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Evaluation of stormwater and snowmelt inputs, land use and seasonality on nutrient dynamics in the watersheds of Hamilton Harbour, Ontario, Canada

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ABSTRACT

Between July 2010 and May 2012, 87 24-hour level-weighted composite samples were collected from a variety of catchment states (rain, snowmelt, baseflow) from all four major tributaries to Hamilton Harbour, Ontario, Canada. Samples were analyzed for phosphorus- and nitrogen-based nutrients, and concentrations were examined for trends with catchment state, land use, and seasonality. Total phosphorus (TP) and phosphate concentrations were consistently higher during rain/melt events relative to baseflow. Nitrogen parameters, however, exhibited either concentrating behavior or little change in concentration across a range in flows (chemostasis) depending on the parameter and catchment. Despite differences in land use among the four watersheds, TP concentrations during rain/melt events did not vary among stations; however, spatial variability was observed for other parameters, especially nitrate which was elevated in watersheds on the north shore of the Harbour. Seasonal variability was generally not observed for TP concentrations, mirroring the lack of temporal trends for TSS. In contrast, elevated concentrations of nitrate and phosphate were observed during the fall and/or winter period, except in the primarily agricultural watershed where concentrations were elevated during the summer growing season. Highly elevated concentrations of ammonia and nitrate were observed in some watersheds during the unseasonably cold winter of 2010–2011 but not in the comparatively warm winter of 2011–2012. Implications of the study are discussed including the inferred potential impacts of climate change on nutrient dynamics given the strong contrasts in weather patterns observed between years, and exploration of the feasibility of mitigation measures given the data trends.

Introduction

Nutrient concentrations in tributaries are an important driver in determining trophic status, as well as the potential eutrophication of downstream water bodies. While every watershed is unique in terms of the magnitude of nutrient concentrations and the dynamics present, some factors commonly understood to influence the observed variability in nutrient concentrations include catchment state (baseflow or high flow conditions), land use, and seasonality. It has been increasingly apparent for suspended sediment and nutrients like total phosphorus (TP) of which 75–90% of the flux is sediment-bound (Horowitz, 2013) that much of the annual load is associated with a few large storm events (Booty et al., 2014; Horowitz, 2013; Macrae et al., 2007; O'Neill, 1979; Old et al., 2003; Richards and Holloway, 1987; Sharpley et al., 1993). Relatively few datasets have been collected during the peak of storms in general due to the brevity of these events, and even fewer data have been collected on extreme events due to their infrequent nature. This is especially important considering that an increase in the intensity of storm events may occur in many regions due to climate change (Kunkel et al., 2013).

Total phosphorus concentrations correlate strongly with flow, as insoluble constituents are generally transported by overland flow, mobilized from the streambed or bank (Gburek and Sharpley, 1998; Green et al., 2007; OMOE, 2012f), or via soil macropores to tile drains (Blann et al., 2009; Macrae et al., 2007; Vidon and Cuadra, 2011). More dissolved forms of phosphorus such as ortho-phosphate have also been linked to overland flow (Tesoriero et al., 2009), albeit concentration peaks during high flow periods are less pronounced relative to TP (Meybeck and Moatar, 2011). In contrast to TP, a greater proportion of total nitrogen (TN) is found in the dissolved phase (Horowitz, 2013) due to relatively high solubility of nitrogen species such as nitrite and nitrate. As such, TN can be transported by both overland and subsurface flow paths depending on the dominant N species present and other

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conditions (Frank et al., 2000; Green et al., 2007; Hill et al., 1999). Furthermore, subsurface leaching of nitrate, and hence transport to groundwater, is generally greater than phosphate due to immobilization of phosphate by clay and other chemical constituents of soil (Reynolds and Davies, 2001).

While a clear association of the various forms of phosphorus with stormwater has been established across watersheds of diverse character, there is much variability in the flow–concentration relationship potentially due to factors such as antecedent conditions (Hirsch et al., 2010; Macrae et al., 2007; Richards, 1998), a non-linear response to extreme precipitation events in terms of either export (Macrae et al., 2007) or discharge thresholds (Wellen et al., 2014). An overarching flow–concentration paradigm for species of nitrogen is even less clear relative to that for phosphorus. Ammonia fluxes have generally been found to increase less rapidly than river flows (diluting process), whereas total Kjeldahl nitrogen (TKN) fluxes increase more rapidly (concentrating process). Nitrate fluxes have been found to follow either process (Meybeck and Moatar, 2011), a duality in behavior which is critical in understanding the sources and transport of this parameter in each watershed. More data are needed on nutrient concentrations across a variety of catchment states, in particular from urban and agricultural watersheds, to further elucidate nutrient-enrichment processes. These landscapes are generally accepted to export greater nutrient fluxes relative to undisturbed natural systems, and event-based study is needed in order to describe current spatial trends and to evaluate the effect of land use change on nutrient fluxes given the ongoing urbanization of formerly agricultural areas.

Understanding the roles of catchment state and land use on observed nutrient concentrations requires an appropriate sampling program. This can be a challenge to many standard monitoring programs because key sampling periods, such as the winter season as well as storm and melt events, are often overlooked. Tributary studies in temperate regions are typically focused on the ice-free season despite year-round flow data due to logistical challenges in collecting samples in snow or through ice. This scarcity of winter data is problematic as the highest annual loads of TP and nitrates in temperate urban and agricultural watersheds have been attributed to the winter period on account of high flows and high concentration relative to equivalent flows in other seasons (Makarewicz et al., 2012; O'Connor et al., 2011; OMOE, 2012f). In addition, many stream monitoring programs are based on the regular collection of water samples irrespective of stream flow conditions, resulting in a bias towards characterization of baseflow conditions. These generate data that are useful from the perspective of the aquatic habitat and examining long-term and spatial trends but are not ideal for nutrient loading studies. Recent studies have recommended event-based sampling with collection of samples during as many high-flow events as practicable (Horowitz, 2013; Makarewicz et al., 2012) and, further, that flow proportional samples be collected in loading studies (Harmel et al., 2003; Makarewicz et al., 2012; Richards, 1998). Although high frequency point-in-time grab samples during high flow events are useful in revealing details of the chemograph, analysis of composite samples consumes less analytical resources and avoids the confounding effects of first flush and hysteresis (Aulenbach and Hooper, 2006; Butcher, 2003; Hirsch et al., 2010; Macrae et al., 2007; O'Connor et al., 2011; Shih et al., 1994).

The primary goal of our study was to characterize nutrient dynamics in the tributaries of Hamilton Harbour where phosphorus and other nutrients play a pivotal role in the eutrophic status and resulting impaired ecology of Hamilton Harbour, a Great Lakes Area of Concern (AOC) under the Canada–United States Great Lakes Water Quality Agreement of 2012 (Government of Canada, 2013a). Although work was prompted by the needs of the Hamilton Harbour Remedial Action Plan (RAP), the applicability of trends found in these watersheds to similar Great Lakes watersheds may mean that such a protracted sampling effort does not need to be repeated in all watersheds with notable nutrient issues. The specific objectives here are to:

1. Assess the difference between baseflow and event flow nutrient concentrations in the four tributary inputs to Hamilton Harbour;
2. Undertake a comparative basin study to evaluate the role of land use in tributary nutrient concentrations; and
3. Evaluate temporal and seasonal trends of nutrients, with a particular focus on late fall, winter, and early spring conditions where relatively less monitoring data are currently available.

Eighty-seven 24-hour periods were sampled over 22 months, making this study one of the most intensive event-based tributary monitoring programs that has been undertaken in Ontario, Canada (Gaynor, 1978; Macrae et al., 2007; Makarewicz et al., 2012) or elsewhere (Maniquiz et al., 2010; Robinson et al., 1996; Zhang et al., 2010).

Material and methods

Watershed summary

This study was undertaken in the watersheds of Hamilton Harbour, a 2150-hectare partially-enclosed Harbour located at the very western end of Lake Ontario, in Ontario, Canada (Fig. 1). Tributary inputs enter the Harbour via Red Hill Creek, Indian Creek, and Grindstone Creek, as well as through the Desjardins Canal, the hydraulic connection between the Cootes Paradise wetland to the west and Hamilton Harbour to the east. In spring 2010, four tributary monitoring stations were installed at downstream locations in Indian Creek and Grindstone Creek, in Burlington, Ontario, and in Red Hill Creek and the Desjardins Canal, in Hamilton, Ontario, cities with 2011 populations of 176,000 and 520,000, respectively (Statistics Canada, 2012). Land use is primarily urban in the Red Hill Creek and Indian Creek watersheds and agricultural in the Grindstone Creek and Cootes Paradise watersheds (Table 1). The soils of the Hamilton Harbour watershed are predominantly loams, sandy loams, and silty loams, with a relatively even split between the four Natural Resources Conservation Service's soil hydrologic runoff groups, meaning there are soils both likely and unlikely to generate runoff throughout the watershed (Wellen et al., 2013).

Several features of each watershed are important in the interpretation of nutrient data collected in this study. All watersheds are traversed by at least one major expressway, and the density of these major roadways is particularly high in the watersheds of Red Hill Creek and Indian Creek where three major expressways are present. Also in the Indian Creek watershed, there are shale extraction quarries and brick manufacturing facilities which have been noted to contribute high sediment loads (Conservation Halton, 2006). Also, the Indian Creek station integrates inputs from multiple urban sub-watersheds as it was located approximately 50 m downstream of the confluence of the Hagar–Rambo diversion channel, an engineered inter-basin transfer of water from the Hagar and Rambo tributaries. An 800 m stretch of Indian Creek also runs underground in a hardened culvert beneath Francis Road in Burlington; similarly, portions of Rambo Creek (also Burlington) and Chedoke Creek (in the Desjardins Canal watershed, Hamilton) are also redirected underground in sections of their watersheds (Cook, 2013).

The Desjardins Canal station is not on a tributary but does integrate inputs from a number of creeks that discharge to the Cootes Paradise wetland including Spencer Creek (235 km^2), Chedoke Creek (25 km^2), Borers Creek (20 km^2) and other small watersheds (10 km^2) (T. Theysmeyer, 2012, pers. comm.). The interpretation of data from the Desjardins Canal station is complicated by several co-occurring processes, including: large tributary inputs during events, in particular from nearby Chedoke Creek; potential flow reversals from Hamilton Harbour during strong easterly winds and low flow conditions; and ongoing wetland processes.

Water quality data from Red Hill Creek and Cootes Paradise via the Desjardins Canal are intermittently influenced by combined sewer

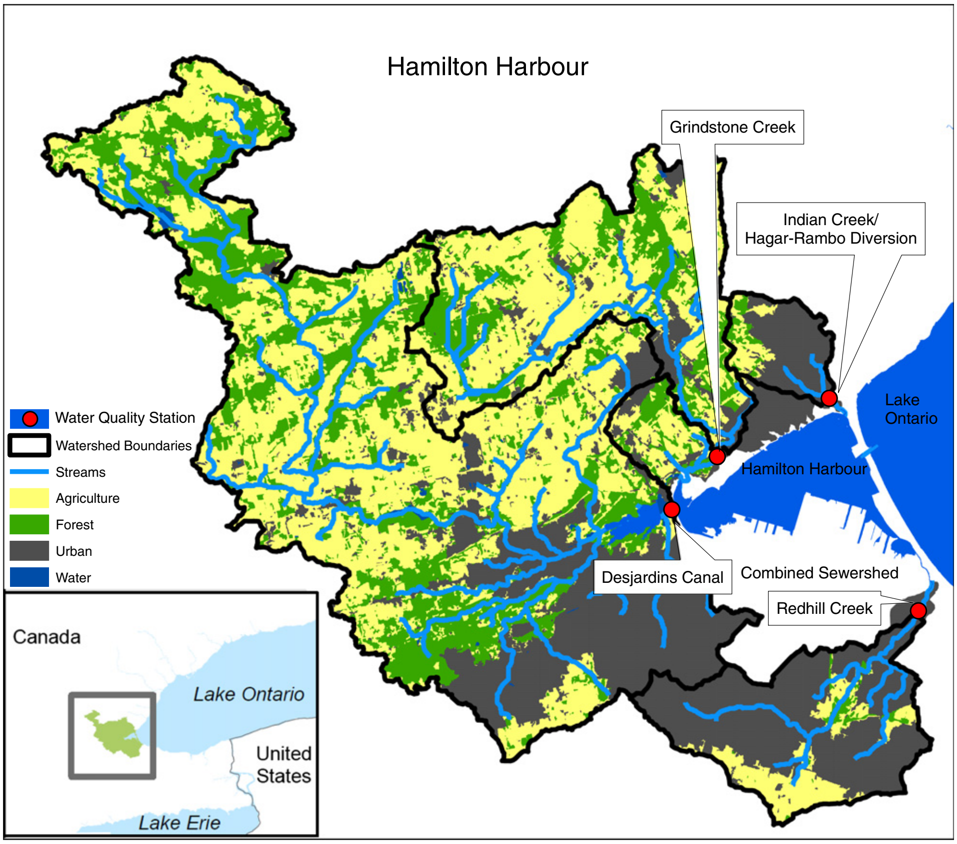

Fig. 1. Location of the four sampling stations in Burlington and Hamilton, Ontario. Also indicated are watershed boundaries, land use and streams.

overflows (CSOs). During the course of this study, the City of Hamilton was undertaking upgrades to the combined sewer system which impacted the number and volume of overflows both to Red Hill Creek and Cootes Paradise. CSO holding tanks are now in operation at many CSO locations, and data on the occurrence and duration of overflow events at these controlled sites are collected by the City of Hamilton; however, no field measured data are available for uncontrolled sites. At the end of the study period (May 2012), Red Hill Creek had two CSO points, located 0.8 km and 4 km upstream from the our monitoring station; both of these are now controlled CSO points. During the July 5, 2010 to May 8, 2012 sampling period of this study, there were 28 overflow events from the Greenhill tank on Red Hill Creek; overflow events from the other CSO locations on Red Hill Creek are unknown until December 2011, when the Red Hill CSO superpipe was brought online, and did not overflow in 2012 (M. Bainbridge, 2014, pers. comm.).

Table 1
Area and land use of the four Hamilton Harbour watersheds.[a]
Land use data from Ontario Ministry of Natural Resources (2008).

	Watershed area (km^2)	Land use (%)			
		Urban	Urban greenspace	Agricultural (pasture and cropland)	Forest
Red Hill Creek	65	66	15	16	3
Indian Creek	23[a]	54	18	17	10
Grindstone Creek	87	6	3	60	29
Desjardins Canal (Cootes Paradise)	290	17	6	47	28

[a] 74% Hagar–Rambo watershed and 26% Indian Creek watershed (Conservation Halton, 2006).

Upgrades were also occurring for CSOs that discharge to Cootes Paradise, and by May 2012, Cootes Paradise had a total of six possible CSO points, of which three of these were controlled CSO points. Of the three, two discharge to Cootes Paradise via Chedoke Creek (Royal tank, Main/King tank) and one directly to the Cootes Paradise wetland (McMaster tank). Between July 5, 2010 and May 8, 2012, there were 30 overflow events from the Main/King tank, and 21 from the Royal tank; the McMaster tank was not brought online until April 2012 so little overflow data are available on this CSO location for the majority of this study (M. Bainbridge, 2014, pers. comm.). The occurrence of overflows is dependent on the nature of each event such as precipitation intensity and antecedent conditions, thus total precipitation amount cannot be used as a predictor of occurrence or the size of overflow events.

Generally, the majority of the population in all four watersheds are serviced by municipal sewers, although some more rural areas in the upper headwaters are serviced by septic systems. The main Hamilton and Burlington wastewater treatment plants (WWTPs) do not influence the waters sampled in this study; however, the Waterdown WWTP servicing Waterdown, Ontario (2009 population: 17,000; Urban Marketing Collaborative, 2010) discharged to Grindstone Creek at a nominal design flow of 2.7 ML/day (HH RAP, 2010) approximately 4.5 km upstream from the sampling site. This plant went offline on August 24, 2010 and although the first nine samples of this study may be influenced by this point source, the results overall do not reflect this source. Of greater relevance, Cootes Paradise and hence water quality at the Desjardins Canal is influenced by the Dundas WWTP, a small tertiary treatment plant with a nominal design flow of 18 ML/day (HH RAP, 2010), that discharges to the west end of Cootes Paradise, approximately 3.8 km west of the Desjardins Canal event-based monitoring station.

2010–2012 weather summary

The Hamilton Harbour watershed is in a temperate climate zone with an annual average precipitation total of 892.6 mm which is distributed relatively evenly among the 12 months of the year although this includes an average snowfall of 126.1 cm between November and April (Government of Canada, 2013b). During the July 2010–May 2012 sampling period, monthly precipitation totals demonstrated some variability from the 1971 to 2000 averages, with July 2010, April 2011, May 2011, and October 2011 as particularly "wet" months and August 2010, December 2010, January 2011, July 2011, February 2012, March 2012 and May 2012 as particularly "dry" months (Government of Canada, 2013b; Hamilton Conservation Authority, unpublished data). There were five very large precipitation events of note, four of which occurred in fall: July 9, 2010 (55.5 mm), September 28, 2010 (40.6 mm), November 16, 2010 (31.6 mm), October 19, 2011 (60.1 mm), and November 29, 2011 (38.5 mm). Some degree of spatial variability also occurred in the actual amount of precipitation that fell in each of the watersheds, as demonstrated in the difference between precipitation amounts measured at the Government of Canada's Royal Botanical Gardens Station in Hamilton and at the Hamilton Conservation Authority's Stoney Creek Station in Stoney Creek, locations which are both below the Niagara Escarpment and approximately 13 km apart. Variability in precipitation amounts among the watersheds was particularly pronounced during summer convective events, which is consistent with the local-scale spatial variability that has been observed in other temperate areas (Booty et al., 2014; Shaw et al., 2010).

Distinct temperature patterns also occurred within the study area during the survey period. The July 2011 and May 2012 monthly average temperatures were approximately 2 °C warmer than average. Anomalous winter conditions also occurred, resulting in two contrasting years in the form of precipitation. Monthly average temperatures during December 2010 to March 2011 were 0.4 °C to 2.1 °C colder than 1971–2000 monthly average temperatures; whereas, monthly average temperatures during November 2011 to March 2012 were 2.8 °C to 6.2 °C warmer than 1971–2000 monthly average temperatures (Government of Canada, 2013b). This inter-annual variability impacted the distribution of precipitation between rain and snow as December 2010–March 2011 monthly average temperatures were below freezing, while during the following winter, only January 2012 had a monthly average temperature below freezing. Very different snowpack conditions were experienced between the two winters in which sampling was conducted, with the winter of 2010–2011 having much greater snow accumulation relative to 2011–2012. As such, melt-event sampling was biased towards the winter of 2010–2011 as very little snow fell during winter 2011–2012.

Water monitoring station set-up and logistics

Event-based sampling is logistically challenging as the initiation of events cannot be predicted with a high degree of precision. Events can happen quickly and the rising limb and peak flow can easily be missed. We used automated sampling technology to address these challenges. The core of each monitoring station consisted of a Teledyne ISCO autosampler (model 6712) with a level bubbler module (model 730), monitoring water level every 15 min. ISCO samplers were equipped with pre-cleaned surgical grade silicone tubing and changed regularly to prevent fatigue from pumping.

All equipment was housed in a hut adjacent to each sampling location and each hut was fitted with power and telephone connections to permit remote programming and data downloads. Heaters and heat-trace lines were also installed at each station to keep the samples and water intake lines from freezing during winter months. Sample water was drawn to the hut along Teflon-lined polyethylene tubing intake lines. Stainless steel strainers with a 1 cm wide mesh were installed on each intake line to prevent intake of large debris and were situated in the main flow of the river. In the three creeks, weights and/or metal brackets were used to secure the intake to the stream bottom. At the Desjardins Canal, the intake was suspended mid-water column with an air-filled float. While collection of water samples representative of the vertical distribution of suspended solids in the water column would be ideal, the impact on results from the sampling set-up employed here would be diminished since clay and silt are generally distributed in the water column homogeneously (Horowitz, 2013), and these fractions account for most adsorbed contaminants.

Sampling events were targeted based on local weather reports, and each ISCO sampler was programmed to initiate sampling following a rise in water level or at a pre-determined time. For high flow events, Red Hill, Indian, and Grindstone Creeks were generally triggered by an approximately 2 cm rise in water level. The Desjardins Canal station could not be programmed to trigger based on level since it does not exhibit a tributary-like hydrograph; instead, this station was triggered at the anticipated start of the storm event. Although the sampling start time and initiation of storm event often did not coincide at the Desjardins Canal station, the majority of the storm flow was generally captured by the 24-hour sampling window, and a sharp rise in water level at nearby and adjacent Grindstone Creek was used to determine the onset of storm event sampling. In general, the direction of water flow is from the wetland to the Harbour; however, flow reversals are possible, particularly during low flow conditions or strong easterly winds (Electronic Supplementary Material (ESM) Appendix S1). Baseflow sampling generally started at uniform times across all four stations and was conducted when no precipitation had been recorded for at least 24–48 h prior to sampling, and the hydrographs showed no recent evidence of runoff.

Sample collection, retrieval, and processing

Once each ISCO sampler was activated to initiate sampling, intake lines were purged and rinsed, and then 1 L of water was collected once an hour, for 24 h. When 24 h was insufficient to capture the entire event (e.g., the spring freshet, large frontal storms), the ISCO was immediately (manually) re-deployed for an additional 24 h. Generally, water levels following storm events returned to baseflow conditions at Red Hill Creek and Indian Creek within 24 h, whereas water levels at Grindstone Creek declined steadily between each event, reflecting the less urban nature of this watershed.

Samples were collected in pre-cleaned 1 L polypropylene ISCO bottles. Upon completion of each event, a visit to each site was conducted to retrieve samples and collect event sampling metadata and additional environmental data on the present condition of each tributary. The temperature, dissolved oxygen, pH, and conductivity of each tributary at the time of sample pickup were measured at each station using a YSI sonde. After sample collection, all 1 L bottles were placed on ice in a cooler and transported back to the Ontario Ministry of the Environment (OMOE) in Toronto, Ontario, where they were stored in a walk-in fridge (4 °C) until sample post-retrieval processing could begin. Samples were generally retrieved within 24 h of the end of each event and processed within 24 h of being brought back to the OMOE. Although this equates to approximately 2–3 days between sample collection and submission to the laboratory, the effects of this holding time on the overall results are expected to be minimal. When nutrient concentrations are high as they are in the Hamilton Harbour watersheds, the relative losses due to lack of preservation are comparatively low (Kotlash and Chessman, 1998).

During approximately every eighth sample pick-up, replicate samples were prepared and a field blank was collected for quality assurance/quality control (QA/QC) purposes. Distilled, deionized water was brought into the field from the lab. At a randomly selected station, 1 L of the lab-grade water was transferred to a spare 1 L plastic ISCO bottle which had been cleaned and stored in the same locations as the bottles which were used for sample collection in the ISCO carousels.

The intent of the blanks was to test for potential field or bottle contamination; laboratory blanks are conducted separately as part of each standard laboratory method. Over the duration of the study, eight field blanks were collected.

Water level data for the duration of each event were downloaded from each station. Discharge data for Indian Creek were also downloaded following each event because a Teledyne ISCO 2150 Flow Module was installed on-site. For the other three stations, however; discharge data were later obtained through the Water Survey of Canada (WSC). Red Hill Creek and Grindstone Creek discharge data were obtained from WSC Hydat flow stations 02HA014 and 02HB012, respectively. For the Desjardins Canal, we used an empirical regression equation developed from Spencer Creek WSC Hydat flow station 02HB007 (ESM Appendix S1).

A 24-hour level-weighted composite sample was prepared for each station. Although flow-composite samples would have ideally been submitted for analysis, real-time flow data and/or rating curves were not available for all stations, and the submission of level-weighted composite samples was preferred over time-weighted composite samples due to a hypothesized reduced sampling bias. Aliquots were drawn from each of the 24 1 L bottles which were proportional to the water level in the tributary at the time of sampling, poured into a pre-cleaned 4 L amber glass mixing bottle, and homogenized. Three 500 mL PET bottles were filled for lab submission. During select events (20 of 87 events), discrete grab samples that were collected from the rising limb, peak, and falling limb of the hydrograph were also submitted for analysis; however, the results in this paper remain focused on the 24-hour level-weighted composite samples. Samples prepared for metals analysis had approximately 10 drops of nitric acid added for sample preservation. The whole water samples were then submitted immediately for analysis to the OMOE's Laboratory Services Branch (LSB), accredited by the Canadian Association for Laboratory Accreditation (CALA) and the Standards Council of Canada (SCC).

Laboratory analysis

All samples and field blanks were analyzed for nutrients, dissolved organic/inorganic carbon, chloride, total suspended solids (TSSs), and 23 trace metals, except for grab samples which were not analyzed for trace metals. Dissolved and total nutrients were analyzed by colourimetry by OMOE's DISNUT3364 [reactive ortho-phosphate, ammonia nitrogen, nitrite nitrogen, nitrite plus nitrate nitrogen] and TOTNUT3367 [TP and total Kjeldahl nitrogen (TKN)] methods, respectively (OMOE, 2010a,b; OMOE, 2012a,b). For simplicity and discussion purposes in this paper, ammonia nitrogen, nitrite nitrogen, and nitrite plus nitrate nitrogen are herein referred to as ammonia, nitrite, and nitrite plus nitrate, respectively. Dissolved organic carbon and inorganic carbon were analyzed by colourimetry through method DCSI3370 (OMOE, 2010c; OMOE, 2012c) and chloride by colourimetry under method CL3016 (OMOE, 2010d; OMOE, 2012d). TSS was analyzed by gravimetry under OMOE's method SS3188 (OMOE, 2010e; OMOE, 2012e) and trace metals by dynamic cell inductively coupled plasma-mass spectrometry (ICP-MS) under method MET3474 (OMOE, 2010f; OMOE, 2011). Although samples were analyzed for a wide suite of parameters, only the phosphorus and nitrogen species are included in the analysis and discussion in this paper; however, summary statistics for trace metals analyzed in the level-weighted composite samples collected during the course of this study are given in ESM Appendix S2.

Concentrations of nitrate and un-ionized ammonia were estimated, as both parameters were not measured directly in this study. Both have been of concern in the Harbour proper and have biological relevance due to potential toxicity. Concentrations of nitrate were estimated from the difference between nitrite plus nitrate, and nitrite concentrations. Un-ionized ammonia concentrations were estimated as the product of the measured ammonia concentration and the fraction of ammonia predicted to be in the un-ionized state as per the temperature and pH of the water measured at the time of sample collection. The fraction (f) was calculated as:

$$f = \left(10^{\mathrm{pKa}-\mathrm{pH}+1}\right)^{-1} \qquad (1)$$

where pKa = 0.09018 + (2729.92/T), and T is the water temperature in Kelvin (temperature in Celsius + 273.16) (OMOEE, 1994). For samples where water temperature and pH data were missing due to inaccessibility of the creek during high storm conditions or ice, pH and temperature data were estimated through averaging the last known value with the next available value. In the case of missing temperature values due to winter ice conditions on the creek surface, temperatures were assumed to be 0 °C.

Quality assurance/quality control

Results of the QA/QC analysis demonstrated good agreement between replicate samples. In cases where the mean coefficient of variation (CV) for all parameters between all replicate samples exceeded 0.08, the data for that sampling event was excluded from subsequent analysis which occurred once. Three outliers believed attributable to reporting errors were also excluded. For seven of the eight submitted field blanks, mean concentrations of parameters tested in the field blanks were generally less than 5% of the mean concentrations measured in the full sample dataset, demonstrating overall minimal field contamination. Elevated field blank concentrations of DOC and nitrite were driven by an unexplained outlier rather than by a persistent contamination trend. Data were not blank-adjusted because this would not change the overall interpretation of results.

Statistical tests

The 24-hour composite sample data at each station were categorized a posteriori on hydrograph response as either baseflow (hydrograph showed no evidence of a runoff event) or rain/melt event, i.e., a high flow event. Several rain events which occurred in late winter/early spring were rain-on-snow events. In this study, however, they were categorized as storm events because the requirement for a snowmelt event was a clear rise in the water level without any recently recorded precipitation. Only four events met the latter condition. For the seasonal tests, winter was categorized as December 22–March 21, spring as March 22–June 21, summer as June 22 to September 21, and fall as September 22 to December 21.

Statistically significant differences between baseflow and rain/melt concentrations for each parameter measured in the 24-hour composite samples were determined by using the Mann–Whitney U-test in the PAST software (Hammer et al., 2001); differences were determined to be significant for p-values less than 0.05. Statistically significant differences among the four stations and among the seasons were determined by computing the Hc, the non-parametric Kruskal–Wallis test statistic (adjusted for ties) in the PAST software; differences were determined to be significant for p-values less than 0.05. Post-hoc pairwise tests were performed using the Mann–Whitney test to determine where statistically significant differences in concentrations exist among the four stations or seasons; differences were determined to be significant for Bonferroni corrected p-values less than 0.05.

Concentration–discharge linear regressions were developed for each parameter at each station following logarithmic transformation of both concentration and paired daily average discharge. The R^2 value, y-intercepts, slopes, and associated 95% confidence intervals were computed in Microsoft Excel using the Data Analysis ToolPak, and values were considered significant for p values less than 0.05.

Results

In total, 87 24-hour periods representing different flow states were sampled between July 5, 2010 and May 8, 2012 of which approximately 23% were baseflow and 77% were rain/melt events (6% of the 77% were melt events).

Variability of nutrient concentrations with catchment state

While nutrient concentration trends with catchment state occasionally differed among watersheds, overall results demonstrated consistently higher concentrations of TSS, TKN, phosphate, and TP during storm/melt events relative to baseflow (Figs. 2 and 3). No differences between baseflow and rain/melt event concentrations were observed for nitrite (except Red Hill Creek where the rain/melt event concentration was elevated) and nitrate (except Indian Creek where the baseflow concentration was elevated). For ammonia concentrations, no significant difference was observed between catchment states for Indian Creek and Grindstone Creek, but elevated concentrations were observed during rain/melt events in Red Hill Creek and the Desjardins Canal. Thus, nitrogen species demonstrated inconsistencies among the four stations between catchment states, whereas all four stations exhibited consistency in TP and phosphate concentration trends with catchment state.

The comparison of the two distinct catchment states – baseflow and storm/melt events – was conducted in part to demonstrate the variability in concentrations that is missed by excluding event-based sampling; however, nutrient concentrations follow a gradient in accordance with variability in flow, rather than demonstrate a distinct binary response. As such, nutrient concentration responses per flow unit were examined along with the slope of the linear regression of the log–log concentration–discharge relationship to indicate the role of chemostasis in the trends observed (Fig. 4; ESM Appendix S3). Chemostasis, or the apparent stability of a constituent's concentration relative to the variability in flow, is recognized in a log–log concentration–discharge plot as a relationship which has a slope between -1 and 0; simple dilution has a slope of -1 and concentrating processes have a positive slope (Godsey et al., 2009).

Like TP and phosphate, many of the nitrogen parameters also exhibited increasing concentrations with increases in flow demonstrating the strong influence of stormwater on the tributaries; however, this behavior was not ubiquitous across watersheds. Significantly negative linear regression slopes between 0 and -1 for the log–log concentration–discharge relationship were observed for nitrate at Indian Creek and Grindstone Creek. The state of chemostasis for nitrate in these two creeks suggests that the mass export of nitrate can be attributed to both groundwater and event flow at these stations. Simple dilution was not observed at any of the stations for any of the parameters. Runoff waters and high flows dilute strong groundwater sources of some nitrogen parameters, but this dilution is much less than would be expected if groundwater were the only source. Apparently, runoff waters are still mobilizing nutrients at rates nearly proportional to the water flux for chemostasis to be observed (Godsey et al., 2009).

Spatial trends

All nutrients included in this study demonstrated significant differences in concentrations for at least one of the four stations sampled, except for TP during rain/melt events ($Hc = 1.7$, $p = 0.6$; Figs. 2 and 3). The station or groups of stations that exhibited the highest median concentration varied by parameter (ESM Appendix S2); and spatial trends among the stations often differed between catchment states, indicating that precipitation events do not always impact watersheds in a similar manner. The different degrees to which stormwater was a driver of elevated nutrient concentrations among the watersheds were emphasized by the differences in slopes among the log–log concentration–discharge relationships: the higher the slope, the stronger the stormwater source (Fig. 4; ESM Appendix S3). In general, the influence of stormwater was greatest at Red Hill Creek for all six parameters and generally least at the Desjardins Canal.

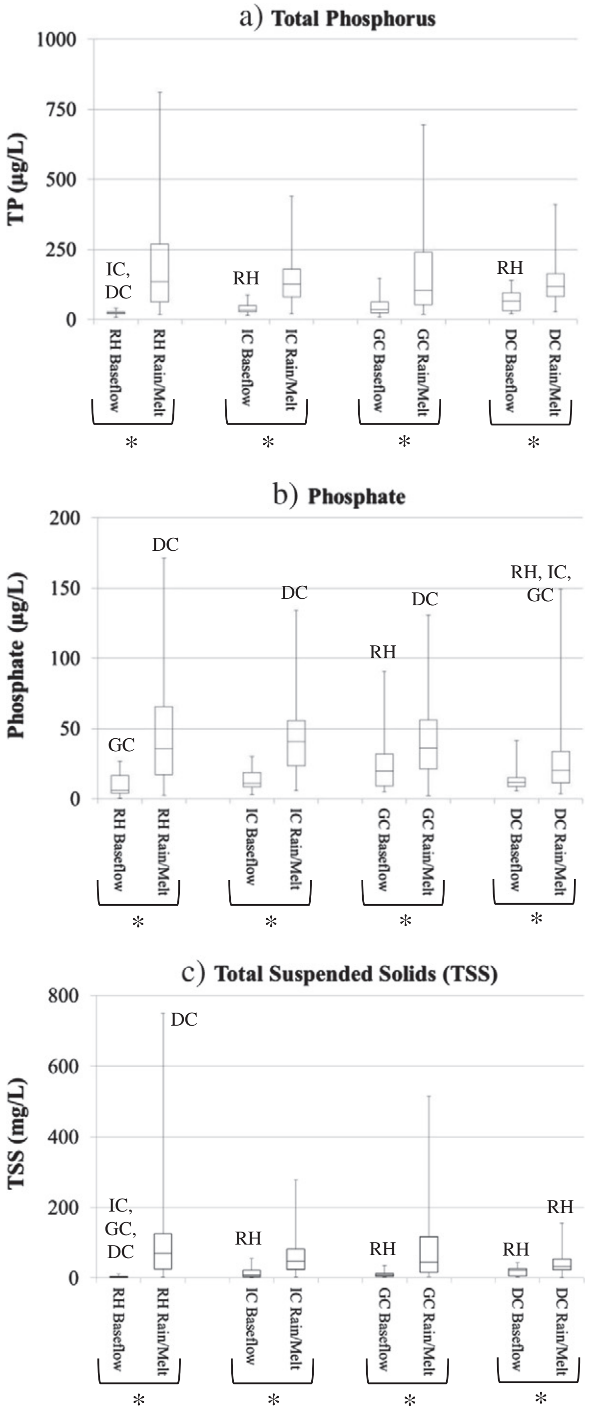

Fig. 2. Boxplots of a) total phosphorus (TP), b) phosphate, and c) total suspended solid (TSS) concentrations among the four Hamilton Harbour watershed stations for baseflow and rain/melt event concentrations measured July 2010–May 2012. Station abbreviations are: RH = Redhill Creek, IC = Indian Creek, GC = Grindstone Creek and DC = Desjardins Canal. Stations for which there were significant differences ($p < 0.05$) according to the post-hoc Mann–Whitney pairwise comparisons using Bonferroni corrected p-values are noted above each boxplot. Significant differences between baseflow and rain/melt concentrations for each station according to the Mann–Whitney U-test ($p < 0.05$) are denoted below each plot with an "*". Boxplots show the minimum, 25th percentile, median, 75th percentile and the maximum values in the dataset.

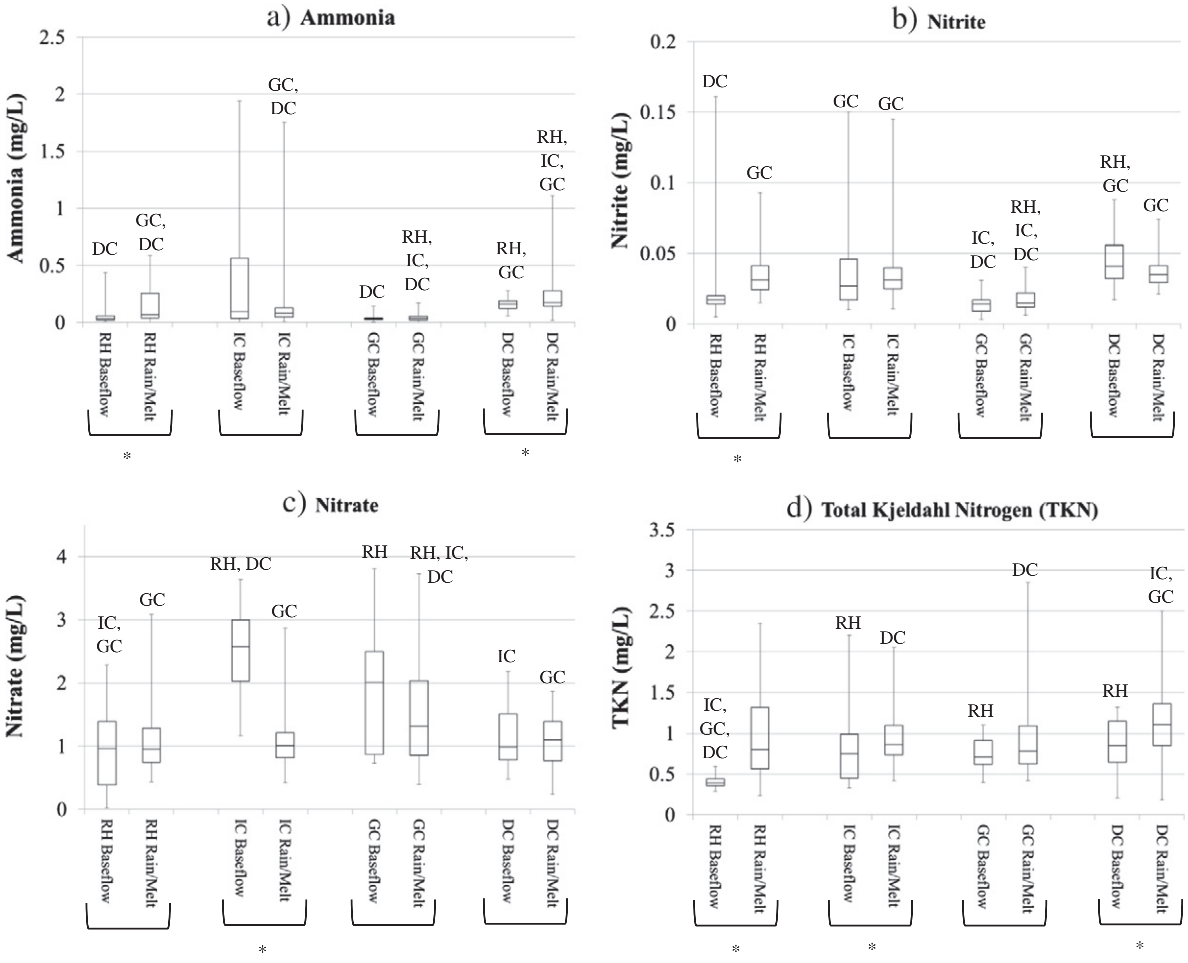

Fig. 3. Boxplots of a) ammonia, b) nitrite, c) nitrate, and d) total Kjeldahl nitrogen (TKN) concentrations among the four Hamilton Harbour watershed stations for baseflow and rain/melt event concentrations measured July 2010–May 2012. Station abbreviations are: RH = Redhill Creek, IC = Indian Creek, GC = Grindstone Creek and DC = Desjardins Canal. Stations for which there were significant differences ($p < 0.05$) according to the post-hoc Mann–Whitney pairwise comparisons using Bonferroni corrected p-values are noted above each boxplot. Significant differences between baseflow and rain/melt concentrations for each station according to the Mann–Whitney U-test ($p < 0.05$) are denoted below each plot with an "*". Boxplots show the minimum, 25th percentile, median, 75th percentile and the maximum values in the dataset.

Significant differences were observed in the slopes of the log–log concentration discharge relationships for TP among the stations except for between Indian Creek and Grindstone Creek and between Grindstone Creek and the Desjardins Canal where 95% confidence intervals overlapped (ESM Appendix S3). These results suggest that overall, the TP concentrations among the Hamilton Harbour watersheds do respond differently to increases in flow.

For phosphate, the highest log–log concentration–discharge slope and the lowest median concentrations during baseflow conditions were observed at Red Hill Creek, similar to TP trends. Unlike TP, however, the highest median phosphate concentration was observed at Grindstone Creek. During rain/melt events, phosphate concentrations were similar among stations except for a statistically significant difference for concentrations at the Desjardins Canal where the median concentration was lower relative to the other three stations. Also of note, Grindstone Creek had the lowest slope of the log–log concentration–discharge regressions for phosphate despite having the highest median baseflow concentration, suggesting relatively less variability in phosphate concentration with flow in this watershed.

During both baseflow and rain/melt events, median ammonia and TKN concentrations were highest at the Desjardins Canal station where concentrations were significantly different than at least one of the other three stations; the highest nitrite concentrations during baseflow were also observed at Desjardins Canal. With regard to ammonia, however, the highest maximum ammonia concentrations measured during the course of the study were at Indian Creek, again an interesting finding given the very high intra-station variability at Indian Creek. Unlike most of the other relationships examined, the log–log concentration discharge slopes were not significant at Indian Creek for TKN, nitrite, or ammonia, illustrating the complexity of the nitrogen dynamics in this watershed.

Nitrate concentrations demonstrated spatial variability among stations, and trends differed relative to the other nitrogen parameters. During baseflow, the highest nitrate concentrations were measured at Indian Creek, although concentrations were not significantly different than those measured at Grindstone Creek. During rain/melt events, the relative spatial pattern in nitrate concentrations among stations was very different relative to baseflow as the highest concentrations were measured at Grindstone Creek and were significantly different than those at the other three stations which had similar nitrate concentrations. The log–log concentration–discharge relationships also demonstrated a difference in nitrate behavior between Red Hill Creek relative to Indian Creek and Grindstone Creek (the relationship at the Desjardins Canal was not significant). Namely, nitrate concentrations exhibited concentrating behavior at Red Hill Creek, while chemostasis in nitrate concentrations was evident at Indian Creek and Grindstone Creek (Fig. 4; ESM Appendix S3).

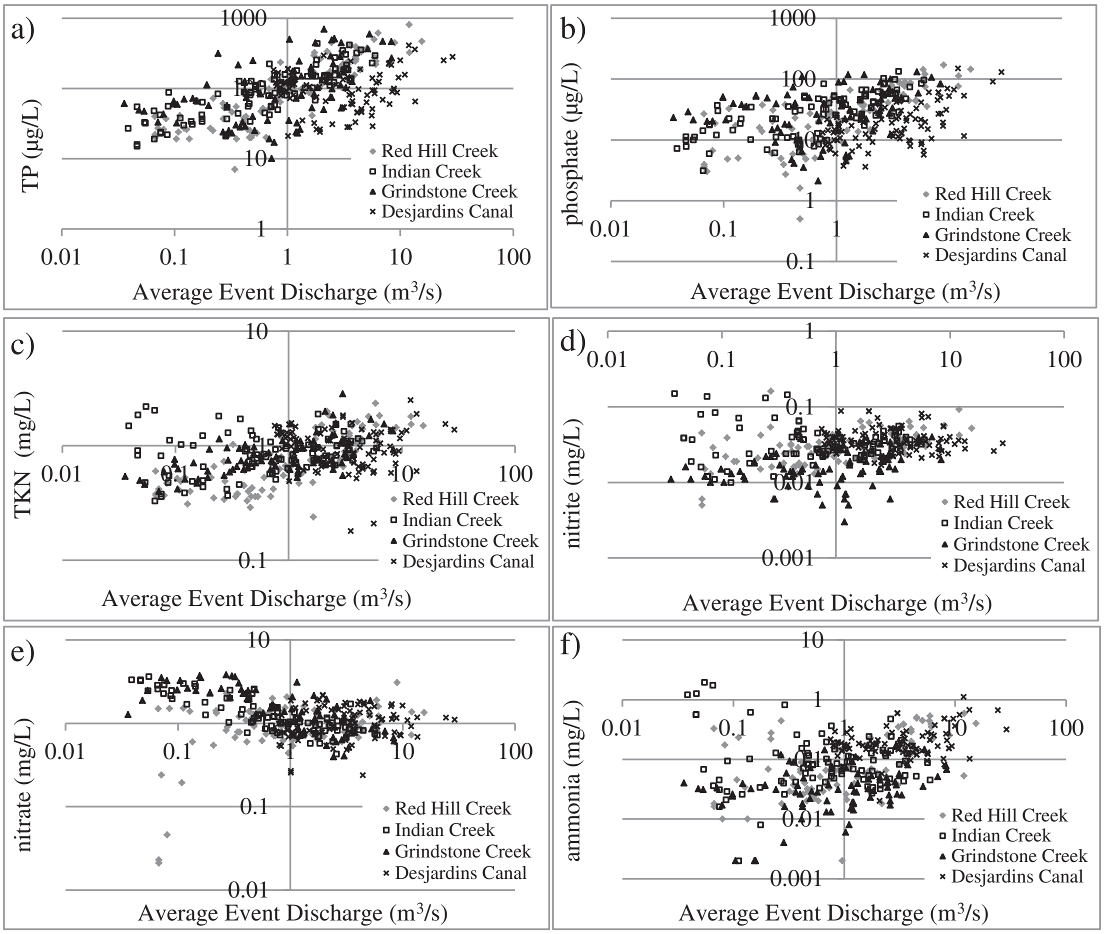

Fig. 4. Relationships between average event discharge and 24-hour level weighted-nutrient concentrations at each of the four stations for a) total phosphorus (TP); b) phosphate; c) total Kjeldahl nitrogen (TKN); d) nitrite; e) nitrate; and f) ammonia.

Temporal and seasonal trends

TP concentrations

Total phosphorus concentrations at Red Hill Creek, Indian Creek, and Grindstone Creek did not demonstrate any clear temporal trends (Fig. 5) or significant differences among seasons for each catchment state, except for between spring and summer TP concentrations during baseflow conditions in Indian Creek, with higher concentrations observed during spring (Table 2). Elevated TP concentrations could occur during any season (Fig. 5) reflecting the similar lack of seasonality in TSS concentrations (ESM Appendix S4). This finding, however, does not preclude the existence of seasonal TP concentration–discharge relationships which were not examined as were beyond the scope of this assessment.

In contrast to the other stations, TP concentrations at the Desjardins Canal demonstrated clear seasonal variability. Regardless of catchment state, TP concentrations were generally lowest in winter, and during baseflow conditions were significantly different from all other seasons. Total phosphorus concentrations tended to increase in spring, and again in summer, then declined during the fall through winter.

Phosphate concentrations

Seasonality was observed in phosphate concentrations in the watersheds of Hamilton Harbour despite the overall lack of seasonality in TP concentrations (Table 2). At Red Hill Creek and Indian Creek for all catchment states and at the Desjardins Canal during rain/melt events, median phosphate concentrations tended to be higher during the fall and/or winter periods relative to spring and summer although statistically significant differences were only observed at Indian Creek and the Desjardins Canal during rain/melt events. The seasonality in phosphate at the Desjardins Canal station is also evident in the proportion of TP composed of phosphate, which is noticeably higher during the winter period (Fig. 5; ESM Appendix S4). In contrast to the two most urbanized watersheds, phosphate concentrations were highest during the summer and/or fall periods at Grindstone Creek for both catchment states and at the Desjardins Canal for baseflow conditions, but again differences were not always statistically significant.

Ammonia concentrations

Relative to TP and phosphate, the nitrogen parameters demonstrated some strong seasonal trends, and further, many differences were observed between the 2010–2011 and 2011–2012 seasons. During baseflow conditions, ammonia concentrations tended to be higher during the winter period at Red Hill Creek, Indian Creek, and Grindstone Creek and during the spring at the Desjardins Canal (Table 2). During rain/melt events, ammonia concentrations in general did not demonstrate any clear seasonality except for at the Indian Creek station, where statistically significant differences were observed between the higher winter/spring concentrations relative to the lower summer/fall concentrations. This trend, however, is clearly driven by the highly elevated ammonia concentrations measured during the winter of 2010–2011.

In December 2010, the ammonia concentrations began to increase in Indian Creek seemingly independent of catchment state and peaked on February 10, 2011 (1.94 mg/L), at which point ammonia concentrations gradually declined during the spring melt period (Fig. 6). This trend was also observed to a lesser degree at the other stations during winter

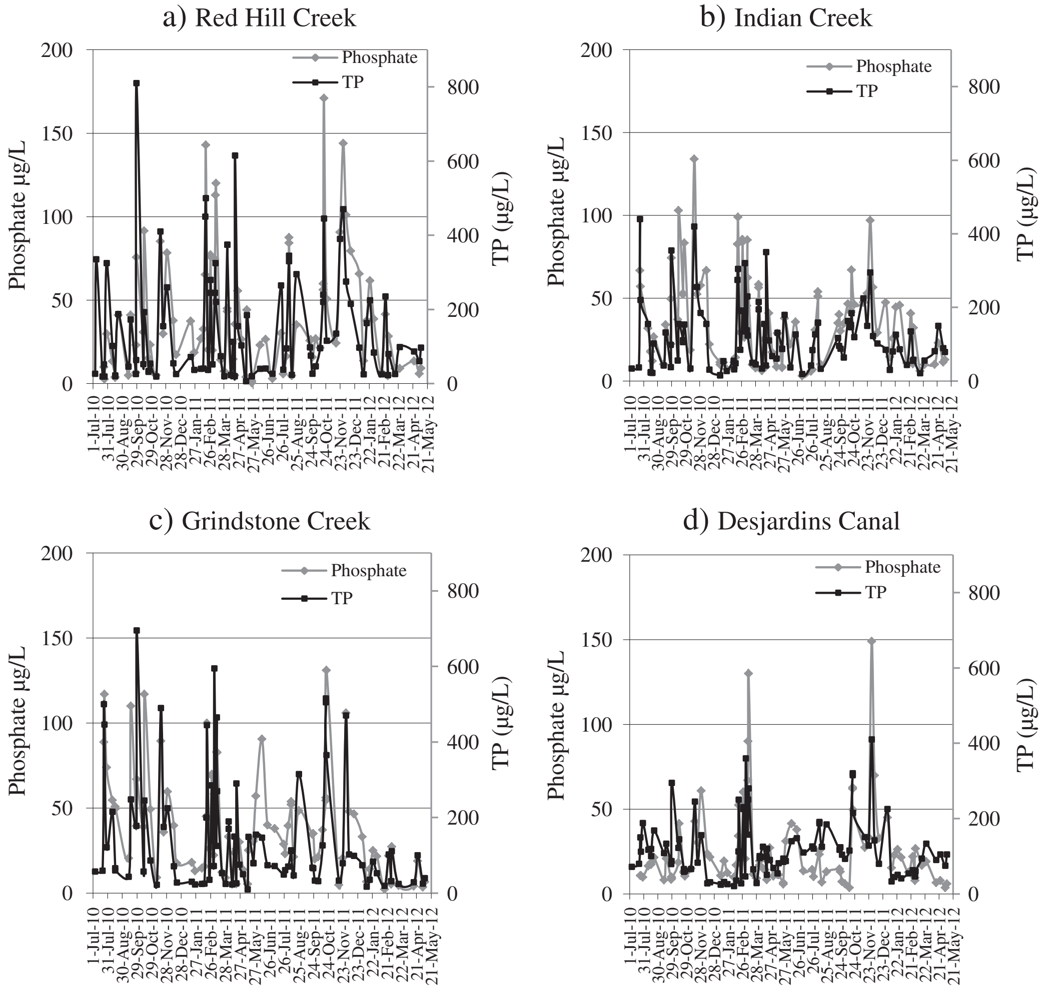

Fig. 5. Time series of total phosphorus (TP) and phosphate concentrations as measured in 24-hour level-weighted composite samples collected from a) Red Hill Creek; b) Indian Creek; c) Grindstone Creek and d) Desjardins Canal during July 2010–May 2012.

2010–2011, but it was not observed at any of the four stations during the following winter of 2011–2012. In addition, ammonia concentrations in Red Hill Creek during summer 2011 were generally higher than those during the previous summer. As ammonia concentrations demonstrated different trends between the 2010–2011 and 2011–2012 years, the seasonal trends observed at the four stations cannot be attributed exclusively to seasonality. Confounding interpretation is the difference in weather conditions – both temperatures and precipitation patterns – between the 2 years in which sampling was conducted.

In addition to total ammonia, un-ionized ammonia concentrations were also examined due to relatively greater toxicity and hence the potential for biological implications. Like total ammonia, un-ionized ammonia concentrations at Indian Creek were also relatively high during winter 2010–2011; however, the magnitude of the un-ionized ammonia concentrations were similar to peaks measured during the summer of 2011, despite total ammonia concentrations being much lower (Fig. 6). A similar temporal trend is also seen in Red Hill Creek where un-ionized ammonia concentrations peaked during the summer period, despite the high total ammonia concentrations observed during the spring freshet of 2011.

In contrast to Indian Creek and Red Hill Creek, the total ammonia concentrations at the Desjardins Canal equate to consistently high un-ionized ammonia concentrations during the biologically active summer period due to both elevated pH and temperature from spring through fall each year. During the course of this study, pH at the Desjardins Canal was as high as 9.16, and a maximum temperature of 27.4 °C was measured. These factors are likely contributing to the relatively high un-ionized ammonia concentrations both spatially and seasonally, despite the spatially unremarkable total ammonia concentrations.

Nitrite and nitrate concentrations

Seasonality was not evident for nitrite concentrations measured in either catchment state; however, nitrate concentrations demonstrated clear seasonal trends at all four stations (Fig. 7; Table 2). Differences in temporal trends between stations were noted for nitrate, suggesting spatial variability in seasonal processes and/or sources. At both the Red Hill Creek and the Desjardins Canal stations, nitrate concentrations for rain/melt events demonstrated strong seasonality with the highest concentrations in winter and the lowest in summer; seasonal nitrate concentrations were significantly different from one another at both these stations except for between spring and fall. Nitrate concentrations during baseflow periods at these stations also demonstrated a similar seasonal cycle as during rain/melt events, but differences were not always statistically significant.

In contrast, nitrate concentrations in Indian Creek demonstrated no statistically-evident seasonality during rain/melt events or baseflow. Nitrate concentrations did, however, tend to be higher during winter for baseflow, like Red Hill Creek and the Desjardins Canal. Nitrate concentrations at Indian Creek had very high event-to-event variability demonstrating the dominant role of catchment state (Fig. 3); and hence, hydrological processes at this station relative to seasonality on influencing ambient nitrate concentrations in the watershed.

Table 2
Summary of seasonal nutrient concentrations in the four Hamilton Harbour watersheds sampled July 2010–May 2012. Seasons with which there were significant differences ($p < 0.05$) according to the Kruskal–Wallis test using post-hoc Mann–Whitney pairwise comparisons (Bonferroni corrected p-values) are noted in parentheses in each column.

		Winter	Spring	Summer	Fall
		Median (Min–Max)	Median (Min–Max)	Median (Min–Max)	Median (Min–Max)
Total phosphorus (TP) μg/L					
Red Hill Creek	Baseflow[a]	37 (25–40)	20 (7–40)	23 (19–27)	26 (19–27)
	Rain/melt events[a]	130 (23–500)	108 (61–615)	137.5 (19–345)	155 (32–810)
Indian Creek	Baseflow	30 (15–85)	53 (37–88) (summer)	28.5 (19–37) (spring)	36 (31–88)
	Rain/melt events[a]	124 (21–320)	110 (34–350)	127 (22–440)	153 (56–420)
Grindstone Creek	Baseflow[a]	23.5 (17–35)	52.5 (10–147)	59.5 (47–72)	28 (22–33)
	Rain/melt events[a]	83 (19–595)	87.5 (23–290)	112.5 (43–500)	126 (32–695)
Desjardins Canal	Baseflow	26 (21–33) (spring, summer, fall)	69.5 (29–140) (winter)	105 (72–125) (winter)	66 (31–104) (winter)
	Rain/melt events	63 (32–360)	95 (65–133) (summer)	140.5 (108–191) (spring)	128 (28–410)
Phosphate (μg/L)					
Red Hill Creek	Baseflow[a]	19.4 (13.7–26.8)	5 (0.5–23)	3.8 (3–4.8)	11.2 (5–17.3)
	Rain/melt events[a]	40.1 (4.8–143)	20.7 (5.9–55.5)	26.6 (2.7–87.6)	50.8 (15.2–171)
Indian Creek	Baseflow[a]	11.2 (7.2–29.3)	8.6 (7.9–22.1)	13.8 (3.1–18)	22.3 (18.7–30.2)
	Rain/melt events	44.6 (6.1–99)	23 (6.3–58.3) (fall)	31.8 (5.9–66.7) (fall)	52.4 (29.2–134) (spring, summer)
Grindstone Creek	Baseflow[a]	13.9 (6.7–26.2)	19.7 (5.3–90.6)	43.7 (21.2–50.9)	17.6 (9.1–20)
	Rain/melt events	25 (2.1–99.9)	21.3 (3.5–57.1) (summer, fall)	50.3 (20.4–117) (spring)	47.3 (4.7–131) (spring)
Desjardins Canal	Baseflow[a]	11.6 (9.8–22.1)	8.8 (5.7–41.4)	15.4 (6.8–18.4)	12.8 (7.2–21.6)
	Rain/melt events	26.2 (7.9–130) (spring, summer)	14.2 (3.6–31) (winter)	14.5 (8.1–37.8) (winter)	31.5 (3.7–149)
Ammonia (mg/L)					
Red Hill Creek	Baseflow[a]	0.273 (0.174–0.439)	0.029 (0.02–0.049)	0.025 (0.016–0.045)	0.022 (0.01–0.068)
	Rain/melt events[a]	0.082 (0.022–0.586)	0.117 (0.037–0.446)	0.065 (0.002–0.501)	0.064 (0.018–0.533)
Indian Creek	Baseflow[a]	0.564 (0.026–1.94)	0.135 (0.026–0.27)	0.034 (0.016–0.068)	0.098 (0.002–0.612)
	Rain/melt events	0.118 (0.04–1.75) (summer, fall)	0.127 (0.042–0.259) (summer, fall)	0.055 (0.021–0.128) (winter, spring)	0.052 (0.008–0.242) (winter, spring)
Grindstone Creek	Baseflow[a]	0.106 (0.013–0.143)	0.037 (0.019–0.057)	0.029 (0.024–0.032)	0.033 (0.004–0.036)
	Rain/melt events[a]	0.050 (0.006–0.171)	0.04 (0.018–0.057)	0.037 (0.002–0.072)	0.025 (0.002–0.011)
Desjardins Canal	Baseflow[a]	0.17 (0.096–0.185)	0.203 (0.121–0.280)	0.160 (0.149–0.193)	0.122 (0.057–0.191)
	Rain/melt events[a]	0.160 (0.081–0.671)	0.161 (0.104–0.271)	0.175 (0.142–0.359)	0.227 (0.02–1.11)
Nitrite (mg/L)					
Red Hill Creek	Baseflow[a]	0.037 (0.015–0.161)	0.016 (0.013–0.018)	0.011 (0.005–0.022)	0.019 (0.013–0.021)
	Rain/melt events[a]	0.031 (0.015–0.057)	0.030 (0.021–0.064)	0.030 (0.019–0.065)	0.034 (0.016–0.093)
Indian Creek	Baseflow[a]	0.039 (0.01–0.15)	0.037 (0.017–0.066)	0.014 (0.012–0.019)	0.038 (0.014–0.071)
	Rain/melt events[a]	0.028 (0.012–0.08)	0.04 (0.021–0.145)	0.027 (0.011–0.137)	0.034 (0.018–0.084)
Grindstone Creek	Baseflow[a]	0.017 (0.005–0.022)	0.014 (0.003–0.031)	0.015 (0.011–0.015)	0.009 (0.006–0.012)
	Rain/melt events[a]	0.016 (0.006–0.039)	0.015 (0.007–0.023)	0.015 (0.01–0.038)	0.015 (0.006–0.04)
Desjardins Canal	Baseflow[a]	0.042 (0.028–0.088)	0.041 (0.021–0.081)	0.044 (0.035–0.088)	0.033 (0.017–0.057)
	Rain/melt events[a]	0.033 (0.021–0.052)	0.033 (0.023–0.074)	0.038 (0.023–0.058)	0.036 (0.024–0.071)
Nitrate (mg/L)					
Red Hill Creek	Baseflow[a]	1.498 (1.415–2.279)	1.077 (0.784–1.394)	0.109 (0.021–0.239)	0.571 (0.046–1.391)
	Rain/melt events	1.39 (1.078–1.985) (spring, summer, fall)	0.825 (0.662–1.298) (winter, summer)	0.676 (0.437–0.985) (winter, spring, fall)	0.911 (0.619–3.083) (winter, summer)
Indian Creek	Baseflow[a]	3.261 (1.7–3.633)	2.136 (1.173–2.574)	2.731 (2.471–2.918)	2.868 (1.967–2.996)
	Rain/melt events[a]	1.056 (0.726–2.86)	0.932 (0.573–1.597)	0.982 (0.573–2.273)	0.976 (0.428–2.476)
Grindstone Creek	Baseflow[a]	2.569 (1.513–3.808)	0.823 (0.726–0.898)	2.482 (2.456–2.505)	2.281 (2.004–3.518)
	Rain/melt events	1.169 (0.405–3.696) (summer)	0.722 (0.396–1.926) (summer, fall)	2.307 (1.269–3.728) (winter, spring)	1.580 (0.516–3.519) (spring)
Desjardins Canal	Baseflow	1.894 (1.401–2.183) (spring, fall)	0.845 (0.478–0.947) (winter)	0.783 (0.768–1.522)	1.001 (0.774–1.473) (winter)
	Rain/melt events	1.526 (0.685–1.868) (spring, summer, fall)	1.02 (0.543–1.542) (winter, summer)	0.654 (0.238–1.246) (winter, spring, fall)	1.050 (0.541–1.626) (winter, summer)
TKN (mg/L)					
Red Hill Creek	Baseflow[a]	0.41 (0.34–0.60)	0.36 (0.29–0.43)	0.42 (0.37–0.53)	0.39 (0.31–0.53)
	Rain/melt events[a]	0.66 (0.36–2.35)	0.85 (0.66–1.83)	0.83 (0.24–1.85)	0.85 (0.38–2.0)
Indian Creek	Baseflow[a]	0.93 (0.39–2.2)	0.7 (0.37–0.83)	0.41 (0.33–0.50)	1.02 (0.49–1.12)
	Rain/melt events[a]	0.75 (0.42–2.05)	1.0 (0.57–1.72)	0.97 (0.48–1.82)	0.84 (0.55–1.9)
Grindstone Creek	Baseflow[a]	0.65 (0.55–0.87)	0.97 (0.53–1.1)	0.7 (0.46–0.93)	0.74 (0.40–0.96)
	Rain/melt events[a]	0.73 (0.55–2.85)	0.85 (0.66–1.24)	0.62 (0.47–1.55)	0.8 (0.42–2)
Desjardins Canal	Baseflow	0.57 (0.49–0.70) (summer, fall)	0.99 (0.21–1.32)	1.16 (0.85–1.28) (winter)	0.84 (0.67–1.31) (winter)
	Rain/melt events	0.725 (0.58–1.9) (summer)	0.96 (0.7–1.27) (summer)	1.36 (1.15–1.58) (winter, spring)	1.16 (0.18–2.5)

[a] Indicates no significant difference among seasons for station and catchment state.

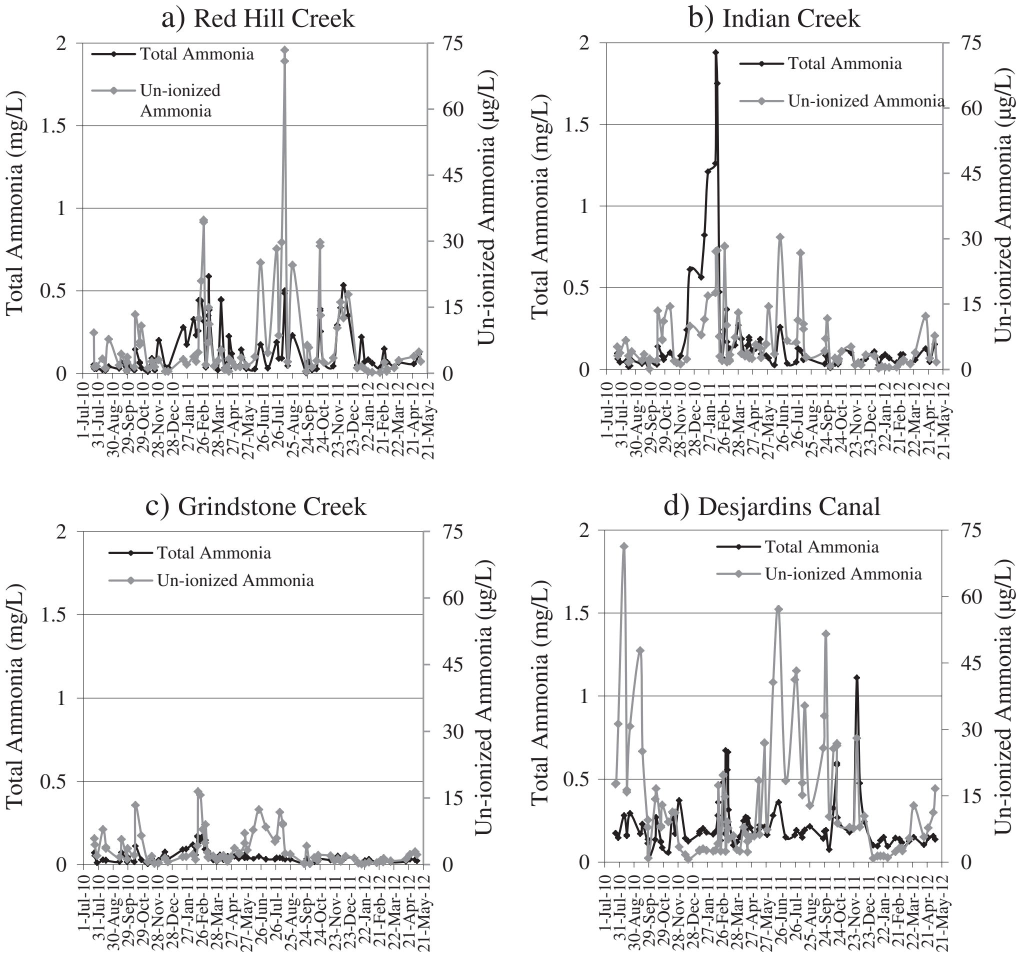

Fig. 6. Time series of un-ionized and total ammonia concentrations in 24-hour level-weighted composite samples collected from a) Red Hill Creek; b) Indian Creek; c) Grindstone Creek and d) Desjardins Canal during July 2010 to May 2012.

Temporal nitrate concentration trends were unique in Grindstone Creek; and while concentrations demonstrated continuity between sequential sampling events and strong seasonality like Red Hill Creek and the Desjardins Canal, the highest concentrations were measured at very different times of the year relative to the other stations. Nitrate concentrations during rain/melt events were highest in summer followed by fall with summer having concentrations significantly different than winter and spring concentrations (Fig. 7; Table 2). The nitrate concentrations during baseflow did not show a clear seasonal trend but did tend to be lowest during spring.

While nitrate concentrations in Grindstone Creek were consistently high during summer and fall, the statistical summary results for winter at this station in particular are highly skewed due to very different concentrations measured between the two winter periods. Highly elevated nitrate concentrations were observed during winter 2010–2011 which were equivalent to nitrate concentrations observed during both summer periods. On the other hand, nitrate concentrations during the following winter of 2011–2012 were approximately 50% lower, a finding also observed to some degree at adjacent Indian Creek (Fig. 7).

Discussion

Implications of climate change

Although not planned a priori, the stark differences in precipitation and temperature patterns between the 2010–2011 and 2011–2012 seasons presented a unique opportunity to examine general differences in nutrient concentrations in the tributaries under very different ambient weather conditions, and in particular, the winter season. These contrasting winter conditions resulted in different TP and phosphate trends for each of the two winters. During December 2010 to February 2011, concentrations were consistently low until mid-February 2011 when concentrations sharply increased in response to melting of the accumulated snowpack and the onset of high flow conditions in the tributaries. On the other hand, throughout the entire winter season of 2011–2012, concentrations continued to fluctuate between the low concentration and approximately half the maximum concentrations observed during winter 2010–2011 in response to winter rain events. The overall meaning of intermittent, event-driven TP and phosphate concentration spikes during a warm winter, relative to a cold winter characterized by a period of quiescent conditions followed by a sudden, yet short-lived period of highly elevated TP and phosphate concentrations from a quick, intense winter melt, is a topic in need of further research. Implications include potential differences in absolute loads due to variability in the magnitude of winter concentrations, as well as differences in timing of nutrient delivery and what that may mean for the formation of spring algal blooms. The data do, however, suggest that winter has the potential to be a period of consistently low phosphorus concentrations if precipitation falls as snow instead of rain, as washoff is minimal, causing minimal entrainment of pollutants and low flow conditions in the tributaries. If precipitation falls as rain instead of snow, which may actually occur more frequently in temperate regions with climate change, phosphorus concentrations in winter have the potential to be equivalent to those observed in other seasons due to the ubiquitous impacts of runoff events.

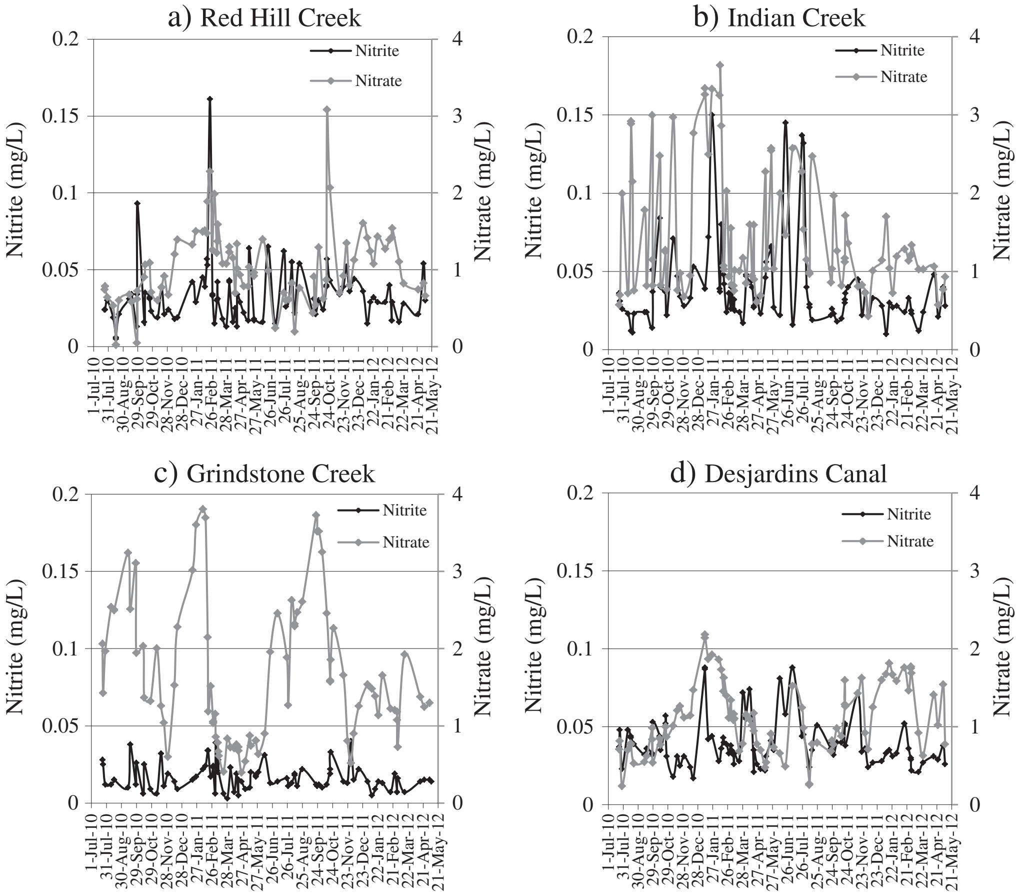

Fig. 7. Time series of nitrite and nitrate concentrations in 24-hour composite samples collected from a) Red Hill Creek; b) Indian Creek; c) Grindstone Creek and d) Desjardins Canal during July 2010 to May 2012.

The difference in weather conditions between the two winters is also believed to have played a role in the differences in nitrogen trends observed between 2010–2011 and 2011–2012. Both nitrate and ammonia concentrations were higher during the unseasonably cold winter of 2010–2011 relative to 2011–2012, especially at Indian Creek for ammonia and at both Indian Creek and Grindstone Creek for nitrate. In fact, the nitrate concentrations during the winter of 2010–2011 at both Indian Creek and Grindstone Creek exceeded the Canadian Water Quality Guideline (CWQG) of 3 mg NO_3-N/L (CCME, 2012). The mechanisms driving the differences in nitrogen dynamics between the two winters are not well understood in part because winter sampling is not traditionally conducted in temperate climates due to logistical constraints. Such data gaps on seasonal nutrient trends the watersheds may have compounding impacts on the understanding of trends in the receiving environment; for example, challenges that have been realized in balancing the nitrate budget in Hamilton Harbour (Ramin et al., 2012). Balancing an annual nutrient budget based on tributary data collected during only a portion of year is problematic when the parameter of interest undergoes marked seasonal variability. In such cases, conventional ice-free sampling programs may not suffice as they do not capture critical time periods. This may even tie into the larger regional scale considering the general increasing trends of nitrite and nitrate in the Great Lakes (United States Environmental Protection Agency, 2012), of which the tributaries in this study are sources to western Lake Ontario. As such, winter sampling is expected to increase in importance for parameters such as TP, phosphate, nitrate and ammonia so that water managers can better gauge potentially changing inter-annual trends and in accordance, implement more meaningful remedial actions to combat eutrophication and potential toxicological impacts under a changing climate.

The potential impacts of climate change on nutrient dynamics in watersheds are likely to be experienced beyond the winter season, although differences between the two summers monitored in this study were not as clear as those observed for winter. The finding of chemostasis for nitrate in Indian Creek and Grindstone Creek suggests that any direct impacts of climate change on creek flows in these watersheds would likely have little impact on nitrate concentrations (Godsey et al., 2009). Another potential impact of climate change on summer nutrient conditions that has been discussed in the literature is an increase of summer soluble reactive phosphorus (SRP) concentrations in creeks during low flow conditions due to temperature-dependent release from riverine sediments. In Grindstone Creek and the Desjardins Canal, TP and phosphate tended to be highest in summer and lowest in winter during low flow conditions, consistent with seasonal patterns observed in the watersheds of the Chesapeake Bay area, Maryland, USA, which were attributed to temperature-dependent release from sediments (Duan et al., 2012). In contrast, TP and phosphate concentrations in Red Hill Creek and Indian Creek during low flow do not support temperature-dependent SRP release from sediments, which appears to contradict Duan and Kaushal's (2013) assertion about the role of urbanization in strengthening temperature-dependent SRP release from sediments.

Challenges of potential mitigation strategies

By parsing out event-to-event, spatial and temporal variability, this study was able to suggest where improvements to stream quality may be possible, and also where implementation of mitigation strategies may be more challenging. This helps to direct the efficient use of resources, especially given the challenge of required buy-in of multiple diverse individuals and agencies for implementation of best management practices (BMPs) in addressing nonpoint sources.

The relative spatial homogeneity in stormwater TP concentrations across the Hamilton Harbour watersheds was unexpected, given the differences in not only land use among these watersheds but also degree of impervious surface coverage or total contributing lawn and road source areas which have also been linked to spatial TP concentration trends in other areas (Bannerman et al., 1993; Butcher, 2003). We suggest that landuse trends in the Hamilton Harbour watershed are being masked by the relatively high variability inherent at each station. Further, differences in the log–log TP concentration–discharge plots suggested that TP concentrations did respond differently to increases in flow. The greater similarity between the plots for Indian Creek and Grindstone Creek (the adjacent watersheds on the north shore of Hamilton Harbour), relative to the plots for Indian Creek and Red Hill Creek (the two urban watersheds) suggests that geological factors may be playing a role in the response of the creeks to increasing flows.

A ubiquitous, clear trend for phosphorus concentrations was observed in the comparison between catchment states. Across all watersheds, rain/melt events had consistently higher TP and phosphate concentrations relative to baseflow; and TP and phosphate concentrations were positively correlated to flow suggesting that stormwater mitigation is needed to reduce phosphorus in the creeks regardless of land use or season. Emphasizing the primary role of rain/melt events in degraded TP concentrations in the tributaries was the finding that despite the highly anthropogenically altered land use of these watersheds, median TP concentrations during baseflow periods (ESM Appendix S2) met or were close to meeting Ontario's Provincial Water Quality Objective (PWQO) for TP of 30 μg/L, set for avoiding excessive plant growth in rivers (OMOEE, 1994). In fact, in Red Hill Creek, the most urbanized of the four watersheds, the PWQO was only exceeded 19% of the time during baseflow periods. In addition, the finding of concentrating nitrate behavior in Red Hill Creek and chemostasis in nitrate concentrations in Indian Creek and Grindstone Creek suggests that at least a portion of the measured nitrate in the creeks is also sourced from stormwater, meaning stormwater mitigation is needed for reducing a broad suite of nutrients.

Stormwater mitigation is particularly important in urban areas such as Red Hill Creek, where the influence of stormwater was generally the greatest, particularly evident through the highest variability in TP concentrations. In the City of Hamilton, ongoing upgrades to the CSOs and combined sewer system are actions expected to result in substantial water quality improvements to the local tributaries and Hamilton Harbour, the downstream receiving environment. For example, intermittent inputs from the Hamilton CSOs upstream from the Red Hill Creek and Desjardins Canal stations during storm events were hypothesized as contributing towards the elevated ammonia concentrations at these two stations during rain/melt events relative to baseflow concentrations. Another special consideration in stormwater mitigation is land use change for watersheds where agricultural lands have become urban, such as Indian Creek. Fink (2005) found that such land use change in Wisconsin, USA, increased TP export due to an increased loss of agriculturally-derived phosphorus-enriched soils from flashy urban hydrology.

In urban areas, stormwater mitigation may mean addressing surface runoff and, in agricultural areas, aspects of tile drainage. Stormwater mitigation aimed at reducing peak flows (e.g., increased infiltration, increased evapotranspiration through tree planting, constructed wetlands, and stormwater retention ponds) reduces both streambed scouring during high flow events and transport of entrained particulates in runoff, much of which are mobilized by kinetic processes. The reduction of particulates to stormwater is important in not only reducing TP, but also phosphate, TKN, ammonia (except Indian Creek), and nitrite concentrations (except Indian Creek and Desjardins Canal), as all had positive and statistically significant correlations with suspended solids (Spearman's $r_s > 0.5$ (P parameters); $r_s > 0.3$ (N parameters); $p < 0.05$). Road-deposited sediment mobilized during storm events may be a source in the urban areas given that it has been found to contain a high level of nutrients including phosphate, nitrate and ammonium (Carraz et al., 2006). A reduction of suspended solids loads to the creeks has cascading benefits in terms of reducing other contaminant inputs (e.g. metals) and improving water clarity, making TSS mitigation an efficient source control measure on several accounts.

While stormwater mitigation is an important measure in improving the nutrient status of the tributaries through reducing transport, source control through the reduction of nutrient use is another vital step. It is hypothesized that in Grindstone Creek, nitrate and phosphate concentrations during rain events were highest in summer and fall due to the application of fertilizers during the growing season, a major nutrient source in agricultural watersheds (Jiang et al., 2010; Mattikalli and Richards, 1996; Shields et al., 2008). Grindstone Creek was the only watershed that demonstrated such seasonal patterns for these parameters, as nitrate and phosphate during melt/rain events tended to be highest during winter and fall in the other three watersheds, likely due to a lack of biological uptake during the non-growing season (Moatar and Meybeck, 2005; OMOE, 2012f; Richardson and Marshall, 1986; Shields et al., 2008). In another agricultural catchment in southern Ontario, Macrae et al. (2007) also found that the strength of the nitrate source (manure applications) was a stronger control than in-creek biological processes. During summer/fall 2010 and summer/fall 2011, nitrate concentrations in Grindstone Creek exceeded the CWQG of 3 mg NO_3-N/L (CCME, 2012) for several weeks suggesting the potential for biological impacts in this watershed. In addition, phosphate and nitrate concentrations were significantly higher during baseflow at Grindstone Creek relative to Red Hill Creek, possibly due to long-term leaching and infiltration of fertilizers in the former. Thus, fertilizer inputs in agricultural areas may have habitat quality implications given that baseflow conditions occur the majority of the time in creeks.

While there are a host of mitigation measures which can be done to improve nutrient concentrations in urban and agricultural watersheds, often times drivers of nutrient concentrations are not as easily addressed. For example, the finding of chemostasis for nitrate at Indian Creek and Grindstone Creek suggests that in addition to stormwater contributions, there are also relatively strong groundwater contributions of nitrate in these watersheds. In particular, baseflow nitrate concentrations in Indian Creek were significantly higher than rain/melt events. While the quality of streams during storm events is commonly associated with current land use practices due to entrainment of constituents from runoff and tile drainage, baseflow conditions in streams, however, reflect both current and historical land-use practices, which present challenges in forming remedial actions.

Groundwater flow paths can be long and hence result in a time lag on the order of decades or even centuries between infiltration of a contaminant into the subsurface and the time it discharges to creeks where it is being measured in current day (Howard and Livingstone, 2000; Meals et al., 2009; Tesoriero et al., 2009). In addition to time-of-travel, there is a legacy of past fertilizer applications due to decades-long leaching of nitrate from soils in formerly agricultural areas (Gaynor, 1978; Sebilo et al., 2013). Such explanations are suspected of being a contributing factor towards the elevated nitrate concentrations in low flow conditions in Indian Creek given the historical agricultural land use in this now primarily urban watershed. Further, soil in the adjacent Grindstone Creek watershed has been found to have much a greater infiltration capacity relative to that in Red Hill Creek (Agriculture and Agri-Food Canada, 2011), which may also mean relatively higher potential for infiltration of nitrate to local groundwater in the Indian Creek watershed.

The lag in discharge of historically contaminated groundwater to surface waters, because of long subsurface flow paths may also help explain alarming disconnects that have been observed between the degree of BMP implementation and mitigation measures in watersheds and accompanying stream water quality (Lemke et al., 2011; OMOE, 2012f). Seasonal factors may be another contributor to disconnects between nutrient inputs and outputs, such as the difference in timing between nutrient applications and loss, particularly for nitrate (Gaynor, 1978). Determining groundwater transit times may assist in correlating land surface practices and stream water quality (Tesoriero et al., 2009) as well as help to predict future stream water quality, trajectories which are useful in planning and watershed management (Pijanowski et al., 2007). While efforts aimed at improving the quality of stormwater have opportunities for observation of relatively immediate improvement, some patience will be required to reap the benefits of efforts made to improve the quality of baseflow conditions, which for some parameters like nitrate are sometimes worse than conditions following storm events. Degraded baseflow quality is responsible for contributing towards consistently elevated pollutant concentrations in urban areas, a phenomenon known as the “urban stream syndrome” (Roy and Bickerton, 2012).

In addition to groundwater as a source of nutrients, making tangible improvements to water quality may be also challenging when ambient conditions out of direct anthropogenic control have a profound influence on water quality. Un-ionized ammonia concentrations at the Desjardins Canal station were approximately two to three times above the Provincial Water Quality Objective (PWQO) and Canadian Water Quality Guideline (CWQG) of 16 μg/L (CCME, 2001; OMOEE, 1994) during each spring to fall period. Interestingly enough, typical summer total ammonia concentrations at the Desjardins Canal station may be of relatively greater biological relevance than the anomalous total ammonia peak during winter 2010–2011 at the Indian Creek station, as the PWQO and CWQG was only briefly and marginally exceeded in Indian Creek. While decreasing inputs of total ammonia to Cootes Paradise is an obvious mitigation measure, high ambient pH and temperatures also play a major role in the proportion of ammonia in the un-ionized state. Intermittent inputs of ammonia to Cootes Paradise, such as through CSO events, have potentially different biological implications depending on the timing of the input because of the strong role of ambient conditions on potential toxicity.

Addressing elevated un-ionized ammonia concentrations involves not just source control but a holistic, ecosystem approach in considering the indirect impacts of ambient water chemistry and physical parameters of the system. The establishment or expansion of vegetated riparian buffer strips could have a positive impact on reducing un-ionized ammonia indirectly through reducing surface water temperatures (Osborne and Kovacic, 1993). Also, because the pH increases during periods of high algal density, actions addressing eutrophication may also have a positive, cascading impact also on addressing un-ionized ammonia concentrations. In this respect, water quality improvements may be synergistic, thus increasing efficiency of implementation.

Ecological processes in Cootes Paradise are also believed to be playing a large role in the TP and phosphate trends observed during this study. The annual cycle of lowest TP concentrations during winter and highest TP concentrations in summer at the Desjardins Canal has been reproduced in modeling scenarios (Cootes Paradise Water Quality Group, 2012), and the observation of both event-to-event variability and seasonality in TP concentrations in this study suggests that multiple processes and/or inputs are likely drivers at this station. While effluent from the Dundas WWTP must contribute towards background TP concentrations in the receiving wetland to some extent, TP concentrations in the final effluent do not follow a seasonal pattern (M. Bainbridge, 2014, pers. comm.); thus, it is more likely that ecological and/or hydrological process are the major influence behind the overall TP seasonality in Cootes Paradise. For example, resuspension of wetland sediments as a contributor to TP concentrations in the water column may be seasonal in nature, with high physical disturbance of the sediment in summer months due to activity of benthivorous fish (e.g., carp) and lower resuspension rates in winter months due to the inability of wind to impact the shallow waters of the wetland due to ice cover (Reynolds and Davies, 2001). In addition to this, the inflowing creeks undergo marked seasonal variability in discharge, with low flow times of year such as summer contributing substantially less dilution and hence result in higher TP concentrations in the wetland, assuming relatively lower TP concentrations in the inflowing creeks than the wetland (T. Theysmeyer, 2014, pers. comm.). In addition, it has been speculated that the lower phosphate concentrations during rain/melt events at the Desjardins Canal station relative to other stations may be reflecting the transformation in Cootes Paradise of phosphorus from its dissolved form (phosphate) to a particulate phase as it is taken up by plankton, similar to that reported by Krieger et al. (2003) for a wetland at the end of a stream in the Lake Erie Basin. Differences in the trends for TP and phosphate concentrations at the Desjardins Canal station speak to different processes occurring for particulate relative to dissolved forms of phosphorus, including bioavailability.

Work done to reduce nonpoint sources of contaminants to streams needs to consider the realities of not only groundwater inputs and the role of ambient conditions but also the additional stress caused by climate change and other factors like invasive species which can often counteract initiatives taken to improve stream water quality. These considerations only emphasize the need for source control where possible and for monitoring programs which when thoughtfully designed will help determine what can be done to achieve tangible improvement in water quality.

Conclusions

Precipitation and snowmelt events were strong and ubiquitous drivers of phosphorus and nitrogen-based nutrients in this study, suggesting runoff and overland sources are a strong influence on stream quality in urban and agricultural watersheds. While concentrations increased as flows increased at all four stations for the phosphorus based parameters and many of the nitrogen-based parameters, nitrate demonstrated a stateof chemostasis in Indian Creek and Grindstone Creek suggesting both runoff and groundwater are likely strong sources of this parameter in these watersheds. Nitrate concentration dynamics were especially unique in Indian Creek as the median concentration was actually higher and significantly different for baseflow periods relative to rain/melt events, the only parameter and watershed to exhibit such distinct groundwater-influenced event-to-event variability.

The inter-basin comparison suggested that spatial factors may be playing a larger role in explaining event-based trends of nitrogen species relative to phosphorus, as no significant differences in TP and phosphate concentrations were found among four of the four stations, and three of the four stations, respectively, during rain/melt events despite differences in land use; intra-station variability was greater than inter-station variability. Compared to TP, phosphate demonstrated relatively greater spatial variability as concentrations were highest in Grindstone Creek during baseflow conditions suggesting agricultural streams may be more eutrophic during baseflow than urban streams, and concentrations were lowest at the Desjardins Canal during rain/melt events suggesting potentially greater biological uptake in the upstream wetland system. In contrast, the Desjardins Canal had the highest ammonia concentrations for both catchment states. Nitrate concentrations were highest in Grindstone Creek during rain/melt events, and in Indian Creek followed by Grindstone Creek during baseflow conditions, suggesting the watersheds on the north shore of Hamilton Harbour are an area of high nitrate concentrations in groundwater and runoff, likely due to both legacy and current nitrogen sources. Factors other than land use, perhaps underlying geology or soil type, can also play a strong a role in catchment functioning.

Seasonal trends were also investigated and TP concentrations like TSS generally did not demonstrate seasonal variability, except at the Desjardins Canal where TP concentrations were highest during summer, potentially a reflection of wetland phosphorus processes. In contrast, phosphate as well as nitrate exhibited seasonal variability, with elevated concentrations during the fall and/or winter period at all stations but Grindstone for phosphate, and at Red Hill Creek and Desjardins Canal for nitrate, attributed to relatively lower biological uptake of these nutrients relative to that during the growing season. Elevated summer phosphate and nitrate concentrations in primarily agricultural Grindstone Creek were attributed to fertilizer applications during the growing season. Ammonia concentrations demonstrated little seasonal variability for rain/melt events except at Indian Creek, where winter and spring concentrations were elevated, at rend also loosely observed during baseflow conditions at all stations.

The results of the 2010-2012 event-based monitoring study in Hamilton Harbour emphasized the importance of including the objectives of a study into the design of a monitoring program. While event-based sampling is necessary to characterize TP concentrations and particulate-associated parameters in general, the same approach is not always needed for many of the nitrogen parameters that exhibit chemostasis, such as nitrate. Empirical data should be screened however, as nitrate in this study was demonstrated to exhibit markedly different trends with flow, even for adjacent watersheds and for those of similar land use. This study also demonstrated that the preparation of level-weighted composite samples is a preferred alternative to time weighted composite samples when flow-composites cannot be prepared, and that studies of temperate climates should include winter sampling as nutrient concentrations at this time of year can be as high as (TP) or higher than (phosphate, nitrate) other times of the year.

Potential impacts of climate change on water quality were explored in this study due to the profound differences in weather between the 2010-2011 and 2011-2012 seasons. Winter TP export changed from a bimodal delivery pattern (quiescent period followed by intense spring freshet) in the unseasonably cold winter, to an export characterized by intermittent inputs of TP during the unseasonably warm winter, reflective of precipitation patterns and subsequent tributary response observed during any other time of the year. The temperature differences between the two winters are also speculated as playing a role in the stark difference in nitrogen concentrations, as elevated concentrations during the unseasonably cold winter, primarily at Indian Creek for ammonia and Grindstone Creek for nitrate, were not observed during the following, relatively warmer winter.

While addressing stormwater through reducing peak flows and source control of particulate are practical mitigation measures for reducing tributary nutrient concentrations, this study also demonstrated some challenges in nutrient reductions due to lack of direct mitigation strategies. Nutrients such as nitrate which are potentially contributed to tributaries from historical land use practices via current day groundwater inputs will continue to contribute towards baseflow issues for some time. Also, reductions in un-ionized ammonia may be possible through an increase in riparian buffer strips to reduce temperatures, and through eutrophication mitigation to reduce ambient pH levels. A more comprehensive understanding of the roles of events, land use and season was gained in this study, and further research will only assist in the ability to devise mitigation measures that will result in improved water quality in urban and agricultural watersheds.

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Appendix A. Supplementary data

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Electronic Supplementary Material

Evaluation of stormwater and snowmelt inputs, landuse and seasonality on nutrient dynamics in the watersheds of Hamilton Harbour, Ontario, Canada

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Appendix S1 – Discharge Data

Discharge data for Red Hill Creek and Grindstone Creek were obtained from Water Survey of Canada (WSC) Hydat flow stations 02HA014 and 02HB012 respectively. The Red Hill Creek Hydat flow station was located approximately one kilometre upstream from the ISCO monitoring station, but since no major inputs are located between the two stations, discharge should be representative of conditions at our site. The Grindstone Creek ISCO monitoring station was co-located within the Grindstone Creek Hydat flow station.

As there is no WSC Hydat flow station on Indian Creek, to obtain discharge at this station, a Teledyne ISCO 2150 Flow Module was installed at the Indian Creek ISCO monitoring station on August 4, 2010. The flow meter was mounted to the bottom of the creek adjacent to the ISCO water intake, and like the level bubbler module, collected discharge data in 15 minute increments. At very low discharge values flow could not be sensed accurately by the current meter and often returned anomalous values (negative or zero discharge). Discharge was also not obtained for brief periods during large storm events. For such days when the flow meter malfunctioned, discharge was estimated through a level-discharge rating curve for that event or assuming equivalent values for periods of similar water levels. Outside of the July 2010 – May 2012 study period, daily average discharge at Indian Creek was estimated by a regression with average event discharge at Red Hill Creek for the 87 24-hour sampling periods captured during July 2010 – May 2012:

$$\log \text{IC flow} = (0.83*(\log (\text{RH flow}))) - 0.14 \qquad r^2 = 0.85\ (p=<0.05)$$

The ANOVA F-test value was statistically significant at the 95% confidence level for this regression (Fig. A1). A similar regression was also conducted for average event flows at Indian Creek and Grindstone Creek ($r^2 = 0.62$); however, the relationship with flows at Red Hill Creek was stronger likely due to the greater similarities in the hydrograph and landuses between Red Hill and Indian Creeks, relative to that observed for Grindstone Creek.

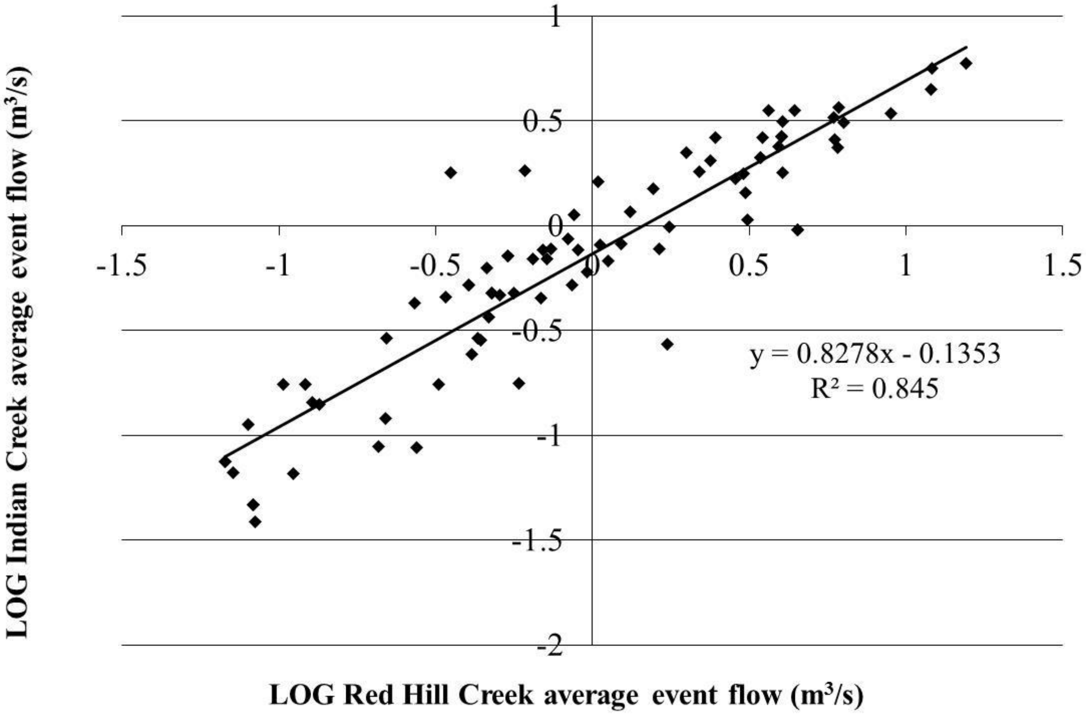

Figure 1: Log-log regression for average event flows at Red Hill Creek and Indian Creek for events that were sampled on the same day at both stations, July 2010 – May 2012

Estimation of discharge out of the Desjardins Canal was made based on an empirical regression with discharge at the Spencer Creek WSC Hydat flow station 02HB007. This relationship between flow at the Canal (outflow of Cootes Paradise to Hamilton Harbour) and Spencer Creek (largest inflow to Cootes Paradise) was developed from Ontario Ministry of the Environment (OMOE) current meter monitoring data collected during summer 2009 at the Desjardins Canal. From April 16 – July 28, 2009 and August 20 – November 19, 2009, two mini ALEC current meters were deployed approximately 9 m apart at mid-depth (approximately 2 m depth) in the Desjardins Canal, approximately 60 m to the east of the 2010-2012 Desjardins Canal ISCO intake line. Flow direction and velocity were recorded every four minutes, and level loggers were also deployed and recorded level every 30 minutes. Discharge was calculated separately for each half of the canal through bisecting the north and south halves of the Canal, and each half of the canal had the cross-sectional area calculated based on the depth profile and the real-time water level, which changed throughout the deployment period (Fig. A2). The daily average cross-sectional area in square metres was calculated as the mean of all 48 cross-sectional areas calculated per day, and the daily average east-west velocity (m/s) was calculated through the mean of all 360 east-west velocity measurements recorded per day. The discharge for one half of the canal corresponding to either the southern or northern current meter was calculated as the product of the daily average east-west velocity in m/s and the daily average cross-sectional area in m^2; to obtain the total discharge at the canal, the northern and southern discharge estimates in m^3/s were summed.

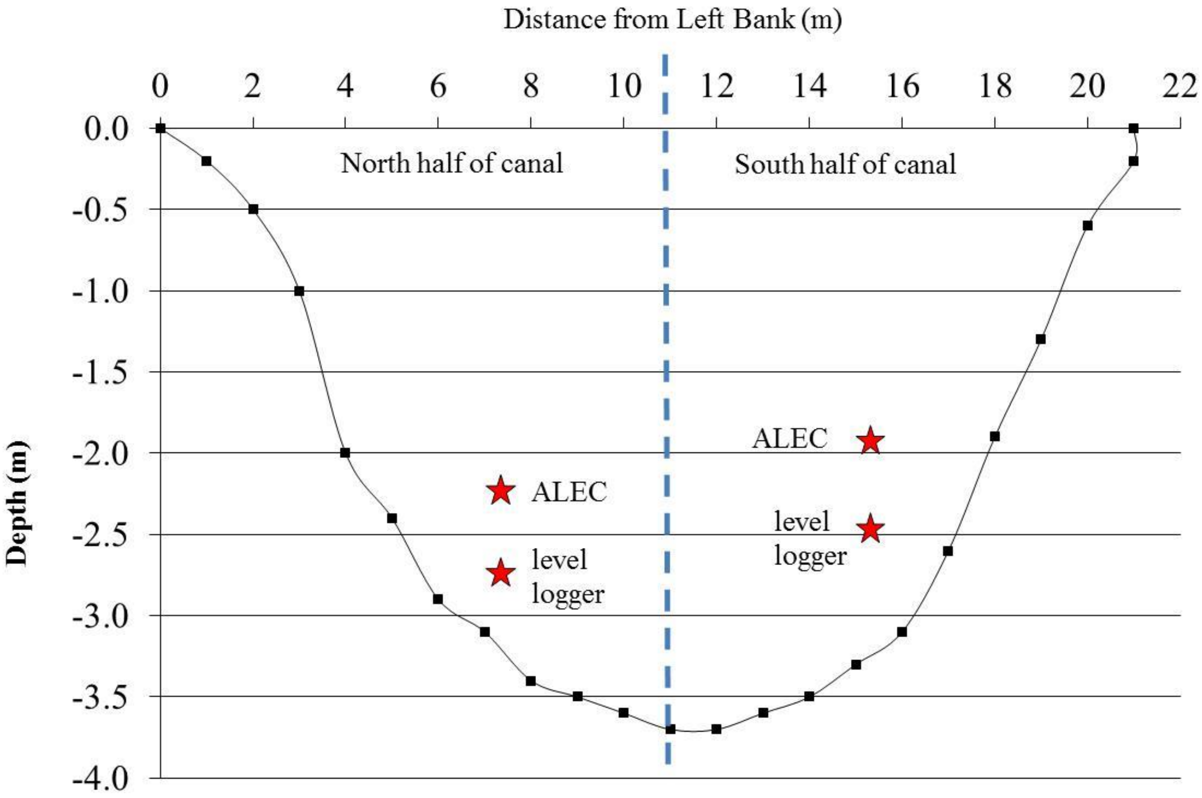

Figure 2: Depth profile and depth positioning of Mini ALEC current meters and level loggers deployed in the Desjardins Canal during summer 2009

The daily discharge values measured at the Spencer Creek Hydat station 02HB007 in summer 2009 were plotted against the daily discharge values calculated at the Desjardins Canal in 2009 to yield a linear regression of y= 1.45X + 0.44 (r^2 = 0.66, $p<0.05$) (Fig. A3). This regression equation was not improved with the addition of discharge values from the Dundas WWTP, likely due to the small discharge values relative to Spencer Creek. The discharge at the Desjardins Canal was found to be more variable relative to Spencer Creek and subject to flow reversals from incoming water from Hamilton Harbour as shown by negative discharge values (Fig. A4). Previous to this method of estimating Cootes Paradise discharge to Hamilton

Harbour, discharge was estimated through assuming that discharge out of Cootes Paradise was equivalent to the sum of the inflows of Spencer Creek (with a correction factor for ungauged streams) and the Dundas WWTP (HH RAP, 2010). Discharge at the Desjardins Canal for the July 2010 – May 2012 study period was calculated from the 2009 regression equation using discharge at the Spencer Creek WSC Hydat Station measured in 15-minute intervals as input values.

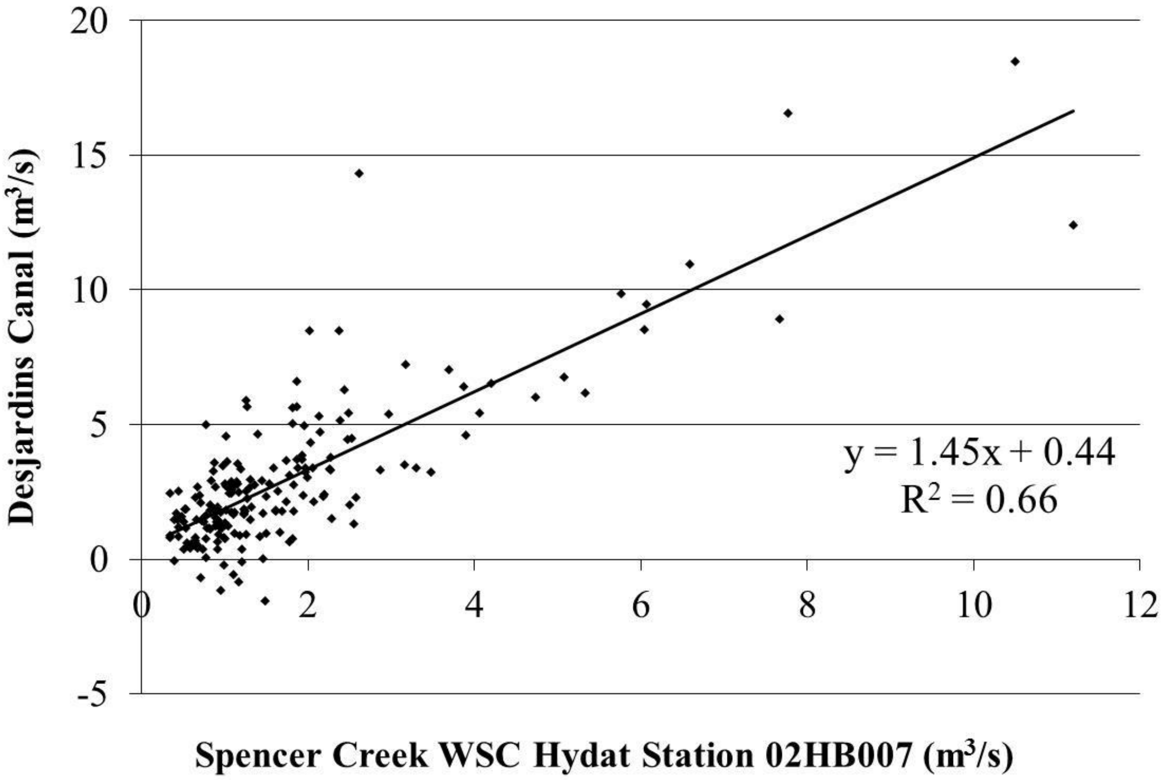

Figure 3: Regression between daily discharge at the Spencer Creek WSC Hydat Station 02HB007 and at the Desjardins Canal for April 16 – July 28, 2009 and August 20 – November 19, 2009.

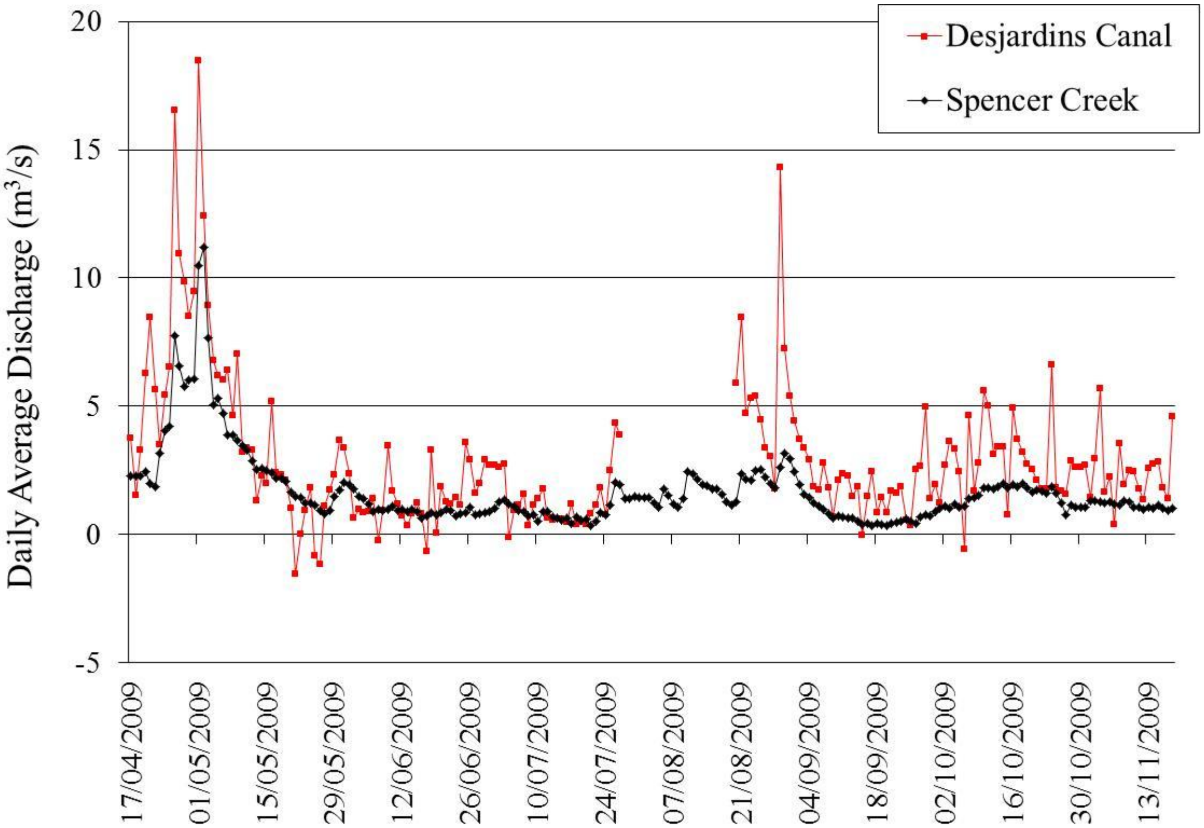

Figure 4: Spencer Creek and Desjardins Canal discharge April – November 2009.

Appendix S2 - Data Summary Table of 24-hour level-weighted composite samples

Table 1: Summary statistics of the 24-hour level-weighted composite samples collected from four stations in the Hamilton Harbour watersheds for 87 events during the period July 2010 – May 2012. Presented are the mean (standard deviation in parentheses), median, and range (minimum – maximum).

Trace Metals (ug/L)

		Silver	Aluminum	Arsenic	Barium
Red Hill Creek	All data	0 (0)	424 (398)	1.26 (0.61)	48.0 (15.2)
	(n= 92)	0	372	1.1	44.8
		0 - 0	22.9 - 2120	0.7 – 4.5	27 - 118
	Baseflow (n=21)	0 (0)	46.7 (17.0)	1.46 (0.94)	57.5 (18.0)
		0	43.7	1.0	51
		0 - 0	22.9 – 78.4	0.7 – 4.5	41.7 - 118
	Rain/melt event (n=71)	0 (0)	535.6 (388.5)	1.20 (0.47)	45.2 (13.2)
		0	487	1.1	41.5
		0 - 0	48.7 - 2120	0.7 – 4.0	27 - 97
Indian Creek	All data (n=97)	0 (0)	325 (246)	4.13 (2.01)	63.8 (19.3)
		0	293	3.5	59.5
		0 - 0	25.4 - 1060	1.3 – 11.5	37.1 - 120
	Baseflow (n=23)	0 (0)	110.1 (88.2)	4.30 (2.64)	87.3 (13.9)
		0	79	3.2	82.2
		0 - 0	25.4 - 318	1.3 – 11.5	68.4 - 116
	Rain/melt event (n=74)	0 (0)	391.9 (241.4)	4.08 (1.79)	56.5 (14.3)
		0	377	3.5	53.8
		0 - 0	45.3 - 1060	2 – 10.6	37.1 - 120
Grindstone Creek	All data (n=89)	0 (0)	349.8 (360.7)	1.16 (0.37)	67.5 (11.3)
		0	213	1.1	66.2

		0 - 0	31.1 - 1940	0.6 – 2.4	43.9 - 106
	Baseflow (n=19)	0 (0)	86.5 (55.8)	1.14 (0.33)	70.1 (8.9)
		0	84.8	1.1	71.8
		0 - 0	31.1 - 271	0.7 – 1.8	53.4 – 84.1
	Rain/melt event (n=70)	0 (0)	421.2 (375.3)	1.17 (0.39)	66.7 (11.8)
		0	263.5	1.1	65.7
		0 - 0	32.3 - 1940	0.6 – 2.4	43.9 - 106
Desjardins Canal	All data (n=95)	0 (0)	197.9 (148.9)	1.26 (0.47)	45.6 (4.99)
		0	151	1.1	46
		0 - 0	19.8 - 753	0.6 – 2.5	36.3 – 61.6
	Baseflow (n=24)	0 (0)	96.7 (45.6)	1.22 (0.40)	45.6 (5.1)
		0	94.1	1.0	46
		0 - 0	19.8 - 183	0.7 – 2.0	36.3 – 59.5
	Rain/melt event (n=71)	0 (0)	232.1 (156.1)	1.27 (0.49)	45.6 (5.0)
		0	194	1.2	46
		0 - 0	25.3 - 753	0.6 – 2.5	37.4 – 61.6
Field Blanks	n=7	0 (0)	1.1 (0.84)	0 (0)	0.23 (0.24)
		0	0.9	0	0.1
		0- 0	0.2 – 2.7	0 - 0	0 – 0.7

Appendix S3 – Summary of concentration-discharge relationships

Table 1: Summary of linear regressions for log-log concentration-discharge relationships

	y-intercept (p-value)	Slope (p-value)	Slope: Lower - upper 95% confidence intervals	R^2	Behaviour suggested by 95% confidence intervals
TP					
Red Hill Creek	89.71 (<0.05)	0.6851 (<0.05)	0.60 – 0.77	0.75	Concentrating
Indian Creek	111.93 (<0.05)	0.5035 (<0.05)	0.44 – 0.57	0.72	Concentrating
Grindstone Creek	97.232 (<0.05)	0.3996 (<0.05)	0.26 – 0.54	0.26	Concentrating
Desjardins Canal	84.425 (<0.05)	0.115 (0.14)	-0.04 – 0.27	0.023	Chemostasis to concentrating (slope not significant)
Phosphate					
Red Hill Creek	22.54 (<0.05)	0.6149 (<0.05)	0.49 – 0.74	0.53	Concentrating
Indian Creek	31.977 (<0.05)	0.4364 (<0.05)	0.34 – 0.53	0.49	Concentrating
Grindstone Creek	28.67 (<0.05)	0.1734 (<0.05)	0.017 – 0.33	0.055	Concentrating
Desjardins Canal	10.663 (<0.05)	0.4858 (<0.05)	0.33 – 0.64	0.31	Concentrating

TKN					
Red Hill Creek	0.7219 (<0.05)	0.3166 (<0.05)	0.26 – 0.37	0.60	Concentrating
Indian Creek	0.8696 (<0.05)	0.0574 (0.063)	-0.0032 – 0.12	0.037	Chemostasis to concentrating (slope not significant)
Grindstone Creek	0.8535 (<0.05)	0.1766 (<0.05)	0.13 – 0.23	0.37	Concentrating
Desjardins Canal	1.0281 (0.69)	-0.047 (0.33)	-0.14 – 0.049	0.010	Chemostasis to concentrating (slope not significant)
Nitrite					
Red Hill Creek	0.0286 (<0.05)	0.2047 (<0.05)	0.13 – 0.28	0.28	Concentrating
Indian Creek	0.0323 (<0.05)	-0.009 (0.82)	-0.090 – 0.071	0.0006	Chemostasis to concentrating (slope not significant)
Grindstone Creek	0.0151 (<0.05)	0.1323 (<0.05)	0.047 – 0.22	0.10	Concentrating
Desjardins Canal	0.0394 (<0.05)	-0.064 (0.12)	-0.15 – 0.018	0.026	Chemostasis to concentrating (slope not significant)
Nitrate					
Red Hill Creek	0.8633 (0.058)	0.2196 (<0.05)	0.11 – 0.33	0.15	Concentrating

Indian Creek	1.1055 (<0.05)	-0.314 (<0.05)	-0.36 - -0.27	0.70	Chemostasis
Grindstone Creek	1.3199 (<0.05)	-0.328 (<0.05)	-0.40 - -0.26	0.53	Chemostasis
Desjardins Canal	0.9063 (0.19)	0.0967 (0.069)	-0.0077 – 0.20	0.036	Chemostasis to concentrating (slope not significant)
Ammonia					
Red Hill Creek	0.0784 (<0.05)	0.4469 (<0.05)	0.29 – 0.60	0.27	Concentrating
Indian Creek	0.0882 (<0.05)	-0.068 (0.42)	-0.23 – 0.098	0.0071	Chemostasis to concentrating (slope not significant)
Grindstone Creek	0.0342 (<0.05)	0.2564 (<0.05)	0.11 – 0.40	0.13	Concentrating
Desjardins Canal	0.1501 (<0.05)	0.1932 (<0.05)	0.062 – 0.32	0.087	Concentrating

ESM Appendix S4 – Temporal and Seasonal Trends

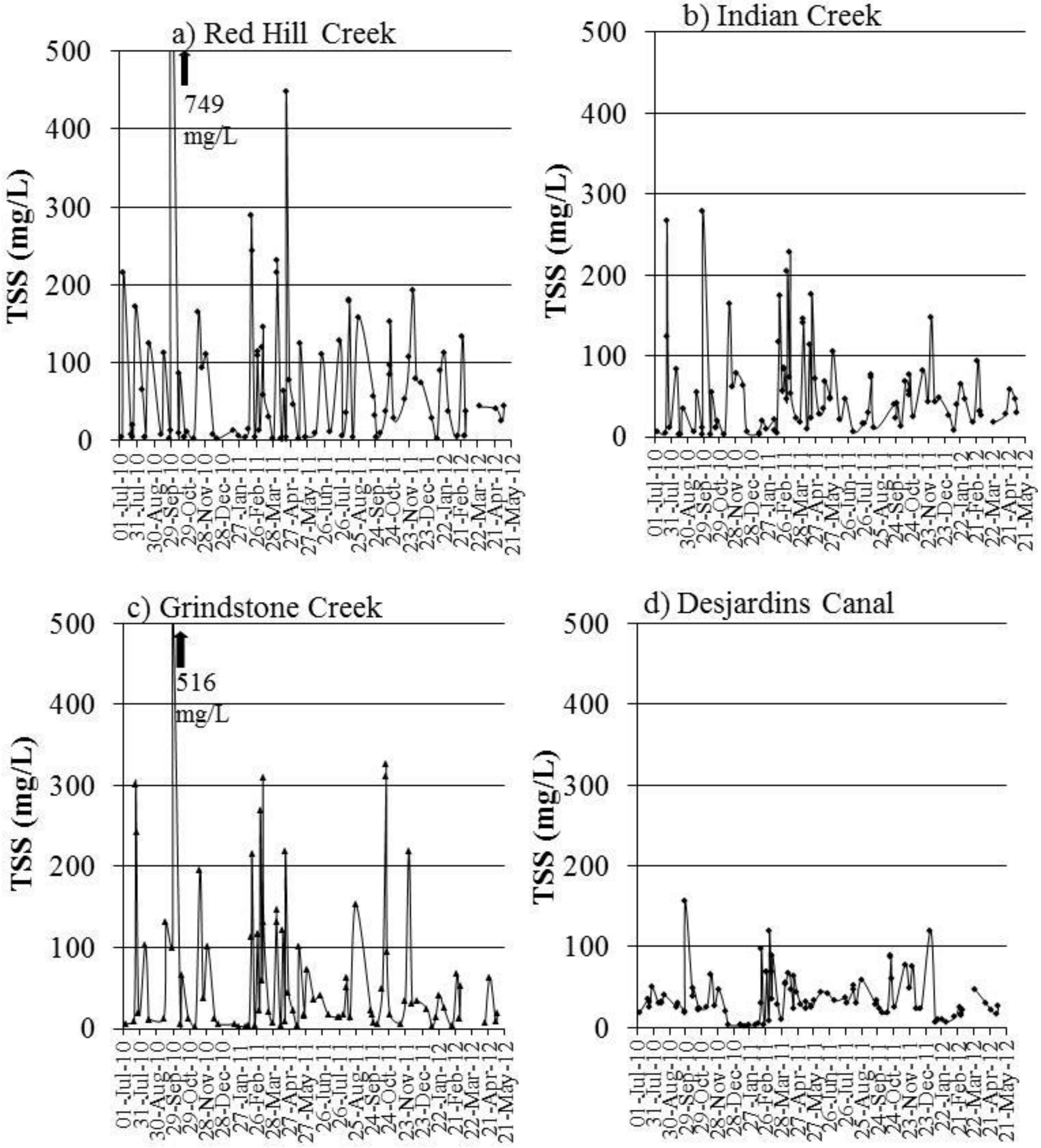

Figure 1: Time series of total suspended solids (TSS) concentrations in 24-hour level-weighted composite samples at a) Red Hill Creek; b) Indian Creek; c) Grindstone Creek and d) Desjardins Canal during July 2010 to May 2012