# **Rachel deCatanzaro and Patricia Chow-Fraser**

Abstract: We surveyed 34 marshes in relatively pristine Precambrian Shield catchments in Georgian Bay and related water chemistry 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) ordered marshes along a gradient with high values corresponding to marshes with large watersheds that contain extensive upstream wetland and that receive relatively high precipitation inputs. 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, ammonia nitrogen, and summer dissolved organic carbon. Stepwise regression models built using catchment- and marsh-level variables explained up to 64% of the variation in water chemistry variables. Average precipitation and snowmelt inputs to the catchments were first to enter the majority of models, alone explaining up to 43% of the variation (in the case of water colour), while drainage area alone explained 44% of the variation in pH. Concentrations of catchment-derived constituents in marshes were highest in spring, reflecting greater loadings from the watersheds, while ionic strength was highest during summer, reflecting increased contributions form other sources (i.e., lake water).

Résumé : Nous avons inventorié 34 marécages dans des bassins hydrographiques relativement peu modifiés dans la baie Géorgienne sur le Bouclier canadien et avons relié la chimie de l'eau à une série de variables à l'échelle du paysage, en particulier aux caractéristiques des marécages et de leur bassin versant. La première composante principale du paysage (qui explique 48 % de la variation) place les marécages le long d'un gradient dont les valeurs supérieures correspondent à des marécages à bassin versant de grande superficie qui contient en amont d'importantes terres humides et qui reçoit de apports relativement élevés des précipitations. Cet axe est en corrélation négative avec la conductivité spécifique, le pH et les concentrations de  $SO_4^{2-}$  et d'azote sous forme de nitrates et en corrélation positive avec le phosphore total, la couleur, les solides en suspension, l'azote sous forme d'ammoniaque et le carbone organique dissous en été. Des modèles de régression pas à pas construits à partir des variables à l'échelle du bassin versant et du marécage expliquent jusqu'à 64 % de la variation des variables de chimie de l'eau. Les apports moyens des précipitations et de la fonte des neiges aux bassins versants sont les premières variables à entrer dans la plupart des modèles, expliquant à elles seules jusqu'à 43 % de la variation (dans le cas de la couleur de l'eau), alors que la surface du bassin versant seule explique 44 % de la variation du pH. Les concentrations des composantes provenant du bassin versant sont le plus élevées au printemps, ce qui indique de plus forts apports à partir du bassin hydrographique, alors que la force ionique est au maximum durant l'été, ce qui reflète les contributions accrues à partir d'autres sources (c'est-à-dire l'eau du lac).

[Traduit par la Rédaction]

## 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

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(Mayer et al. 2004). Urban and agricultural development can be particularly detrimental, causing increases in nutrient loadings and turbidity (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 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 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

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et al. 1991; Dillon and Molot 1997; Eimers et al. 2008) have provided some insight into the 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., D'Arcy and Carignan 1997; Dillon and Molot 1997; Prepas et al. 2001). Precipitation can play a large role in the export of nutrients and sediments to streams and lakes by generating runoff that interacts with catchment features and promotes flushing of allochthonous materials (Allan et al. 1993; Schiff et al. 1998; Eimers et al. 2008). 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). 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 (e.g., spring snowmelt), lake water inflow and mixing in the wetland is reduced, and the chemistry of the marsh is more heavily influenced by runoff chemistry (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 (see Duxbury 1979).

Coastal marshes of the Precambrian Shield portion of eastern Georgian Bay are among the least human-disturbed in the Great Lakes Basin (Chow-Fraser 2006; Cvetkovic et al. 2010) and afford a unique opportunity to study water chemistry dynamics in the absence of major anthropogenic perturbations. Expansion of road networks and incremental cottage and residential development are expected to continue (see deCatanzaro et al. 2009), and many climate models have predicted changes in precipitation patterns and a drop in Lake Huron water level (see Mortsch and Quinn 1996; Lofgren et al. 2002), making the establishment of reference conditions of critical importance for this area. The majority of the marshes form in lacustrine protected embayments, which are characterized as having strong surface-water connections with the lake (see Albert et al. 2005). Climatic conditions promote snow accumulation during winter, resulting in high hydrologic flow from watersheds during spring snowmelt, and this could have important consequences for the relative influences of watershed versus lake on the hydrology and chemistry of coastal marshes (Morrice et al. 2004).

This is the first paper to examine the relative effects of watershed features and processes (including precipitation inputs) and marsh morphology on reference water chemistry of coastal marshes in eastern Georgian Bay. We predict that marshes with larger drainage areas receiving higher precipitation and snowmelt inputs would have water chemistry that more closely reflects processes in watersheds of the Precambrian Shield with respect to sediment and nutrient retention and export. On the other hand, the chemistry of marshes with weak hydrologic connection to uplands would be more similar to that of open Georgian Bay. We also expect features such as catchment slope to play a major role, whereby water chemistry would reflect higher nutrient and sediment export from steeply sloped catchments. Secondly, we examine seasonal changes in marsh water chemistry by (i) comparing discrete survey data from each of the marshes in spring and summer and (ii) monitoring continuous changes in water chemistry at a representative marsh from ice-out to early autumn. Consistent with previous studies, we expect the highest concentrations of catchment-derived constituents in marshes during spring, when snowmelt produces high discharge and nutrient loadings to downstream areas. Our results will help to reveal the relative importance of watershed versus Great Lakes influences on water quality of these pristine systems that are known to support high biodiversity of plants, fish, and species at risk (Croft and Chow-Fraser 2009; Cvetkovic et al. 2010; deCatanzaro and Chow-Fraser 2010) and will inform the discussion on how best to adapt to changes in precipitation and runoff patterns in this region associated with climate change.

# Materials and 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 (Fig. 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 secondgrowth deciduous and coniferous forests of the Great Lakes -St. Lawrence Forest region, characterized by species such as eastern white pine (Pinus strobus), red pine (Pinus resinosa), eastern hemlock (Tsuga canadensis), white spruce (Picea glauca), sugar maple (Acer saccharum), northern red oak (Quercus rubra), and American beech (Fagus grandifolia). Extensive wetland complexes form in topographic depressions and along streams and tributaries flooded as a result of beaver (Castor canadensis) activity.

Within this area, the offshore Georgian Bay water is alkaline and has high specific conductivity (COND; N. Diep, Ontario Ministry of the Environment, Great Lakes Unit of the Water Monitoring and Reporting Section, 125 Resources Road, Etobicoke, ON M9P 3V6, unpublished data; Table 1) owing to the influence of dissolved ions from easily eroded Palaeozoic limestone that surrounds 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 around 7.0 µg·L-1 in spring to 3.9  $\mu g \cdot L^{-1}$  in summer, while sulphate (SO<sub>4</sub><sup>2-</sup>) is over 10 mg·L<sup>-1</sup> and nitrate nitrogen (TNN) over 200  $\mu$ g·L<sup>-1</sup> during the ice-free season. Concentrations of ammonia nitrogen (TAN), dissolved organic carbon (DOC), colour (COL), and total suspended solids (TSS) are all low in the open-water areas. The climate is characterized by extremes of cold and dry or hot and humid weather. Winter temperatures are below freezing for up to 4 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 typically occur in March and April (Weiler 1988).

### Landscape analyses

Analyses of landscape variables were performed in ArcGIS 9.2 (ESRI, Redlands, California, USA). We delineated marsh



**Figure 1.** Map of the 34 study sites (*b*) and their location in the Great Lakes basin (*a*). Black Rock marsh watershed is highlighted in panel (*b*) and shown in greater detail in panel (*c*).

 Table 1. Means and ranges of water chemistry variables (spring-summer averaged) in offshore open-water sites and in coastal marshes.

		Open water	$(n = 11)^a$	Coastal mars	sh $(n = 33)$
Parameter	Abbreviation	Mean	Range	Mean	Range
Group 1					
Total phosphorus ( $\mu g \cdot L^{-1}$ )	TP	5.5	4.0-7.8	16.4	9.3-33.8
Soluble reactive phosphorus ( $\mu g \cdot L^{-1}$ )	SRP	0.6	0.5-1.0	5.2	2.4-10.9
Total ammonia nitrogen ( $\mu g \cdot L^{-1}$ )	TAN	8	4-12	15	5–90
Dissolved organic carbon $(mg \cdot L^{-1})$	DOC	2.5	2.0-3.1	16.6	8.3-69.1
Colour (mg $Pt \cdot L^{-1}$ )	COL	5	1–9	116	43-337
Total suspended solids $(mg \cdot L^{-1})$	TSS	0.8	0.6–1.3	2.8	0.9–11.4
Group 2					
Total nitrate-nitrite nitrogen ( $\mu g \cdot L^{-1}$ )	TNN	225	190-259	18	8-85
Sulphate $(mg \cdot L^{-1})$	SO4 <sup>2-</sup>	11.1	7.5-12.8	1.4	0.5-6.0
Specific conductivity ( $\mu$ S·cm <sup>-1</sup> )	COND	180	159-196	36	15-92
рН		8.1	8.0-8.2	6.7	6.1–7.5

Note: Back-transformed geometric means are reported for variables that were log<sub>10</sub>-transformed.

<sup>a</sup>Offshore data were obtained from the Ontario Ministry of the Environment in 2005 (N. Diep, Ontario Ministry of the Environment, Great Lakes Unit of the Water Monitoring and Reporting Section, 125 Resources Road, Etobicoke, ON M9P 3V6, unpublished data).

drainage basins by using digitized contours and spot elevations of Ontario base maps (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 (Table 2). We determined average slope (SLOPE) for each watershed

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)
WET	Total area of wetland (bog, fen, swamp, marsh, beaver ponds) located upstream of the coastal marsh
SLOPE	Mean drainage basin slope
DBA/AQUAT	Drainage ratio (ratio of drainage basin area to aquatic marsh area)
PROPWET	Proportion of the drainage basin occupied by upstream wetland
PREC <sub>07, 14, 30</sub>	Catchment inputs of precipitation and snowmelt over 7-, 14-, or 30-day periods prior to sampling

 Table 2. Description of landscape variables used in analyses.

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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 identify and quantify wetland areas within each catchment, we used the McMaster Coastal Wetland Inventory (P. Chow-Fraser, unpublished data). 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 (see Midwood and Chow-Fraser 2010). Because the marshes were situated in welldefined embayments, the lakeward boundary of the marsh was drawn across the mouth of the embayment. We used this to calculate drainage ratio (DBA/AQUAT). We also determined the width of the opening that connects the marsh to Georgian Bay (OPEN) through which surface water can flow.

#### Meteorological and water level data

Daily precipitation values were obtained from the Environment Canada weather station in Parry Sound, 20 km north of the study area. These data were used to calculate the cumulative precipitation inputs to catchments over 7-, 14-, and 30day periods prior to sampling at each marsh. For spring sampling dates, we also used the change in recorded snow depth over these periods to calculate the areal water equivalent and obtain an estimate of the volume of meltwater generated from spring snowpack. We used a snowpack density of 0.35 g·cm<sup>-3</sup>, a value typical for the late spring in south-central Ontario (Logan 1973). The sum of the precipitation inputs and areal water equivalent from the change in snowpack were taken to be the total precipitation and meltwater inputs to the catchment over the 7-, 14-, and 30-day periods (PREC<sub>07</sub>, PREC<sub>14</sub>, and PREC<sub>30</sub>). Lake-level data (averaged over 1-day intervals; LVL) were obtained from the Parry Sound station maintained by the Canadian Hydrographic Services (Parry Sound, Ontario).

# Field sampling

## Marsh surveying

Sampling surveys were conducted twice in 2009. The first sampling period occurred during the week following ice-out in mid-April, towards the end of the snowmelt period. We were unable to sample Hennessy Bay (HNB) in spring, but all of the other 33 sites 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 0830 and 1800.

Samples were collected adjacent to the longest axis of the watershed, near the 0.5 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 global positioning system (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 (Fig. 1). BLR is a 4.7 ha marsh located downstream of a moderately sloped (4.4%), 271.5 ha drainage basin containing 70.1 ha of upstream wetland. Upstream surface waters have low mid-summer pH (5.16–6.45) and COND (3–15  $\mu$ S·cm<sup>-1</sup>) and high TP (11.9–61.9  $\mu$ g·L<sup>-1</sup>) and COL (170–345 mg Pt·L<sup>-1</sup>). The ISCO sampler collected daily water samples in the marsh that 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 and (or) calibrated with standards in the field during site visits (generally every 20–24 days).

#### Sample processing

Water samples for total ammonia nitrogen ( $NH_3-N + NH_4^+-N$ ; TAN), total nitrate-nitrite nitrogen ( $NO_3^--N + NO_2^--N$ ; Published by NRC Research Press

Note: Subscript "avg" refers to spring-summer average.

								PRECavg (	m <sup>3</sup> )	
Site	Latitude (°N), longitude (°W)	Aquatic marsh (ha)	Meadow marsh (ha)	Marsh opening (m)	Drainage basin (ha)	Upstream wetland (ha)	Slope (%)	7-day	14-day	
MS1	44.952, 79.851	4.4	1.1	126	15.3	2.0	8.9	801	2961	- 1
MS2	44.946, 79.894	0.9	0.1	63	122.2	17.8	3.2	6414	23 700	
CG1	44.952, 79.913	3.6	0.4	107	22.3	0.0	5.9	1955	9316	
CG2	44.959, 79.912	3.0	0.6	181	168.0	35.7	4.1	8 823	32602	
LNB	44.969, 79.895	2.2	4.9	93	496.9	82.0	5.5	26088	96 403	
LSP	44.979, 79.932	5.5	0.8	94	133.1	29.6	2.5	8869	25 822	
RDB	44.985, 79.921	4.0	0.9	40	43.1	1.9	5.3	2 264	8 368	
PGI	44.992, 79.926	1.0	0.7	33	26.5	0.0	6.9	1 392	5 145	
RBH	44.994, 79.922	2.6	0.3	63	70.8	12.3	5.8	3 717	13 735	
INB	44.997, 79.922	1.3	4.4	8	262.5	49.0	4.7	13 781	50923	
PTC	45.005, 79.929	1.5	2.3	79	86.8	0.0	4.5	4 558	16842	
GHR	45.006, 79.913	0.4	0.8	64	584.4	141.9	5.6	30 682	113 377	
MR1	45.014, 79.944	17.0	10.5	304	476.6	104.7	3.2	25 021	92 457	
MR2	45.012, 79.951	0.9	8.8	179	121.9	0.0	2.0	6 399	23 644	
BRI	45.018, 79.982	2.6	1.5	49	95.6	21.9	2.1	5 019	18 548	
DVB	45.045, 79.999	0.8	0.3	24	15.4	2.0	0.9	1346	7 132	
TB1	45.028, 79.983	4.7	3.4	56	173.5	31.6	2.9	11 274	79 440	
TB2	45.042, 79.990	1.8	1.0	108	8.4	0.0	0.6	546	3 848	
TB3	45.052, 79.958	0.9	0.2	106	11.9	0.1	1.9	775	5 4 5 8	
TB4	45.057, 79.995	0.4	0.2	26	13.7	0.0	3.9	891	6276	
TL1	45.035, 79.954	2.6	0.2	58	91.6	8.7	2.1	5 953	41949	
TL2	45.047, 79.914	0.9	0.9	102	274.2	37.3	6.0	17 826	125 602	
THB	45.052, 79.970	1.2	1.0	57	29.8	0.0	0.7	1936	13639	
CFR	45.048, 79.988	2.8	2.2	236	82.1	9.7	2.0	5 338	37615	
BLR	45.043, 79.973	4.7	4.5	26	271.5	70.1	1.8	17 651	124 369	
ALB	45.053, 80.002	1.5	0.9	79	15.6	0.0	4.4	1012	7 1 3 0	
MRB	45.118, 79.978	20.4	13.8	310	354.6	36.8	5.9	22 698	08689	
WB1	45.138, 80.014	25.6	5.5	257	61.2	1.0	9.7	3917	11903	
WB2	45.129, 79.984	3.0	2.5	153	37.9	9.4	7.6	2 426	7372	
MB1	45.115, 80.017	6.7	1.3	52	141.5	12.9	5.6	9058	27 526	
MB2	45.113, 80.035	1.9	3.5	147	554.4	102.0	3.8	35 482	107 832	
MB3	45.126, 80.009	1.2	0.3	50	6.8	0.0	8.7	434	1319	
BLB	45.131, 80.026	1.0	1.9	108	41.2	6.0	5.3	2 638	8017	
HNB	45.141, 80.041	1.2	0.3	74	66.4	10.3	6.2	4 247	12906	

Table 3. Landscape characteristics for the 34 sampled marshes.

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0.54	0.14	-0.47	-0.42	-0.44	).10 .		0.4	-0.02	0.51	TSS
1.00	0.20	-0.48	-0.60	-0.75	).40	_ _	0.5	0.05	0.61	COL
	1.00	-0.19	-0.11	-0.01	).18 -		-0.3	0.52	0.40	DOC
		1.00	0.61	0.58	).19	0	-0.20	-0.09	-0.40	pH
			1.00	0.86	).11	7	-0.3	-0.02	-0.49	COND
				1.00	).29	7	-0.4	0.13	-0.54	$SO_4^{2-}$
					1.00	9	-0.09	-0.19	-0.02	TNN
						0	1.00	-0.33	0.22	TAN
								1.00	0.20	SRP
									1.00	TP
COL	DOC	pH	COND	$SO_4^{2-}$	NN	Т	TAN	SRP	TP	
								S.	try variable	(b) Water chemis
0.95	0.99	0.65	0.72	0.17	0.55	0.28	-0.06	0.88	0.99	PREC <sub>30</sub>
1.00	0.95	0.59	0.71	0.12	0.49	0.22	-0.25	0.84	0.95	PREC <sub>14</sub>
	1.00	0.64	0.71	0.17	0.54	0.29	-0.08	0.88	0.99	PREC07
		1.00	0.46	0.00	0.23	0.19	-0.05	0.81	0.65	PROPWET
			1.00	-0.20	0.11	-0.47	-0.22	0.67	0.72	DBA/AQUAT
				1.00	0.36	0.48	0.15	0.16	0.16	OPEN
					1.00	0.53	0.06	0.40	0.55	MED
						1.00	0.22	0.19	0.28	AQUAT
							1.00	-0.05	-0.06	SLOPE
								1.00	0.88	WET
									1.00	DBA
PREC <sub>14</sub>	PREC <sub>07</sub>	PROPWET	DBA/AQUAT	OPEN	MED	AQUAT	SLOPE	WET	DBA	

1.00

TSS

1.00

Table 4. Pearson's correlation coefficients for landscape variables (a) and for spring-summer-averaged water chemistry variables in coastal marshes (b).

PREC<sub>30</sub>

	DBA	WET	SLOPE	AQUAT	MED	OPEN	DBA/AQUAT	PROPWET	PREC <sub>07</sub>	PREC <sub>14</sub>	PREC <sub>30</sub>
TPavg	0.46	0.41	0.36	0.52	0.41	0.19	0.05	0.27	0.47	0.32	0.46
SRPavg	0.25	0.24	0.05	0.03	-0.04	-0.07	0.21	0.13	0.24	0.20	0.24
TNNavg	-0.40	-0.34	0.46	0.15	-0.11	0.20	-0.48	-0.25	-0.40	-0.42	-0.40
$TAN_{avg}$	0.35	0.22	0.04	0.29	0.49	0.49	0.11	0.07	0.37	0.36	0.36
$SO_4^{2-}$ avg	-0.61	-0.55	0.02	-0.20	-0.43	-0.10	-0.42	-0.38	-0.64	-0.62	-0.63
CONDavg	-0.60	-0.54	-0.14	-0.22	-0.28	-0.24	-0.39	-0.32	-0.62	-0.60	-0.60
$pH_{avg}$	-0.67	-0.57	-0.28	0.02	-0.31	-0.09	-0.63	-0.46	-0.63	-0.54	-0.66
DOCsp	0.00	0.06	-0.17	-0.06	-0.24	-0.24	0.04	0.11	-0.10	-0.03	0.00
DOCsu	0.38	0.46	0.22	0.10	0.00	0.04	0.28	0.44	0.49	0.27	0.35
DOCavg	0.19	0.28	0.01	0.00	-0.16	-0.13	0.18	0.29	0.16	0.10	0.18
COLavg	0.63	0.58	-0.15	0.25	0.53	0.16	0.40	0.45	0.66	0.63	0.63
$TSS_{avg}$	0.50	0.43	0.28	0.30	0.46	0.37	0.28	0.49	0.50	0.37	0.49
Mater Cia											

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Table 6. Pearson correlations of landscape variables with the first two principal component axes (n = 34).

	Variance	17 11	
Ax1s	explained (%)	Variable	r
PC1	47.7	DBA	0.97
		PREC <sub>07</sub>	0.97
		WET	0.94
		PROPWET	0.77
		DBA/AQUAT	0.69
		MED	0.58
PC2	23.5	AQUAT	0.86
		OPEN	0.70
		DBA/AQUAT	-0.63
		MED	0.53
		SLOPE	0.43

TNN), COL, and SO<sub>4</sub><sup>2-</sup> 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 preweighed 0.45 µm GF/C filters, which were frozen until subsequent analysis. Filtrate was split, and a portion was frozen and stored for later analysis of soluble reactive phosphorus (SRP) content. A second portion was 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 using persulfate 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 analyses and statistics

Statistical analyses were performed in SAS JMP 7.0 (SAS Institute Inc., Cary, North Carolina), with  $\alpha = 0.05$ . SO<sub>4</sub><sup>2–</sup>, TAN, and TNN values that fell below the detection limit (1 mg·L<sup>-1</sup>, 10  $\mu$ g·L<sup>-1</sup> and 10  $\mu$ g·L<sup>-1</sup>, 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<sub>10</sub>- or square-root-transformed as appropriate, with the exception of water level, for which it was necessary to square the data. Spring TSS for WB1 was excluded because strong winds on the morning of collection resulted in an unusually high value. 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. Springsummer averages of water chemistry variables at each surveyed site 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. In the case of BLR, data used in these analyses were from discrete samples taken during the same

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Figure 2. Plots of water chemistry variables against landscape PC1 (su, summer; avg, spring-summer averaged concentrations). Only variables with statistically significant relationships to PC1 are shown.

spring and summer sampling periods as the other 33 marshes.

Because of 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) into synthetic axes that best explain the variation (Shaw 2003). Since all precipitation measures were highly correlated with each other, we used only the averaged 7-day cumulative precipitation and snowmelt inputs in the PCA. Axes with an eigenvalue greater than one were retained

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 Table 7. Models built from forward stepwise regressions.

RIGHTSLINKA)

Parameter	и	Equation	$r^2 a$	$r^{2}_{\rm adj}$
log <sub>10</sub> COND <sub>avg</sub>	33	$2.320 - 0.208\log_{10}(\text{PREC}_{07avg})^{***}$	0.38	0.36
$\log_{10} \mathrm{SO}_{4}^{2-}$ avg	33	$1.505 - 0.369\log_{10}(\text{PREC}_{07avg})^{****}$	0.41	0.39
pHavg	33	8.023 - 0.263log10(DBA)* - 0.0711(SLOPE)** - 0.317log10(DBA/AQUAT)**	0.44, 0.55, 0.64	0.61
log <sub>10</sub> COL <sub>avg</sub>	33	$1.062 + 0.275 \log_{10}(PREC_{07avg})^{****}$	0.43	0.41
log <sub>10</sub> TSS <sub>avg</sub>	33	$-0.718 + 0.270\log_{10}(\text{PREC}_{07avg})^{**} + 0.0398(\text{SLOPE})^{*}$	0.25, 0.36	0.32
log <sub>10</sub> TP <sub>avg</sub>	33	$0.770 + 0.0956\log_{10}(AQUAT)^{*} + 0.0926\log_{10}(PREC_{07avg})^{**} + 0.0166(SLOPE)^{*}$	0.28, 0.39, 0.48	0.42
log <sub>10</sub> TNN <sub>avg</sub>	33	$1.333 - 0.188\log_{10}(DBA/AQUAT)^* + 0.0451(SLOPE)^*$	0.23, 0.35	0.31
log <sub>10</sub> TAN <sub>avg</sub>	33	$0.573 + 0.307 \log_{10}(\text{OPEN})^* + 0.191 \log_{10}(\text{MED})^*$	0.24, 0.36	0.31
$\log_{10} \mathrm{DOC}_{\mathrm{su}}$	34	$0.520 + 0.173 \log_{10}(\text{PREC}_{07su})^{**}$	0.24	0.21
Note: Subscript te	srms indica	e the following: su, summer; avg, spring-summer averaged. *, $P < 0.05$ ; **, $P < 0.01$ ; ***, $P < 0.001$ ; *	***, P < 0.0001.	
<sup>a</sup> Cumulative for ea	ach variable	e entered.		

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 landscape variables in forward stepwise multiple regression analyses to generate explanatory models for water chemistry variables. Only variables having statistically significant effects were retained in the models.

To look for seasonal variation, we used paired t tests to determine whether water chemistry variables differed in their concentrations between spring and summer surveys and also to look for differences in the precipitation and snowmelt inputs to the catchments during the two periods. We used the continuous data from Black Rock marsh to further examine seasonal variation in water chemistry in relation to hydrology. This was accomplished by using forward stepwise multiple regressions (in the same manner as above) to determine the effects of day of year, lake level, and precipitation and snowmelt inputs on daily averages of total phosphorus, colour, specific conductivity, and pH.

# 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 3). 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 exceptions 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 measurements of precipitation and snowmelt inputs to catchments (Table 4*a*).

Compared with the offshore, water in coastal marshes was high in TP, SRP, TAN, TSS, COL, and DOC (group 1; Table 1) and low in pH, COND, TNN, and SO<sub>4</sub><sup>2–</sup> (group 2). Variables in group 1 were positively correlated with each other and negatively correlated to variables in group 2 (Table 4*b*). The strongest relationships were between COND and each of SO<sub>4</sub><sup>2–</sup> (r = 0.86), pH (r = 0.61), and COL (r =-0.60) and between COL and each of TP (r = 0.61) and SO<sub>4</sub><sup>2–</sup> (r = -0.75). Although spring–summer-averaged DOC was not significantly correlated with 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 5). Averaged concentrations of COND,  $SO_4^{2-}$ , pH, COL, TSS, and often TP were generally correlated to the same set of landscape variables, with many of these variables showing the strongest relationships to drainage basin area and precipitation and snowmelt inputs; correlations were positive for variables measuring loading (TSS, TP, COL) but negative for variables measuring ionic strength (pH, COND,  $SO_4^{2-}$ ).

Parameter	Spring	Summer	t	Р
Precipitation and sno	owmelt inputs to catchments			
$PREC_{07}$ (m <sup>3</sup> )	4 902 (534-57 104)	2 992 (170-40 909)	-2.78	0.0089
$PREC_{14}$ (m <sup>3</sup> )	27 746 (1 438-202 664)	9 935 (1 201–98 130)	-11.69	< 0.0001
$PREC_{30}$ (m <sup>3</sup> )	84 762 (8 269–675 822)	53 715 (4 409–461 821)	-23.65	< 0.0001
Water chemistry par	ameters			
TP ( $\mu g \cdot L^{-1}$ )	15.2 (8.4–44.3)	17.1 (10.2–28.8)	1.92	NS
SRP ( $\mu g \cdot L^{-1}$ )	5.5 (1.5-15.8)	4.4 (1.3–10.7)	-2.04	0.0494
TAN ( $\mu g \cdot L^{-1}$ )	11 (5-40)	16 (5–160)	2.11	0.0427
TNN ( $\mu g \cdot L^{-1}$ )	23 (10-120)	11 (5–50)	-6.57	< 0.0001
$SO_4^{2-}$ (mg·L <sup>-1</sup> )	1.0 (0.5-5.0)	1.7 (0.5–7.0)	3.56	0.0012
COND ( $\mu$ S·cm <sup>-1</sup> )	26 (8–74)	45 (15–114)	6.95	< 0.0001
pH	6.8 (5.8-8.1)	7.0 (6.2–8.2)	1.31	NS
DOC (mg·L <sup><math>-1</math></sup> )	18.5 (7.4–97.0)	13.2 (5.9-44.3)	-3.08	0.0042
COL (mg Pt·L <sup>-1</sup> )	120 (65–250)	103 (11-424)	-1.41	NS
TSS $(mg \cdot L^{-1})^a$	2.5 (0.7-20.0)	2.5 (0.7–17.1)	0.10	NS
<sup>a</sup> WB1 excluded.				

Table 8. Comparison of spring and summer means (and ranges) of precipitation and snowmelt inputs to catchments and of water chemistry variables using paired t tests (NS, not significant).

WD1 excluded.

Both TP and TNN were positively related to watershed slope, and TP was also positively related to size of the aquatic marsh. Summer DOC showed positive relationships to DBA, PREC, and upstream wetland variables (WET and PROP-WET), whereas spring and averaged DOC and SRP concentrations were not significantly related to any of the landscape variables examined.

### Landscape principal components

PCA on landscape variables yielded two axes with eigenvalues greater than one, together explaining 71.2% of the variation in the data set (Table 6). PC1 explained 47.7% of the variation in the data and was highly positively correlated with DBA, PREC<sub>07</sub>, WET, PROPWET, and DBA/AQUAT and weakly correlated with MED. High scores on PC1 are therefore interpreted as marshes that drain large watersheds with large areas of upstream wetland and that receive high precipitation inputs. PC2 explained an additional 23.5% of the variation and showed strong positive correlations with AQUAT and OPEN, a strong negative correlation with DBA/AQUAT, and weak positive correlations with MED and SLOPE; high PC2 scores are therefore most strongly associated with large, open marshes.

PC1 was strongly related to several water chemistry variables; it was positively related to TP, COL, and TSS and to summer DOC and negatively related to TNN,  $SO_4^{2-}$ , COND, and pH (Fig. 2). It also showed a weak positive relationship with TAN concentrations ( $r^2 = 0.12$ , P = 0.0494). PC2 was not as strongly related to water chemistry variables; however, it was significantly positively related to TP ( $r^2 = 0.16$ , P = 0.0216), TAN ( $r^2 = 0.13$ , P = 0.0397), and TNN ( $r^2 = 0.13$ , P = 0.0368).

### Stepwise regression models using landscape variables

Stepwise regressions identified sets of factors that can best explain the variation in water chemistry variables (Table 7). Landscape variables explained the most variation (64%) in pH; of this, DBA alone explained 44%. PREC<sub>07</sub> was first to enter the models for COND, COL, TSS, TP,  $SO_4^{2-}$ , and

summer DOC. In the cases of COND,  $SO_4^{2-}$ , COL, and DOC<sub>su</sub>, no other landscape variables had significant effects. Drainage slope had significant effects for several variables, including TSS, TP, and TNN (positive relationships) and pH (negative relationship). Size of the aquatic marsh also entered the model for TP. Unlike other chemistry variables, TAN was most closely related to marsh-level variables; MED and OPEN together explained 36% of variation in averaged TAN concentrations.

### Seasonal patterns in marsh water chemistry

Total precipitation and snowmelt inputs to catchments over 7-, 14-, and 30-day periods leading up to sampling were all significantly higher in spring than summer, largely due to contributions from snowmelt in spring (paired *t* tests; Table 8). TP, pH, COL, and TSS did not differ significantly between the April and July sampling periods when all sites were considered (paired *t* tests; Table 8). Mean SRP, TNN, and DOC concentrations were all lower in the summer compared with spring, with TNN showing the largest and most significant decline (from 23 to 11 µg·L<sup>-1</sup>). TAN, SO<sub>4</sub><sup>2–</sup>, and COND were all significantly higher during the summer; mean COND concentrations showed the greatest increase, from 26 µS·cm<sup>-1</sup> in spring to 45 µS·cm<sup>-1</sup> in summer.

Consistent with the broader surveys, continuous monitoring at Black Rock marsh revealed an increase in COND throughout the spring and summer, from around 20  $\mu$ S·cm<sup>-1</sup> in mid-April to nearly 80  $\mu$ S·cm<sup>-1</sup> in late summer, before declining in early fall (Fig. 3). Stepwise regression models showed that COND was positively related to day of year and water level and negatively related to PREC<sub>30</sub>; together, these variables explained 69% of the variation in COND (Table 9). Water pH fluctuated between 6.1 and 6.9 throughout the monitoring period and was not significantly related to day of year, water level, or PREC. TP ranged between 14 and 25  $\mu$ g·L<sup>-1</sup> during the months of April to July, after which it began to decline; the lowest 5-day averaged concentration was 9· $\mu$ g·L<sup>-1</sup> in early October. Day of year was the only variable to enter the model for TP (negative relationship), explaining Figure 3. 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. Panel (a) shows daily precipitation (bars) and water level (line) during the study period.

32% of the variation in daily concentrations. COL was highest in spring (up to 250 mg Pt·L<sup>-1</sup>), and declined in summer and early fall to a low of around 56 mg Pt·L<sup>-1</sup> in early October. Both day of year and water level entered the model for COL (negative relationships), together explaining 49% of the variation.

# 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 areas of unique water chemistry due in large part to

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the unique geological setting. Precambrian Shield watersheds export large quantities of sediment, DOC, phosphorus, 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 portion 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 contrast, the sedimentary bedrock that underlies the majority of Great Lakes watersheds, including the southern and western portion of Georgian Bay, results in relatively alkaline, well-buffered lake water. Compared with runoff from the crystalline Shield rock, Georgian Bay water is low in phosphorus, but is a relatively rich source of dissolved ions, including sulphate and nitrate, and has a high pH. The resulting gradation in water chemistry from land to water in eastern Georgian Bay results in distinct patterns in water chemistry (groupings of watershed- vs. lake-derived variables).

# Landscape influences on marsh water chemistry

We found that larger drainage basins tended to contain more upstream wetland both in terms of absolute area and as a proportion of the total watershed and received higher precipitation and snowmelt inputs. 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 PC1 scores) had higher concentrations of TP, COL, TSS, TAN, H<sup>+</sup>, and DOC, but lower concentrations of COND, TNN, and SO<sub>4</sub><sup>2-</sup>. Since PCA could not elucidate the degree to which watershed size alone versus other factors (e.g., precipitation and snowmelt inputs or amount of upstream wetland) influenced water chemistry, we relied on the relative strength of each independent variable in regression analyses to provide further insight.

Stepwise regressions identified precipitation and snowmelt inputs to catchments (the product of drainage area and precipitation + snowmelt) as the strongest predictor of the majority of marsh water chemistry variables, including SO<sub>4</sub><sup>2-</sup>, COND, TP, COL, TSS, and summer DOC, while drainage area was the strongest predictor of pH. Previous studies on inland lakes have found drainage area to have a strong influence on nutrient and sediment loadings; TSS, DOC, and COL largely originate from terrestrial sources, thus larger watersheds tend to produce higher loadings to downstream waters (Curtis and Schindler 1997; Dillon and Molot 2005; Eimers et al. 2008). Similarly, a positive relationship between TP and watershed size is attributed to the fact that a larger drainage area theoretically results in higher P loading because of weathering and atmospheric deposition (Schindler 1971). Our finding that water chemistry variables showed a stronger relationship to short-term (7-day) precipitation and snowmelt inputs to catchments than to drainage area alone demonstrates that hydrologic flushing has a dominant role in export of catchment-derived constituents to downstream marshes. Additionally, higher precipitation and

Parameter	n	Equation	$r^2 a$	$r^2_{\rm adj}$
log <sub>10</sub> COND	187	-0.0787 + 0.00256DATE**** $-0.346$ log <sub>10</sub> (PREC <sub>30</sub> )**** $+ 0.831$ (LVL) <sup>2</sup> ****	0.49, 0.63, 0.69	0.68
log <sub>10</sub> COL	187	2.584 - 0.00215DATE**** - 0.850(LVL) <sup>2</sup> ****	0.42, 0.49	0.48
log <sub>10</sub> TP	187	1.457 – 0.00137DATE****	0.32	0.32

Table 9. Models built from forward stepwise regressions for seasonal water chemistry data at Black Rock marsh.

**Note:** \*\*\*\*, *P* < 0.0001.

<sup>a</sup>Cumulative for each variable entered.

snowmelt inputs to catchments tends to result in higher discharge (Yao et al. 2008; Buttle and Eimers 2009), which can reduce the seiche-induced inflow of lake water to a marsh (Trebitz et al. 2002). Consequently, marshes with high measures of  $PREC_{07avg}$  tended to have lower water pH, COND, TNN, and  $SO_4^{2-}$  concentrations because of reduced buffering and ionic loadings from the lake.

Other factors may also affect the amount of lake water influence in a marsh. The openings to several of the marshes in our study occurred within larger shoreline embayments, which themselves experience varying degrees of mixing with the offshore water. Thus, examining the position of marshes in relation to broader shoreline morphology would likely account for some additional variation in water chemistry characteristics, as would examining the degree of site-to-site variation in seiche amplitude (see Trebitz et al. 2002). In addition, the opening width that connects the marsh to the lake may influence the amount of mixing that occurs via longshore currents; however, we did not find evidence of this effect in our study, possibly owing to the presence of overriding factors.

While summer DOC was best explained by 7-day precipitation and snowmelt inputs to catchments and also showed a moderately strong relationship to area of upstream wetland, spring DOC was not significantly related to landscape variables. This may be partly a result of variation in the seasonality of sources of DOC. Wetlands are widely reported to be a major source of DOC to downstream waters during runoff events (Dillon and Molot 1997; Kothawala et al. 2006; Eimers et al. 2008), and DOC production and leaching from peat is highest during summer months (Hongve 1999). Variation in spring concentrations, however, may be largely a function of catchment variables not examined in our study, such as the area of deciduous forest cover; deciduous leaf litter can be a major source of DOC between autumn and spring thaw (Hongve 1999). Some research also indicates that distinguishing among wetland types may have yielded stronger relationships between upstream wetland variables and water chemistry variables (including DOC), 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 TNN, TP, TSS, and pH, with positive relationships with each variable except pH. A positive relationship between TNN 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, which they attributed to less opportunity for export of dissolved P in steep catchments. Our observation of higher concentrations of TSS 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 positively related to TP, TNN, and TAN. While the mechanism behind these relationships is not clear, we speculate that the finding of higher nutrient levels in large marshes may be related to the storage and release of these nutrients in marsh sediments and organic matter (Bowden 1987; Craft et al. 1989). Marshes in our study generally support dense submerged aquatic vegetation that can filter and cause settling of organic and inorganic particulate matter entering from the watershed and can also play a role in the transfer of nutrients between sediments and the water column (Nichols 1983). Detailed bathymetric information would have allowed us to estimate residence times, which could have explained additional variation in some water-chemistry parameters; however, digital elevation models for such remote locations do not currently exist.

#### Seasonal trends in marsh water chemistry

Knowledge of seasonal variation in marsh water chemistry is important in temperate coastal areas, where snowmelt plays a major 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). During spring, snowmelt results in high hydrologic flow from watersheds, and this can increase runoff contribution and reduce the influx of lake water into coastal bays and wetlands (Trebitz et al. 2002; Morrice et al. 2004). Spring runoff from Precambrian Shield catchments delivers large 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). Consistent with these studies, we found higher concentrations of DOC and SRP in April than in July surveys and a continued decline in TP and colour during the late summer and early fall at Black Rock marsh; together, these results indicate higher loadings of catchmentderived constituents during spring and early summer.

In contrast with 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). 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), and specific conductivity is also relatively conservative (Cox et al. 2007). Thus, increased inflow of lake water likely contributes to the increase in dissolved ions (higher specific conductivity and SO<sub>4</sub><sup>2-</sup> concentrations) during summer. Higher rates of evapotranspiration and increased amounts of runoff in the form of shallow groundwater rather than overland flow may also contribute to the seasonal variation in specific conductivity.

At Black Rock marsh, lake level had a significant effect on daily fluctuations in COND and COL, whereby COL decreased and COND increased with an increase in lake level. This may indicate that seiche-induced inflow of lake water acts to dilute runoff and increase ionic loadings to the marsh; however, frequent (e.g., hourly) measurements of in-marsh water level and water chemistry through the duration of a seiche cycle would be necessary to provide a clearer understanding of the magnitude of seiche-induced influences on water chemistry of these marshes (see Morrice et al. 2004). Since tributaries in the study area tend to have very low conductivity (<10  $\mu$ S·cm<sup>-1</sup>) relative to the lake, increased hydrologic flows from the watershed following rain events likely contributed to the negative relationship between PREC<sub>30</sub> and COND at Black Rock marsh.

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). Although lake water potentially acts as a major source of nitrate during summer, there are high rates of biotic assimilation and denitrification that can reduce TNN concentrations relative to springtime levels (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 and early fall suggests either net P export from the marsh to the Bay or sequestration of P in marsh sediments (e.g., through senesce of plankton; Nichols 1983). Further research is required to first verify the generality of this trend and then determine causality.

### Implications

Eastern Georgian Bay is one of the few areas in the Great Lakes where it remains possible to study water chemistry in relation to natural watershed dynamics while establishing true baseline conditions against which future impacts can be assessed. Within a landscape ecology framework, our study draws on 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 have contributed a better understanding of the factors controlling reference chemistry of these ecosystems, something that is of recognized importance in the field of ecosystem conservation and management. The relationships established will be useful for identifying areas that could have high sensitivity to watershed disturbances. For example, our results strongly suggest that marshes with large, steeply sloped watersheds would be more sensitive to intensive land development that adds nutrients or promotes soil erosion in their watershed, and that these detrimental effects may be most evident in spring or following periods of high precipitation, when marsh water concentrations of catchment-derived constituents are highest. Future climate change will likely affect the timing and magnitude of nutrient and ion loadings to these marshes because of anticipated changes in precipitation and runoff patterns throughout the Great Lakes region; the majority of climate change models predict overall dryer catchments around Lake Huron and less snowfall and snowpack accumulation because of more winter precipitation falling as rain (Mortsch and Quinn 1996; Lofgren et al. 2002). As knowledge of coastal wetland dynamics continues to advance, we will become better equipped to manage these valuable habitats and predict and prevent the detrimental effects of human stressors and climate change impacts.

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