was in mid-April during the week following ice-out, towards the end of the snowmelt period. All sites except HNB were visited at this time. The second round of sampling occurred over a 10-day period in mid-July; this corresponded with conditions of tributary baseflow and the time during which many sampling programs are conducted to assess Great Lakes water quality (e.g., Chow-Fraser 2006; Trebitz et al 2007; Morrice et al 2008). Sampling was not undertaken during or within 48 h following notable (>5 mm) rain events. The time of day during which sampling occurred varied from site to site, but fell between the hours of 08:30 and 18:00 h.

Samples were collected adjacent to the longest axis of the watershed, near the 0.5 m to 1.0 m depth contours, depending on accessibility and site morphology. We sampled at roughly the same locations during spring and summer surveys (locations were marked on a map and GPS points were taken). Efforts were made not to disturb submerged vegetation. A YSI 6600 multiprobe (YSI, Yellow Springs, Ohio, USA) was used to measure COND and pH *in situ*. Water samples for nutrient and suspended solids analysis were collected at mid-depth and kept cold until they could be processed or frozen at the end of the day.

Continuous monitoring

Following ice-out in mid-April, an ISCO 6720 automatic water sampler and a YSI 6600 multiprobe were installed at Black Rock marsh (BLR) in Tadenac Bay (Figure 2.1). BLR is a second-order marsh located downstream of a series of wetlands that have resulted from construction of beaver dams. Upstream surface waters have low mid-summer pH (5.16-6.45) and COND (3-15 $\mu S\ cm^{-1}$), and high TP (11.9-61.9 $\mu g\ L^{-1}$) and COL (170-345 mg L^{-1} Pt). The ISCO sampler collected daily water samples in the marsh which were later analysed for COL and TP, and the probe stored hourly measurements of COND and pH. The probe was calibrated in the lab before deployment and COND and pH were checked/ calibrated with standards in the field during site visits (generally every 20-24 days). Meteorological data were obtained from the nearest Environment Canada weather station in Parry Sound and an on-site ISCO 647 rain gauge.

Sample processing

Water samples for total ammonia nitrogen (NH_3–N+ NH_4^+–N; TAN), total nitrate-nitrite nitrogen (NO_3^-–N+ NO_2^-–N; TNN), COL and SO_4^{2-} were processed on the day of collection with a Hach DR/890 colorimeter and Hach reagents and protocols. During this time, samples for TSS were also filtered through pre-weighed 0.45 μm GF/C filters, which were frozen until subsequent analysis. Filtrate was frozen and stored for later analysis of soluble reactive phosphorus (SRP) content, and acidified with nitric acid (to a pH< 2) and refrigerated at 4°C for later analysis of DOC content. Raw water samples were frozen and stored for TP analyses.

During laboratory processing, TP samples were digested by persulfate digestion in an autoclave. SRP samples (undigested) and digested TP samples were then analysed according to the molybdenum blue method (Murphy and Riley 1962), with absorbance readings taken on a Genesys spectrophotometer. TSS filters were dried in a drying oven at 100°C for 1 h, placed in a desiccator for 1 h, and weighed. Preserved DOC samples were analysed with the NPOC method in a Shimdzu TOC-VCHP Analyser.

Data analysis and statistics

Statistical analyses were performed in SAS JMP 7.0, with α=0.05. SO_4^{2-}, TAN and TNN values that fell below the detection limit (1 mg L^{-1}, 10 μg L^{-1} and 10 μg L^{-1}, respectively) were assigned half the detection limit value, a technique commonly used to treat data with concentrations below detection (e.g., Trebitz et al. 2007). Variable data with non-normal distributions were $\log_{10}$- or square root (sqrt)- transformed as appropriate. Spring TSS for WB1 was excluded due to an abnormally high value resulting from wind-stirring of sediment on the day of collection. We used Pearson correlation matrices to examine relationships among landscape variables and among water chemistry variables. Pearson correlation was also used in initial examination of bivariate relationships between landscape and water chemistry variables. Means of water chemistry variables were used with the exception of DOC; we used summer DOC because preliminary analyses revealed that only summer concentrations were significantly related to landscape variables.

Due to multicollinearity among landscape variables, we used two statistical methods to aid interpretation of relationships between landscape and water chemistry variables. First, we conducted a Principal Components Analysis (PCA) using a correlation matrix to condense transformed landscape variables (Table 2.2) into synthetic axes that best explain the variation (Shaw 2003). Axes with an eigenvalue greater than one were retained for further analysis. We interpreted principal component (PC) axes by using Pearson correlation to examine the strength of the relationships between the landscape variables and each retained PC axis. We then regressed water chemistry variables against PC site scores. This technique allowed us to focus on the shared contributions of all explanatory variables (Graham 2003). Secondly, we used the same set of landscape variables in a forward stepwise multiple regression analysis to generate explanatory models for water chemistry variables. Only variables having statistically significant effects were retained in the models. Strong collinearity among sets of landscape variables sometimes resulted in one variable (e.g., DBA) being excluded due to prior introduction of a closely related variable (e.g., ORDER) into the model. In such cases, we also present alternative models that produced nearly equivalent or improved adjusted r^2-values.

We used mixed-model ANOVAs to determine whether water chemistry variables differed in their concentrations between spring and summer surveys, and between marshes with different degrees of hydrologic connectivity to the watershed. Catchments were categorized as low order (zero and first order) or high order (second and third order). The analyses were performed with order (low vs. high) as the between-subjects factor and season (spring vs. summer) as the within-subjects (repeated measures) factor. Continuous data from Black Rock marsh was averaged over five-day intervals and used along with discrete survey data to examine seasonal trends in marsh chemistry.

For each marsh, we used specific conductivity to estimate the proportion of marsh water (marsh) that was derived from offshore Georgian Bay (Bay) relative to the proportion that was derived from watershed runoff (runoff) using the formula:

$$\% \text{ Bay} = 100\text{x} \ ([\text{COND}_{\text{marsh}}] - [\text{COND}_{\text{runoff}}]) \ / \ ([\text{COND}_{\text{Bay}}] - [\text{COND}_{\text{runoff}}])$$

We used conductivity due to the large difference in concentrations of tributary and Bay water, and because it is a relatively conservative natural tracer (e.g., Cox et al 2007). Conductivity of the Bay is around 162 $\mu S\ cm^{-1}$ in spring and 198 $\mu S\ cm^{-1}$ in summer (Table 2.1). Conductivity of tributary runoff is generally low in this area (3-15 $\mu S\ cm^{-1}$; DeCatanzaro unpubl.), and we used a conservative value of 7 $\mu S\ cm^{-1}$.

Results

Landscape and water chemistry characteristics

Watersheds ranged broadly in size from 6.8 ha (MB3) to 584.4 ha (GHR), with a mean of 146.4 ha (Table 2.3). Twenty catchments were classified as high order (second or third order) and 14 as low order (zero or first order). Several of the smaller watersheds did not contain any upstream wetland, while GHR, MR1 and MB2 each contained over 100 ha of wetland upstream of the marsh. Typical of other regions in Georgian Bay, most aquatic marshes in this study were smaller than 10 ha in size, with the exception of MR1, MRB and WB1. Mean watershed slope ranged from 0.6% (TB2) to 9.7% (WB1), with an average of 4.4%. There was considerable collinearity among landscape variables, with the strongest correlations occurring between DBA and both ORDER (r=0.84) and WET (r=0.88) and between WET and WET/AQUAT (r=0.89; Table 2.4A).

Means and ranges of water chemistry variables (spring, summer and seasonal average) for all sites are given in Table 2.1. Compared with the offshore, water in coastal marshes was high in TP, SRP, TAN, TSS, COL and DOC and low in pH, COND, TNN and SO_4^{2-}. Several of the water chemistry variables were significantly correlated with each other (Table 2.4B). The strongest relationships were between COND and each of SO_4^{2-} (r=0.86), pH (r=0.61) and COL (r=-0.60), and between COL and each of TP (r=0.61) and SO_4^{2-} (r=-0.75). Although mean DOC was not significantly correlated with mean COL, summer concentrations of DOC and COL were significantly positively correlated with each other (r=0.48, *P*=0.0038).

Pearson correlations revealed several trends in relationships between landscape and water chemistry variables (Table 2.5). Mean COND, SO_4^{2-}, pH, COL, TSS, and often TP, were generally correlated to the same set of landscape variables, with concentrations of many of these variables showing the strongest correlations to ORDER and DBA; these relationships were positive in the case of COL, TSS and TP, and negative in the case of COND, SO_4^{2-} and pH. Both TP and TNN were positively related to SLOPE, and TP was also positively related to AQUAT. Summer DOC showed positive relationships to DBA and upstream wetland variables (WET, PROPWET, WET/AQUAT), whereas spring and mean DOC concentrations were not significantly related to landscape variables. TAN was positively correlated with DBA, MED and OPEN, while SRP was not significantly related to any landscape variable.

Landscape principal components

Principal Components Analysis of landscape variables yielded 2 axes with eigenvalues greater than one, together explaining 70.6% of the variation in the dataset (Table 2.6). PC1 explained 48.0% of the variation in the data and was highly positively correlated with WET, DBA, WET/AQUAT, ORDER, PROPWET and DBA/AQUAT, and weakly correlated with MED. High scores on PC1 are therefore interpreted as marshes that drain large, high-order watersheds with large areas of upstream wetland. PC2 explained an additional 22.6% of the variation, and showed strong positive relationships with AQUAT, OPEN and MED, a strong negative relationship with DBA/AQUAT and weak positive relationship with SLOPE; high PC2 scores are therefore most strongly associated with large, open marshes with greater exposure to wind and wave action.

PC1 was strongly related to several water chemistry variables; it was positively related to mean TP, COL and TSS, and to summer DOC, and negatively related to mean TNN, SO_4^{2-}, COND and pH (Figure 2.2). PC2 was not as strongly related to water chemistry variables; however, it was significantly positively related to mean TP (r^2=0.20, P=0.0091), TAN (r^2=0.17, P=0.0170) and TSS (r^2=0.15, P=0.0286).

Stepwise regression models

Stepwise regressions identified sets of factors that can best explain the variation in water chemistry variables (Table 2.7). ORDER was first to enter the models for COND (r^2=0.39), COL (r^2=0.44), TSS (r^2=0.29) and TP (r^2=0.29) while DBA was first to enter the models for SO_4^{2-} (r^2=0.38) and pH (r^2=0.44). In the majority of cases, alternative models that used the other predictor (either DBA or ORDER) resulted in only slightly lower r^2. For COND and SO_4^{2-}, no other landscape variables had significant effects in the models. SLOPE had significant effects for pH, TSS and TP, while AQUAT entered the model for pH and one of the models for TP, and MED entered one of the models for COL.

Both SLOPE and DBA/AQUAT entered into the stepwise regression model for mean TNN. Unlike other chemistry variables, mean TAN was most closely related to marsh-level variables; MED and OPEN together explained 36% of variation in TAN concentrations. Because the landscape variables examined in our study were not significant predictors of spring or mean DOC, but were significant for summer DOC, we only performed stepwise regression for summer concentrations. WET was the first and only variable entered into the stepwise regression; however, a nearly equivalent model containing WET/AQUAT produced only a slightly lower r^2.

Seasonal patterns in marsh water chemistry

The mixed-model ANOVAs revealed that TP, pH, COL and TSS did not differ significantly between the April and July sampling periods (Table 2.8, Figure 2.3). SRP, TNN and DOC concentrations were all lower in summer compared with spring, while TAN, SO_4^{2-} and COND were higher in summer. Marshes in high-order catchments had significantly higher TP, SRP and COL, and lower SO_4^{2-}, COND and pH compared with marshes in low-order catchments; however, no interaction effects were observed, and both classes showed the same overall trends with respect to increasing or decreasing concentrations between spring and summer.

Continuous monitoring at Black Rock provided a more detailed picture of the dynamics of key water chemistry variables at a second-order marsh from April through October (Figure 2.4). Consistent with the broader surveys, COND at this site increased throughout the spring and summer, from around 20 $\mu S\ cm^{-1}$ to nearly 80 $\mu S\ cm^{-1}$, before declining in early fall. Water pH fluctuated between 6.1

and 6.9 throughout the monitoring period. TP ranged between 14 $\mu g\ L^{-1}$ and 25 $\mu g\ L^{-1}$ through the months of April to July, after which it began to decline; the lowest five-day averaged concentration was 9 $\mu g\ L^{-1}$ in early October. COL was highest in spring (up to 250 mg L^{-1} Pt), and declined in summer and early fall to a low of 56 mg L^{-1} Pt in early October. There was a decline in COND and increase in TP and COL towards the end of the monitoring period which coincided with a period of high rainfall.

Estimates of runoff and Bay water mixing

Estimates of lake water contributions based on specific conductivity concentrations in the marshes were low. Georgian Bay water constituted between 1% (at MRB) and 43% (at ALB) of marsh water in April, with a mean of 11%. In July, the estimated contribution of water from offshore Georgian Bay ranged from 4% (at TL2) to 56% (at BRI), with a mean of 20%.

Discussion

Watershed runoff versus Georgian Bay water

Marshes examined in our study lie at the transition between Precambrian Shield watersheds and Georgian Bay, and represent critical ecotones and areas of unique water chemistry. Precambrian Shield watersheds export significant quantities of sediment, DOC, P and colour to downstream surface waters (Gergel et al 1999; Dillon and Molot 2005; Eimers et al 2008). Catchment soils and wetlands also tend to retain a large percentage of atmospherically-derived nitrate

(Devito et al 1989; Dillon and Molot 1990), and under some conditions (e.g., sustained high water table) can retain sulphate (Devito 1995). Consequently, runoff tends to be highly coloured, acidic and relatively phosphorus-rich, but low in dissolved ions (Allan et al 1993). By comparison, Georgian Bay water is alkaline and relatively low in phosphorus, but is a relatively rich source of dissolved ions, including sulphate and nitrate. Because coastal marshes are influenced by temporally variable watershed contributions and intrusion of Georgian Bay water, both watershed landscape variables and season were important factors affecting water chemistry in this study.

Landscape influences on marsh water chemistry

We found that larger drainage basins tended to be of higher order, containing more upstream wetland both in terms of absolute area and as a proportion of the total watershed. Thus, marshes were ordinated along a gradient related to degree of watershed influence, that is, potential to generate runoff that is subject to land-based processes such as nutrient and ion uptake, transformation and release in soils and wetlands (Devito et al 1989; Allan et al 1993). Sites with larger watershed influence (higher PC 1 scores) had higher concentrations of TP, COL, TSS, H^+ and DOC, but lower concentrations of COND, TNN and SO_4^{2-}. Since PCA could not elucidate the degree to which watershed size alone versus other factors (e.g., proportion of the watershed that is upstream wetland or the strength of hydrologic flows) influenced water chemistry, we relied on the relative strength of each independent variable in regression analyses to provide further insight.

Stepwise regressions identified DBA and ORDER as the strongest predictors of the majority of marsh water chemistry variables including SO_4^{2-} and pH (DBA) as well as COND, TP, COL and TSS (ORDER). In this study, DBA and ORDER were often interchangeable as predictors in regression equations. Previous studies on inland lakes have found these variables to be important due to their influence on nutrient loadings. In such systems, suspended solids, TP, COL and DOC often showed a positive relationship with drainage area or drainage ratio (Schindler 1971; Curtis and Schindler 1997) and strength of the surface drainage network (Kirchner 1975; Devito et al 2000). This positive association is because TSS, DOC and COL are produced and exported over land, and thus, the larger the watershed, the higher the loadings to downstream waters (Dillon and Molot 2005; Eimers et al 2008). Similarly, we attribute the positive relationship between TP concentration and watershed size to the fact that a larger drainage area theoretically results in higher P loading through atmospheric deposition (Schindler 1971). Stream networks can be important for delivering constituents to downstream surface waters by promoting hydrologic flushing from nutrient-rich surface soils and wetlands (Devito et al 2000); this may partly explain why ORDER was sometimes a stronger predictor of marsh water chemistry variables than was DBA.

In coastal marshes, drainage area can also affect water chemistry by influencing marsh hydrology. In Precambrian Shield landscapes, larger watersheds produce higher discharge (Yao et al 2008; Buttle and Eimers 2009), which in turn reduces the potential for seiche-induced inflow of lake water to the marsh; this may be particularly evident when tributary networks provide a strong hydrologic link between the watershed and marsh (Trebitz et al 2002; Figure 2.5A, C). The highly significant negative relationships between COND and both DBA and ORDER strongly support the theory that marshes with large, high-order watersheds contain a lower proportion of water of lake origin, and can explain why these marshes have lower water pH, TNN and SO_4^{2-} concentrations.

Summer DOC was the only water chemistry variable that was most strongly related to the amount of upstream wetland. This is consistent with a number of published studies that show an increase in lakewater DOC with increasing area of wetland in the watershed (Dillon and Molot 1997; Gergel et al 1999; Eimers et al 2008), and supports suggestions that wetlands are a major source of DOC exported to streams and lakes (Kothawala et al 2006). Gergel et al (1999) found that the relationship between DOC in lakes and wetland cover in the watershed was strongest late in the ice-free season, and this is consistent with our observation that spring DOC concentrations failed to show the same relationship to wetland variables as did summer concentrations. This can be explained by the fact that DOC production and leaching from peat is highest during summer months (Hongve 1999). Some research also suggests that distinguishing among wetland types may yield stronger relationships between upstream wetland variables and water chemistry variables, since young beaver ponds often have a different effect on runoff chemistry than do mature swamps and fens (Devito et al 1989; Kothawala et al 2006).

Slope contributed significantly to explanatory models for mean TNN, TP, TSS and pH, with positive relationships with each variable except pH. A positive relationship between nitrate levels and slope of the drainage basin has also been observed in other freshwater systems of the Precambrian Shield (Dillon et al 1991; D'Arcy and Carignan 1997); it has been hypothesized that in steeper catchments, fewer areas with saturated soils develop during high runoff, resulting in less opportunity for denitrification and assimilation of nitrate in upper soil horizons (D'Arcy and Carignan 1997). Similarly, less development of anoxic soil conditions in steep catchments can explain the negative relationship between slope and pH. Consistent with our findings, Dillon et al (1991) found a positive relationship between TP export in Precambrian Shield streams and catchment slope, even though it was not statistically significant. By contrast, D'Arcy and Carignan (1997) found a negative relationship, and they attributed this to less opportunity for export of dissolved P in steep catchments. That we also observed higher concentrations of suspended solids in marshes with steeper catchments makes us more confident about a positive relationship, and we suggest that increased sediment export from steep slopes may provide a mechanism for greater export of sediment-bound P to downstream marshes.

Marsh-level variables were generally only weakly related to water chemistry variables. Landscape PC2 ordered marshes along a gradient where high scores corresponded to large, open marshes; this axis was weakly but positively related to TP, TSS and TAN. The positive relationship between TSS and PC2 scores may be the result of greater wind and wave exposure at large, open marshes. This higher TSS may contribute to higher sediment-bound P in the water column. Additionally, high levels of phosphorus and ammonium in larger marshes may be related to storage and release of these nutrients in marsh sediments and organic matter (Bowden 1987; Craft et al 1989).

Seasonal trends in marsh water chemistry

Knowledge of seasonal variation in marsh water chemistry is important in temperate coastal areas, where snowmelt plays a significant role in water and nutrient budgets (Barica and Armstrong 1971). Past studies examining seasonal patterns in coastal marsh water chemistry are few, and tend to be limited to single-site observations (e.g., Mitsch and Reeder 1992; Morrice et al 2004). Our data suggest that, on average, a higher percentage of marsh water was derived from runoff during early spring compared with summer surveys. During spring snowmelt, high hydrologic flow from watersheds can increase runoff contribution and reduce the influx of lake water into coastal bays and wetlands (Trebitz et al 2002; Morrice et al 2004; see Figure 2.5A, C). Spring runoff from Precambrian Shield catchments delivers significant quantities of DOC, colour and P to downstream waters (Dillon and Molot 2005; Eimers et al 2008), but is not a major source of dissolved ions, nitrates and sulphates (Allan et al 1993). Marshes in our study had higher concentrations of DOC and SRP in April than in July surveys.

This, coupled with the trends towards decreased TP and COL later in summer and early fall at Black Rock, demonstrates that coastal marshes receive higher loadings of catchment-derived constituents during spring and early summer.

In contrast to the spring scenario, influx of lake water into coastal wetlands is generally highest during summer, when tributaries are at baseflow (Trebitz et al 2002; Morrice et al 2004; Figure 2.5B, D). Georgian Bay water represents a source of conductivity, alkalinity, nitrates and sulphates to coastal marshes. While nitrates may be used up rapidly in these carbon-rich systems through biotic processes of assimilation and denitrification (Bowden 1987), particularly in the marsh-lake water mixing zone (Morrice et al 2004), sulphates are less readily reduced in the presence of nitrates (Whitmire and Hamilton 2005). This could explain the higher COND and SO_4^{2-} concentrations during summer.

Our estimates of lake-water mixing in the marshes were low, particularly in spring, and we attribute this partly to the morphology of the shoreline in eastern Georgian Bay. The openings to several of the marshes occurred within larger shoreline embayments, which themselves experience varying degrees of mixing with the offshore water. Thus, a portion of the water that enters the marsh during seiche events would have originated as runoff from the surrounding landscape. Examining the position of marshes in relation to broader shoreline morphology may account for some additional variation in water chemistry characteristics. In addition, positioning sampling stations closer to the wetland mouth would have resulted in larger estimates of lake water contributions, particularly for large wetlands that experience more seiche-induced inflow (Trebitz et al 2002).

In addition to watershed and lake influxes, seasonal changes in bioavailable nutrients are influenced by internal marsh processes. Rates of biogeochemical reactions are generally higher in summer, when temperatures are high and biological activity is at its peak (Mitsch and Reeder 1992; Spieles and Mitsch 2000). During summer, although lake water potentially acts as a major source of nitrate, high rates of biotic assimilation and denitrification can explain the lower TNN in marshes of both high- and low- order catchments relative to spring concentrations (Bowden 1987; Morrice et al 2004). Meanwhile, increased organic matter mineralization during the summer may increase production of ammonium (Bowden 1987), contributing to higher summer TAN concentrations. TP in the marshes was not significantly different between April and July, but lower SRP in the water column in July suggests more P was tied up in organic forms at this time; this trend has also been observed in Old Woman Creek in Lake Erie (Mitsch and Reeder 1992). The decrease in TP at Black Rock marsh later in summer suggests either net P export from the marsh to the Bay or sequestration of P in marsh sediments.

Implications

Within a landscape ecology framework, our study draws on existing knowledge of hydrology and biogeochemistry of Precambrian Shield catchments, and of coastal hydrology and nutrient dynamics, to interpret observed patterns in water chemistry of coastal marshes. In doing so, we contribute to a better understanding of the factors controlling reference chemistry of these ecosystems, something which is of recognized importance in the field of ecosystem conservation and management. The relationships established may be useful for identifying areas that could have high sensitivity to watershed disturbances. Based on our findings, we might expect that marshes with strong hydrologic connections to uplands may be more sensitive to intensive land development that adds nutrients or promotes soil erosion in their watershed, since runoff has a greater influence on marsh water chemistry at these sites, and because they may already have naturally higher concentrations of phosphorus and sediment. Furthermore, these detrimental effects may be most evident in spring when marsh water concentrations of catchment-derived constituents are highest. As knowledge of coastal wetland dynamics continues to advance, we will become better equipped to manage these valuable habitats and predict detrimental effects of human stressors.

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Table 2.1: Seasonal means (and ranges) of water chemistry variables in offshore open water areas and in coastal marshes examined in this study. Offshore data were obtained from the Ministry of the Environment (2005; unpubl.). Back-transformed geometric means are reported for variables that were $\log_{10}$-transformed. TP= total phosphorus; SRP= soluble reactive phosphorus; TAN= total ammonia nitrogen; TNN= total nitrate-nitrite nitrogen; COND= specific conductivity; DOC= dissolved organic carbon; COL= colour; TSS= total suspended solids

	Spring		Summer		Spring-summer average	
Parameter	Open water (*n*=11)	Coastal marsh (*n*=33)	Open water (*n*=11)	Coastal marsh (*n*=34)	Open water (*n*=11)	Coastal marsh (*n*=33)
TP ($\mu g\ L^{-1}$)	7.0 (5.5-12.0)	15.2 (8.4-44.3)	3.9 (2.0-5.5)	17.1 (10.2-28.8)	5.5 (4.0-7.8)	16.4 (9.3-33.8)
SRP ($\mu g\ L^{-1}$)	0.5 (0.5-0.5)	5.5 (1.5-15.8)	0.7 (0.5-1.5)	4.4 (1.3-10.7)	0.6 (0.5-1.0)	5.2 (2.4-10.9)
TAN ($\mu g\ L^{-1}$)	10 (4-17)	11 (5-40)	6 (2-14)	16 (5-160)	8 (4-12)	15 (5-90)
TNN ($\mu g\ L^{-1}$)	240 (209-273)	23 (10-120)	210 (164-252)	11 (5-50)	225 (190-259)	18 (8-85)
SO_4^{2-} ($mg\ L^{-1}$)	11.1 (8.7-13.1)	1.0 (0.5-5.0)	11.7 (10.8-12.5)	1.7 (0.5-7.0)	11.1 (7.5-12.8)	1.4 (0.5-6.0)
COND ($\mu S\ cm^{-1}$)	162 (126-190)	26 (8-74)	198 (192-203)	45 (15-114)	180 (159-196)	36 (15-92)
pH	8.0 (7.8-8.2)	6.8 (5.8-8.1)	8.2 (8.2-8.3)	7.0 (6.2-8.2)	8.1 (8.0-8.2)	6.7 (6.1-7.5)
DOC ($mg\ L^{-1}$)	2.7 (2.0-3.5)	18.5 (7.4-97.0)	2.3 (1.9-2.8)	13.2 (5.9-44.3)	2.5 (2.0-3.1)	16.6 (8.3-69.1)
COL ($mg\ L^{-1}Pt$)	7 (0-14)	120 (65-250)	3 (1-4)	103 (11-424)	5 (1-9)	116 (43-337)
TSS ($mg\ L^{-1}$)	0.6 (0.5-1.5)	2.5 (0.7-20.0)	0.9 (0.6-1.7)	2.5 (0.7-17.1)	0.8 (0.6-1.3)	2.8 (0.9-11.4)

Table 2.2: Description of landscape variables used in analyses.

Variable	Description
AQUAT	Size of coastal marsh (aquatic portion)
MED	Total area of meadow marsh connected to the aquatic marsh
OPEN	Width of surface water connection to Georgian Bay
DBA	Drainage basin area (excluding aquatic marsh)
ORDER	Catchment/ marsh order, defined using Strahler stream order (Strahler 1952)
WET	Total area of wetland (bog, fen, swamp, marsh, beaver ponds) located upstream of the coastal marsh
SLOPE	Mean drainage basin slope
DBA/AQUAT	Ratio of drainage basin area to aquatic marsh area
WET/AQUAT	Ratio of upstream wetland area to aquatic marsh area
PROPWET	Proportion of the drainage basin occupied by upstream wetland

Table 2.3: Landscape characteristics for the 34 marshes. Samples were collected in both spring and summer for all marshes except HNB (no spring sample).

Site Code	Latitude, longitude	Aquatic marsh (ha)	Meadow marsh (ha)	Marsh opening (m)	Drainage basin (ha)	Upstream wetland (ha)	Slope (%)	Order
MS1	44.952, -79.851	4.4	1.1	126	15.3	2.0	8.9	0
MS2	44.946, -79.894	0.9	0.1	63	122.2	17.8	3.2	2
CG1	44.952, -79.913	3.6	0.4	107	22.3	0.0	5.9	1
CG2	44.959, -79.912	3.0	0.6	181	168.0	35.7	4.1	3
LNB	44.969, -79.895	2.2	4.9	93	496.9	82.0	5.5	3
LSP	44.979, -79.932	5.5	0.8	94	133.1	29.6	2.5	2
RDB	44.985, -79.921	4.0	0.9	40	43.1	1.9	5.3	1
PGI	44.992, -79.926	1.0	0.7	33	26.5	0.0	6.9	1
RBH	44.994, -79.922	2.6	0.3	63	70.8	12.3	5.8	2
INB	44.997, -79.922	1.3	4.4	8	262.5	49.0	4.7	2
PTC	45.005, -79.929	1.5	2.3	79	86.8	0.0	4.5	2
GHR	45.006, -79.913	0.4	0.8	64	584.4	141.9	5.6	2
MR1	45.014, -79.944	17.0	10.5	304	476.6	104.7	3.2	3
MR2	45.012, -79.951	0.9	8.8	179	121.9	0.0	2.0	1
BRI	45.018, -79.982	2.6	1.5	49	95.6	21.9	2.1	2
DVB	45.045, -79.999	0.8	0.3	24	15.4	2.0	0.9	2
TB1	45.028, -79.983	4.7	3.4	56	173.5	31.6	2.9	3
TB2	45.042, -79.990	1.8	1.0	108	8.4	0.0	0.6	0
TB3	45.052, -79.958	0.9	0.2	106	11.9	0.1	1.9	0
TB4	45.057, -79.995	0.4	0.2	26	13.7	0.0	3.9	0
TL1	45.035, -79.954	2.6	0.2	58	91.6	8.7	2.1	2
TL2	45.047, -79.914	0.9	0.9	102	274.2	37.3	6.0	3
THB	45.052, -79.970	1.2	1.0	57	29.8	0.0	0.7	0
CFR	45.048, -79.988	2.8	2.2	236	82.1	9.7	2.0	1
BLR	45.043, -79.973	4.7	4.5	26	271.5	70.1	1.8	2
ALB	45.053, -80.002	1.5	0.9	79	15.6	0.0	4.4	0
MRB	45.118, -79.978	20.4	13.8	310	354.6	36.8	5.9	3

Table 2.3: (Continued).

Site Code	Latitude, longitude	Aquatic marsh (ha)	Meadow marsh (ha)	Marsh opening (m)	Drainage basin (ha)	Upstream wetland (ha)	Slope (%)	Order
WB1	45.138, -80.014	25.6	5.5	257	61.2	1.0	9.7	2
WB2	45.129, -79.984	3.0	2.5	153	37.9	9.4	7.6	1
MB1	45.115, -80.017	6.7	1.3	52	141.5	12.9	5.6	2
MB2	45.113, -80.035	1.9	3.5	147	554.4	102.0	3.8	3
MB3	45.126, -80.009	1.2	0.3	50	6.8	0.0	8.7	0
BLB	45.131, -80.026	1.0	1.9	108	41.2	6.0	5.3	1
HNB	45.141, -80.041	1.2	0.3	74	66.4	10.3	6.2	2

Table 2.4: Pearson correlation coefficients for landscape variables (A; n=34) and for spring-summer mean water chemistry variables (B; n=33).

(A) Landscape variables

	DBA	ORDER	WET	SLOPE	AQUAT	MED	OPEN	DBA/ AQUAT	WET/ AQUAT	PROP WET
DBA	1.00									
ORDER	**0.84**	1.00								
WET	**0.88**	**0.75**	1.00							
SLOPE	-0.06	-0.03	-0.05	1.00						
AQUAT	0.28	**0.35**	0.19	0.22	1.00					
MED	**0.55**	**0.35**	**0.40**	0.06	**0.53**	1.00				
OPEN	0.16	0.17	0.16	0.15	**0.48**	**0.36**	1.00			
DBA/AQUAT	**0.72**	**0.52**	**0.67**	-0.22	**-0.47**	0.11	-0.20	1.00		
WET/AQUAT	**0.77**	**0.65**	**0.89**	-0.04	-0.16	0.13	-0.11	**0.82**	1.00	
PROPWET	**0.65**	**0.61**	**0.81**	-0.05	0.19	0.23	0.00	**0.46**	**0.79**	1.00

(B) Water chemistry variables

	TP	SRP	TAN	TNN	SO_4^{2-}	COND	pH	DOC	COL	TSS
TP	1.00									
SRP	0.20	1.00								
TAN	0.22	-0.33	1.00							
TNN	-0.02	-0.19	-0.09	1.00						
SO_4^{2-}	**-0.54**	0.13	**-0.47**	0.29	1.00					
COND	**-0.49**	-0.02	**-0.37**	0.11	**0.86**	1.00				
pH	**-0.40**	-0.09	-0.26	0.19	**0.58**	**0.61**	1.00			
DOC	**0.40**	**0.52**	**-0.38**	-0.18	-0.01	-0.11	-0.19	1.00		
COL	**0.61**	0.05	**0.51**	**-0.40**	**-0.75**	**-0.60**	**-0.48**	0.20	1.00	
TSS	**0.51**	-0.02	**0.40**	-0.10	**-0.44**	**-0.42**	**-0.47**	0.14	**0.54**	1.00

Table 2.5: Pearson correlations between landscape variables and water chemistry variables.

	DBA	ORDER	WET	SLOPE	AQUAT	MED	OPEN	DBA/ AQUAT	WET/ AQUAT	PROP WET
TP_{mean}	**0.46**	**0.53**	**0.41**	**0.36**	**0.52**	**0.41**	0.19	0.05	0.26	0.27
SRP_{mean}	0.25	0.34	0.24	0.05	0.03	-0.04	-0.07	0.21	0.26	0.13
TNN_{mean}	**-0.40**	-0.30	-0.34	**0.46**	0.15	-0.11	0.20	**-0.48**	**-0.36**	-0.25
TAN_{mean}	**0.35**	0.28	0.22	0.04	0.29	**0.49**	**0.49**	0.11	0.04	0.07
$SO_4{}^{2-}{}_{mean}$	**-0.61**	**-0.60**	**-0.55**	0.02	-0.20	**-0.43**	-0.10	**-0.42**	**-0.47**	**-0.38**
$COND_{mean}$	**-0.60**	**-0.63**	**-0.54**	-0.14	-0.22	-0.28	-0.24	**-0.39**	**-0.47**	-0.32
pH_{mean}	**-0.67**	**-0.51**	**-0.57**	-0.28	0.02	-0.31	-0.09	**-0.63**	**-0.61**	**-0.46**
DOC_{sp}	0.00	0.05	0.06	-0.17	-0.06	-0.24	-0.24	0.04	0.11	0.11
DOC_{su}	**0.38**	0.33	**0.46**	0.22	0.10	0.00	0.04	0.28	**0.45**	**0.44**
DOC_{mean}	0.19	0.21	0.28	0.01	0.00	-0.16	-0.13	0.18	0.32	0.29
COL_{mean}	**0.63**	**0.66**	**0.58**	-0.15	0.25	**0.53**	0.16	**0.40**	**0.45**	**0.45**
TSS_{mean}	**0.50**	**0.54**	**0.43**	0.28	0.30	**0.46**	**0.37**	0.28	**0.36**	**0.49**

Table 2.6: Pearson correlations of landscape variables with the first two principal component axes (*n*=34).

Axis	Variance explained (%)	Variable	*r*	*P*
PC1	48.0	WET	0.96	<0.0001
		DBA	0.95	<0.0001
		WET/AQUAT	0.90	<0.0001
		ORDER	0.85	<0.0001
		PROPWET	0.81	<0.0001
		DBA/AQUAT	0.75	<0.0001
		MED	0.45	0.0078
PC2	22.6	AQUAT	0.90	<0.0001
		OPEN	0.71	<0.0001
		MED	0.61	0.0001
		DBA/AQUAT	-0.54	0.0010
		SLOPE	0.37	0.0333

Table 2.7: Models built from forward stepwise regressions. Where strong collinearity resulted in alternative models with similar r^2_{adj}, the alternative models are presented.

Parameter	n	Equation	r^{2a}	r^2_{adj}
$\log_{10} COND_{mean}$	33	1.740 – 0.112(ORDER)***	0.39	0.37
$\log_{10} COND_{mean}$	33	1.922 – 0.194log$_{10}$(DBA)***	0.35	0.33
$\log_{10} SO_4^{2-}{}_{mean}$	33	0.798 – 0.342log$_{10}$(DBA)***	0.38	0.36
$\log_{10} SO_4^{2-}{}_{mean}$	33	0.452 – 0.182(ORDER)***	0.36	0.34
pH_{mean}	33	8.023 – 0.580log$_{10}$(DBA)**** – 0.071(SLOPE)** + 0.317log$_{10}$(AQUAT)**	0.44, 0.55, 0.64	0.61
$\log_{10} COL_{mean}$	33	1.861 + 0.120(ORDER)**** + 0.140log$_{10}$(MED)*	0.44, 0.54	0.51
$\log_{10} COL_{mean}$	33	1.593 + 0.253log$_{10}$(DBA)***	0.39	0.37
$\log_{10} TSS_{mean}$	33	0.033 + 0.151(ORDER)*** + 0.038(SLOPE)*	0.29, 0.39	0.35
$\log_{10} TSS_{mean}$	33	-0.208 + 0.256log$_{10}$(DBA)** + 0.039(SLOPE)*	0.25, 0.36	0.31
$\log_{10} TP_{mean}$	33	1.017 + 0.067(ORDER)*** + 0.020(SLOPE)**	0.29, 0.43	0.40
$\log_{10} TP_{mean}$	33	0.949 + 0.086log$_{10}$(DBA)* + 0.098log$_{10}$(AQUAT)* + 0.016(SLOPE)*	0.21, 0.38, 0.47	0.41
$\log_{10} TNN_{mean}$	33	1.333 – 0.188log$_{10}$(DBA/AQUAT)* + 0.045(SLOPE)*	0.23, 0.35	0.31
$\log_{10} TAN_{mean}$	33	0.573 + 0.307log$_{10}$(OPEN)* + 0.191log$_{10}$(MED)*	0.24, 0.36	0.31
$\log_{10} DOC_{su}$	34	1.013 + 0.030sqrt(WET)**	0.21	0.19
$\log_{10} DOC_{su}$	34	1.019 + 0.155log$_{10}$(WET/AQUAT+1)**	0.20	0.18

[a]Cumulative for each variable entered

*P<0.05, **P<0.01, ***P<0.001, ****P<0.0001

Table 2.8: Mixed-model ANOVA *F* value results for water chemistry variables. Effects of season (spring [Sp]/ summer [Su]), order (high [H]/ low [L]), and their interaction are given.

Parameter	*F* Order	*F* Season	*F* Order x Season	Order relationship	Season relationship
TP	8.684**	3.500	0.000	H>L	
SRP	4.965*	4.748*	1.077	H>L	Sp>Su
TAN	0.410	4.894*	0.776		Su>Sp
TNN	1.893	45.366****	1.506		Sp>Su
SO_4^{2-}	10.182**	11.951**	0.004	L>H	Su>Sp
COND	10.756**	45.039****	0.304	L>H	Su>Sp
pH	8.864**	1.692	0.023	L>H	
DOC	3.245	9.130**	0.017		Sp>Su
COL	7.640**	2.436	1.060	H>L	
TSS[a]	3.199	0.001	1.003		

[a]WB1 excluded
*P<0.05, **P<0.01, ***P<0.001, ****P<0.0001

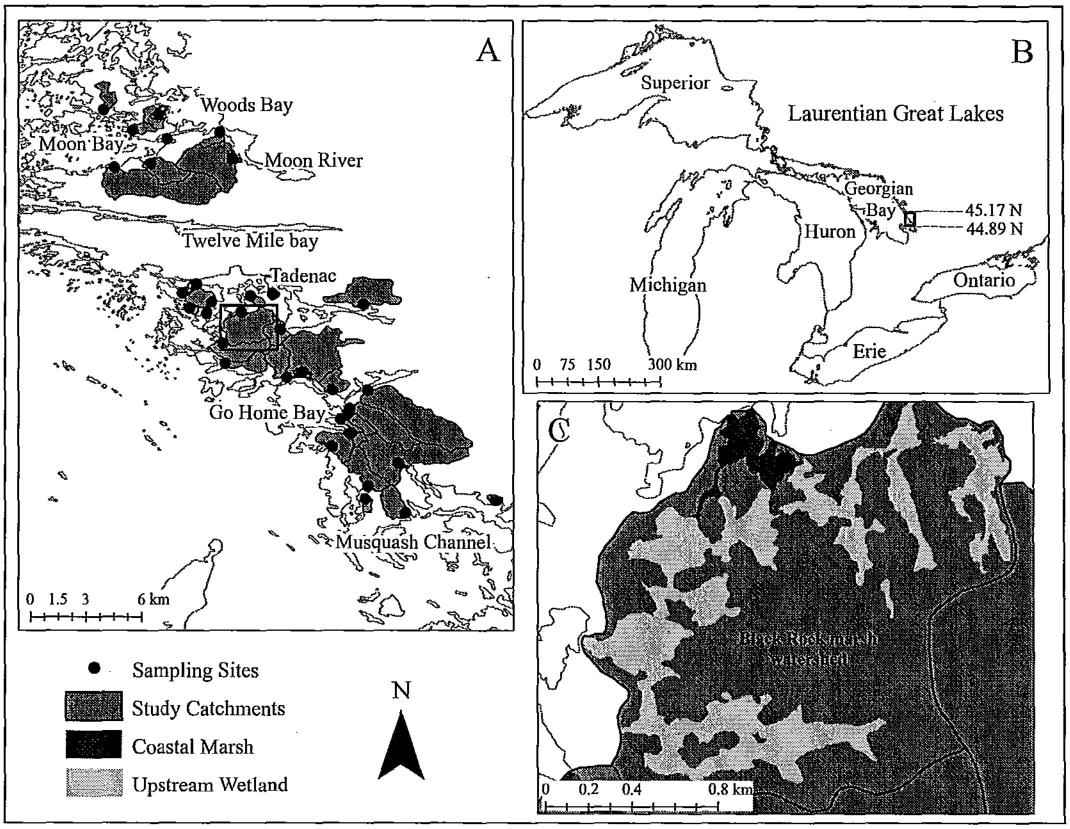

Figure 2.1: Map of the 34 study sites (A) and their location in the Great Lakes basin (B). Black Rock marsh watershed is highlighted in (A) and shown in greater detail in (C).

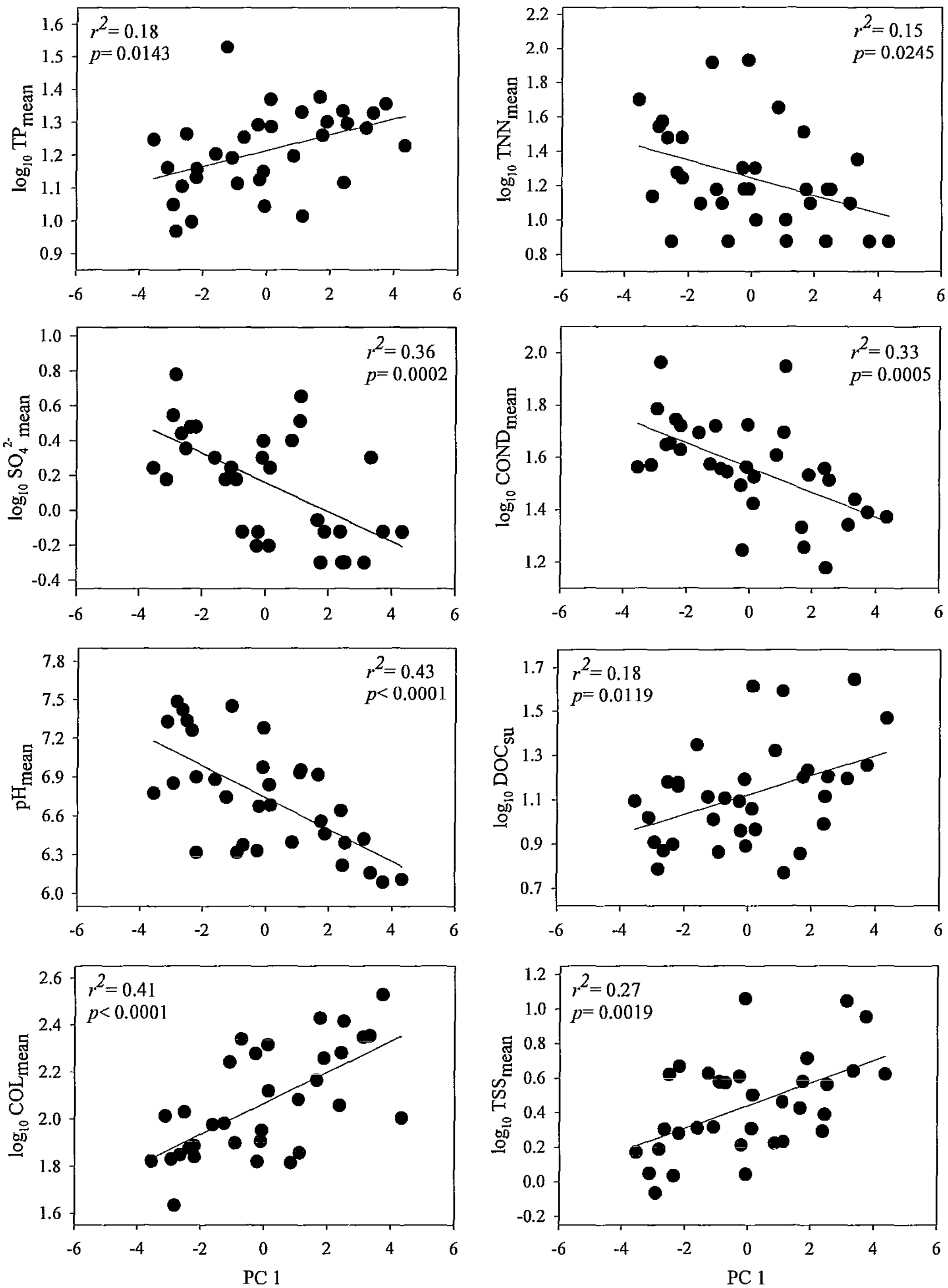

Figure 2.2: Plots of water chemistry variables against landscape PC1. Only variables with statistically significant relationships to PC1 are shown.

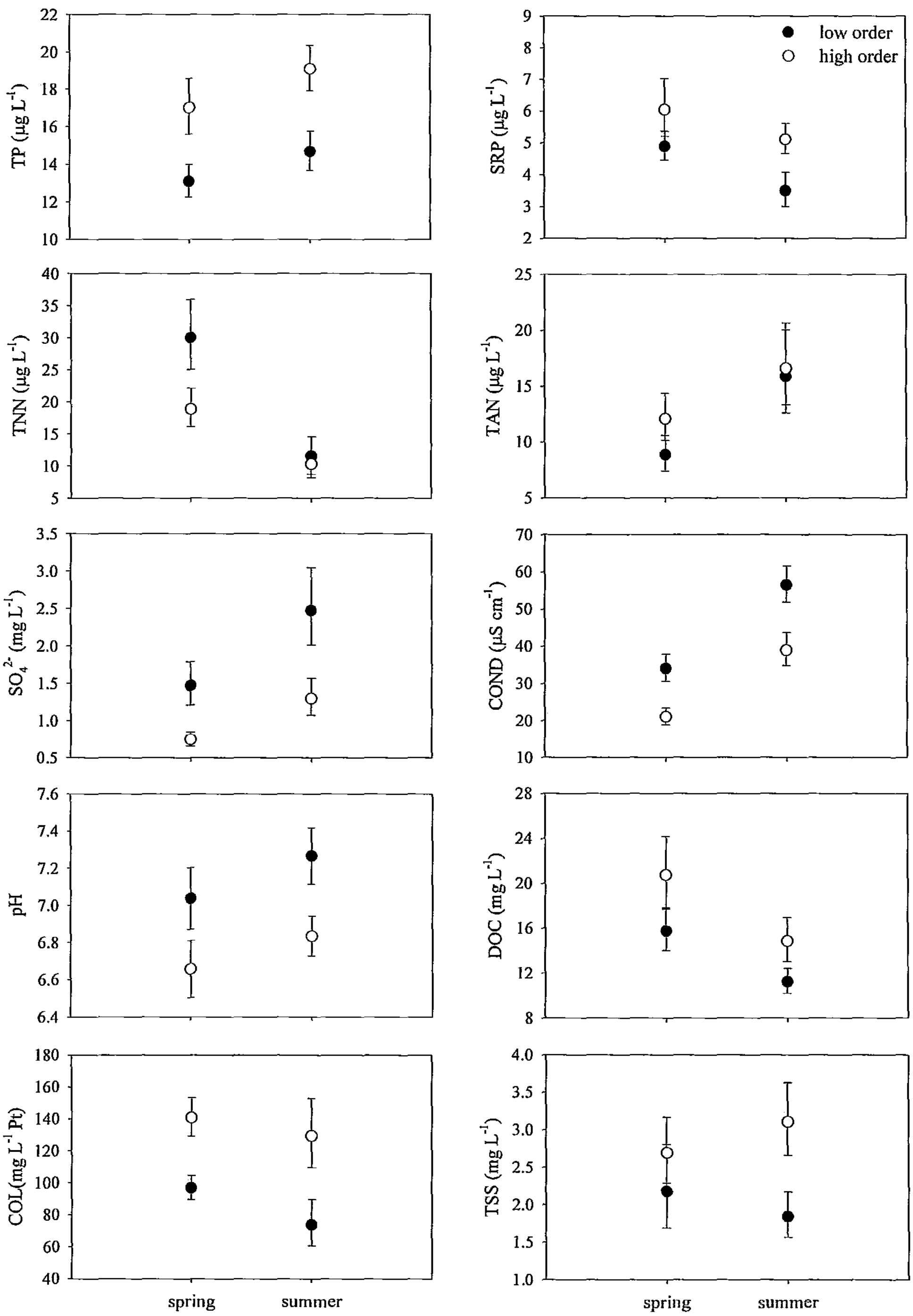

Figure 2.3: Back-transformed means (points) and SE (vertical bars) of water chemistry variables in marshes draining high- and low-order catchments in spring and summer.

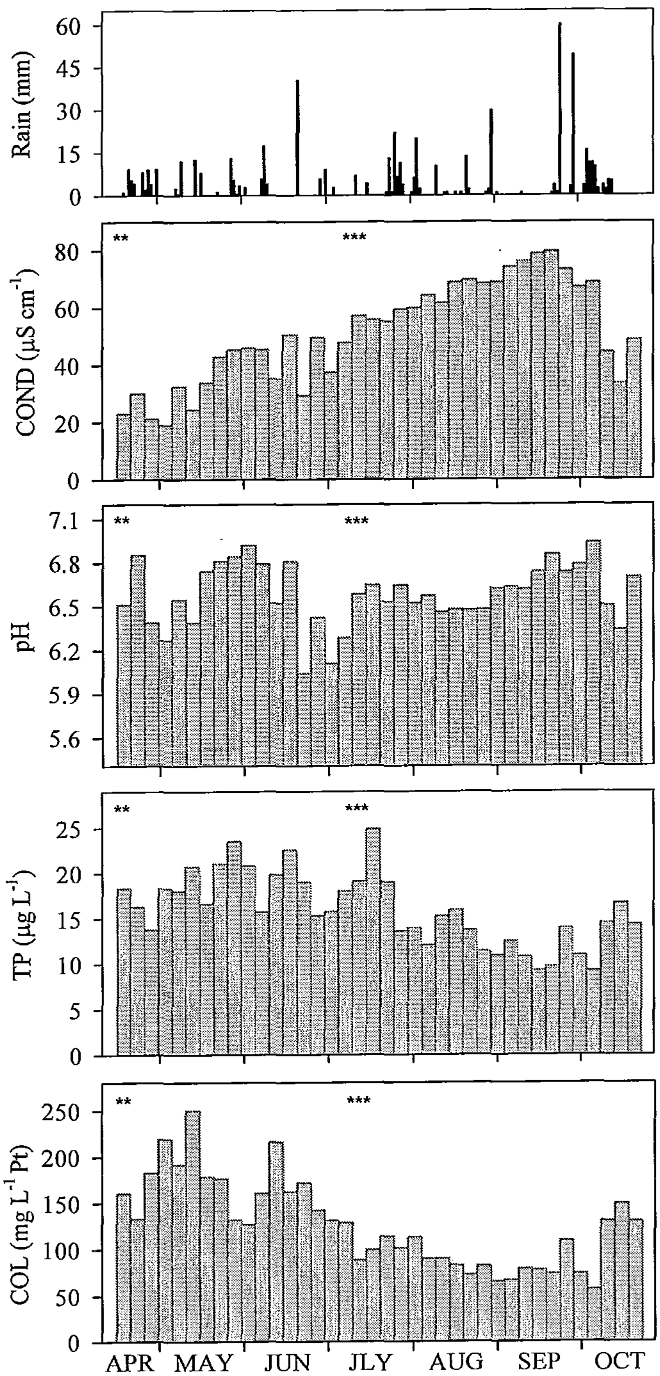

Figure 2.4: Trends in key water chemistry variables at Black Rock marsh from mid-April to mid-October. Asterisks were used to indicate timing of discrete sampling surveys across all marshes. The top panel shows daily rainfall during the study period.

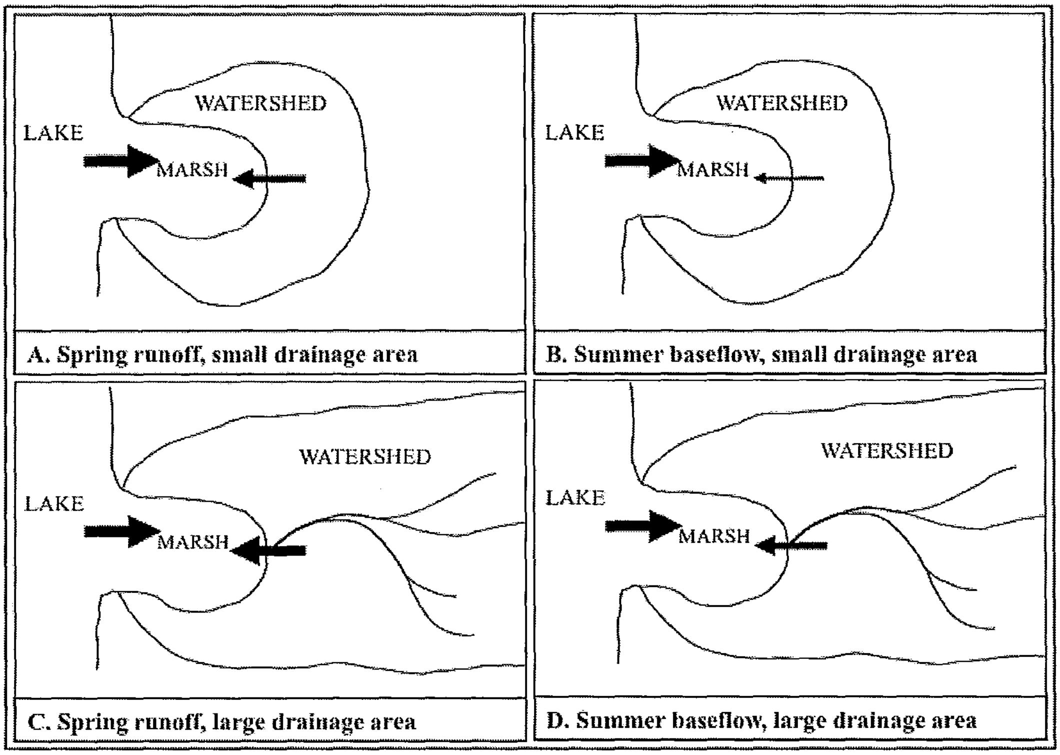

Figure 2.5: Conceptual diagram to explain variation in marsh water chemistry based on differing hydrologic scenarios. Sizes of the arrows represent the relative magnitude of flow rates. Watershed discharge (solid arrows pointing from watershed to marsh) increases with the size of the watershed, and is higher during spring snowmelt compared with summer baseflow. For similar-sized embayments, periodic seiche-induced flows (solid arrows pointing from lake to marsh) are assumed roughly constant across sites and seasons, although the chemistry of water moved by seiches may vary. The relative influence of lake chemistry on marsh water chemistry is greatest under scenario B, when inputs from the watershed are relatively small. Marsh water chemistry will most closely reflect runoff chemistry under scenario C, when high rates of discharge reduce the intrusion of lake water.

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