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## Exploring spatial trends and causes in Lake Ontario coastal chemistry: Nutrients and pigments

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### ABSTRACT

An ordination approach integrating chemical water quality and biological parameters proved to be an effective method that identified six regional clusters of differing water quality in the nearshore of Lake Ontario. This approach allows for an evaluation of potential factors that contribute to the water quality observed. Creeks and rivers with high dissolved nutrients, low suspended solids, and low biological production as chlorophyll were included in Cluster 1, while Cluster 2 included four bays associated with eutrophic conditions. The shoreside sites along the south shore of Lake Ontario (Cluster 3) had high total phosphorus (TP), chlorophyll, and phycocyanin relative to the offshore and moderate P limitation, suggesting that any P entering these systems from tributaries will stimulate phytoplankton and benthic algal growth. Long Pond and the Genesee River shoreside (Cluster 4) had elevated TP, total suspended solids, and total Kjeldahl nitrogen and high chlorophyll and phycocyanin concentrations. In general, offshore waters and the eastern nearshore and embayments of Lake Ontario (Clusters 5 and 6) had relatively low P, N, chlorophyll, and phycocyanin levels and were the most severely limited for P (N/P = molar ratio 82). Phosphorus loads to embayments and perhaps to the nearshore may be creating regional areas where N-limitation is likely, which tends to favor the growth of Cyanobacteria and may be associated with hepatotoxin production. From a management perspective, such analyses identify regions stressed by nutrients and provide possible causal relationships enabling the targeting of regions of the lake and its watershed for remediation.

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### Introduction

Lake Ontario's nearshore region encompasses 1020 km of shoreline with Canadian and American shorelines of nearly equal length (537 km Canada; 483 km USA) (Coordinated Great Lakes Physical Data, 1977). Over 150 tributaries discharge into the lake and have a regional impact on nearshore water quality (Makarewicz et al., 2012d). The Niagara River provides the largest total phosphorus (TP) load to Lake Ontario, but the cumulative TP load of other tributaries (2606 mT/yr) was 234% higher than that of wastewater treatment plants (WWTPs) and 67.5% of the 1982 Niagara P load (Makarewicz et al., 2012d). Tributary discharge plumes, a pervasive feature of the nearshore, create a spatially variable nearshore nutrient chemistry, with the predominating alongshore currents frequently orienting water quality gradients parallel to the shoreline away from tributary mouths. Much of this P and sediment load occurs during hydro-meteorologic events (Makarewicz et al., 2013; Long et al., 2014). For example, total suspended solid (TSS) concentrations increased by as much as 2690%, TP by 1159%, and soluble reactive phosphorus (SRP)

by 265% during events on the Genesee River, a major tributary of Lake Ontario (Makarewicz et al., 2013). The plumes of river water into the nearshore zone of large lakes generate a constant but variable source that increases the inventory of TP, bioavailable P, and other nutrients in the nearshore (Makarewicz et al., 2012b). This transport of nutrients and sediments from watersheds via streams to lakes is important in determining the timing and extent of nutrient availability and in structuring the biological communities such as the benthic algae *Cladophora* and the dreissenid mussels found in the nearshore region. In addition, frequent upwellings, especially notable on the north shore of Lake Ontario, contribute to the periodic onshore-offshore gradients in water quality and the highly changeable conditions over time (Howell et al., 2012b; Yerubandi et al., 2012). The individual and cumulative impact of these tributaries entering Lake Ontario is potentially great in the embayments and drowned river mouths and along the nearshore of the coastal region and is increasingly being recognized as a driver of nearshore conditions (Makarewicz and Howell, 2012).

For example, Makarewicz et al. (2012c) demonstrated that spring thermal bar development, P, and suspended solid flux from a river contribute to elevated turbidity and P concentrations on the shoreside of the thermal front and are not transported to the lakeside of the thermal front. Conversely, while turbidity and TP increase, biological mechanisms reduce silica and nitrate on the shoreside relative to the offshore

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of the thermal front. Pavlac et al. (2012) identified a clear chlorophyll maximum at this thermal front. The elevated P levels of the nearshore are of concern as P is believed to limit the growth of both the planktonic and the benthic alga *Cladophora* in Lake Ontario and can be expected to stimulate growth and contribute to the occurrence patterns of algae over the nearshore. The potential role of the shoreside of the thermal front as a potential incubator, with its warmer temperatures and elevated nutrient levels for algal growth, is discussed by Vodacek (2012).

Another cause of variability within the nearshore is effluent from wastewater treatment plants (WWTPs). Although much is known about nutrient influx from WWTPs, Helm et al. (2012) working in the Greater Toronto area, demonstrated that organic wastewater-chemicals are greatest in the vicinity of WWTPs. Ibuprofen, carbamazepine, and especially caffeine concentrations exhibited more uniform distributions both within and between study nearshore sites, suggesting that transport via alongshore currents may contribute to a regional background of the relatively more persistent organic wastewater associated chemicals that may not be captured in onshore–offshore gradient studies (Helm et al., 2012). Clearly, nutrients would also be carried by these currents and contribute to a regional background of elevated nutrients.

Nearshore TP concentrations can exceed the Great Lakes Water Quality Agreement (GLWQA) objectives for P near the shoreline, but P concentrations a few kilometers offshore are within the GLWQA objectives. Nutrients, chlorophyll, and even temperature were more variable and reached higher levels in the nearshore than in the offshore (Makarewicz and Howell, 2007; Makarewicz et al. 2012a). A recurring pattern was a drop in these features away from the shoreline with little or subtle decline beyond 1 to 3 km from the shore. Wide variability in nutrients, major ions, suspended solids, and *Escherichia coli* was observed over the nearshore; variability correlated with proximity to the shoreline and within geographic areas. Howell et al. (2012a) and Makarewicz et al. (2012a) have suggested that a thin band of water with a unique but variable water chemistry compared to both offshore waters and tributaries may extend up to 4 km into the open waters along the southern coast of Lake Ontario during the late spring and summer. For example, at the Rochester nearshore sites in June, temperature, specific conductance, TP, and turbidity were elevated out to at least 3–4 km from the shoreline (Makarewicz et al., 2012a,b). Levels of suspended solids, nutrients, major ions, *E. coli*, and dissolved organic carbon were higher and more variable among tributary, embayment, and shoreside (0- to 1.2-m depth) areas compared with the open nearshore (~3-m depth to 5 km offshore) (Howell et al., 2012a).

Here we develop information on the persistent structure of the nearshore zone of southern Lake Ontario based on monitoring data from May 2003 to September 2013 in an ongoing study generally referred to as the Lake Ontario Nearshore Nutrient Study (LONNS) – a part of the binational Cooperative Science and Monitoring Initiative (CSMI). A total of 39 sites were monitored focusing on the nearshore, tributaries, embayments, and two stations in the open waters of Lake Ontario with analyses focused primarily on nutrients (phosphorus and nitrogen), total suspended solids, chlorophyll, and phycocyanin. Ongoing work on the nearshore of Lake Ontario has demonstrated that the nearshore zone is highly variable, complex, dynamic, and influenced by runoff from the watershed and the larger open lake (Makarewicz and Howell, 2012). With the documented variability and complexity of the coastal region of Lake Ontario, was a persistent spatial pattern evident in coastal water quality? Our objective was to consolidate collected data on coastal water quality in Lake Ontario to recognize a general spatial pattern associated with landforms and levels of anthropogenic stress; that is, to categorize contrasting water regimes along the south shore of Lake Ontario. An ordination approach using chemical and biological measures was used to integrate, evaluate, and identify not only regions of the lake that have differing water quality but also the correlated causes associated with the differences observed.

## Methods

### Nearshore monitoring

The Lake Ontario Nearshore Nutrient Study (LONNS) refers to a monitoring program undertaken from 2003 to 2013 (2003, 2004, 2005, 2007, 2009, and 2013). Water samples were collected monthly from May through September in each year (with occasional samples from October and November) from 39 sites along the southern shore of Lake Ontario from the Niagara River in the west to Chaumont Bay in the east using a Van Dorn type water sampler (Fig. 1) (e.g., Makarewicz et al., 2012a). Sites were selected to cover a wide variety of habitat types that included rivers, embayments, coastal shoreside waters, and offshore waters along the southern and eastern shores of Lake Ontario. Sites east of Port Bay were sampled from 2005 to 2013 only, while the remaining sites were sampled from 2003 to 2013. Embayments (Braddock Bay, Chaumont Bay, Henderson Harbor, Little Sodus Bay, Irondequoit Bay, Long Pond, Port Bay, Sackets Harbor, Sandy Pond, Sodus Bay) and creeks and rivers (e.g., Niagara River, Twelvemile Creek, Eighteenmile Creek, Oak Orchard Creek, Salmon River, Sandy Creek, Genesee River, Salmon Creek at Pultneyville, Oswego River) were sampled at a depth of 1 m at either the mouth of the river or, if an embayment, near the outlet to Lake Ontario. Raw and filtered water samples were stored on ice, transported to the laboratory, stored in a refrigerator at 4 °C, and logged into the laboratory database upon arrival.

Shoreside sites, where water samples were taken at a wadeable depth (~0.5 to 1 m) with a Van Dorn-type water bottle from docks, piers, boats, and by wading into the water, represented water conditions that beachgoers and lakeside home owners encounter. For samples obtained by wading, precautions were taken to avoid resuspension of sediments by waiting 3 min before taking a sample. Nearshore lake currents are generally west to east, west of Oswego, NY, and south to north, north of Oswego, NY. To reduce the river or embayment influences on water quality, nearshore water samples were taken west of a tributary west of Oswego and south of a tributary north of Oswego, NY.

Two open-water sites north of Sandy Creek [LO-30 m (30-m water depth, 2.4 km from shoreline) and LO-100 m (100-m water depth, 7.8 km from the shoreline)] were sampled generally biweekly, unlike the other sites where monthly samples were taken, at a 1-m depth from May through September (occasionally October). At all sites, water samples were analyzed for total phosphorus (TP), soluble reactive phosphorus (SRP), combined nitrate and nitrite ( $\text{NO}_3 + \text{NO}_2$ ), total Kjeldahl nitrogen (TKN), chlorophyll (Chl), and total suspended solids (TSS). A Seabird CTD (Model 25 SBE, Sea-Bird Electronics) (offshore sites) or a Hydrolab D55 (shoreside sites) was deployed to measure dissolved oxygen, pH, turbidity, temperature, specific conductance, and fluorometric measures of chlorophyll (Chl) and phycocyanin (Phy).

In vivo pigment fluorescence measured by fluorometers was calibrated using an exponential phase culture of *Chlorella vulgaris* (for chlorophyll) grown in ASM media (McLachlan and Gorham, 1961) or *Microcystis aeruginosa* (for phycocyanin) grown in BG-11 media (ATCC). Fluorometers were recalibrated using a secondary standard of Rhodamine WT (Keystone Aniline Corporation, IL) in water, and the calibration was checked immediately before deployment for each cruise. In addition, approximately 20% of the raw water samples were run for chlorophyll by extraction (Wetzel and Likens, 2000) on a Turner Designs TD 700 Fluorometer for quality control purposes. The TD 700 was calibrated with a chlorophyll extract that was analyzed spectrophotometrically and serially diluted following the APHA 10200 H 3b1 method. A solid standard was used to ensure that the machine calibration was consistent.

### Chemistry

Water samples were analyzed at the State University of New York at the Brockport Water Quality Laboratory. From each sample bottle,

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