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Increasing nitrate concentrations in streams draining into Lake Ontario

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ABSTRACT

Nitrate (NO_3-N) concentrations in offshore waters of Lake Ontario increased by approximately 60% between the 1970s and 2000s, although the drivers are unclear. Here, we show that NO_3-N concentrations also increased significantly in at least one season at 13 of 15 large southern Ontario tributaries (8.4 to 2779 km^2) that drain into Lake Ontario and have no known upstream wastewater treatment plants. Average NO_3-N concentrations more than doubled between the 1970s and 2000s at some streams. Only the two most urbanized streams did not show any increase in NO_3-N and NO_3-N declined at the most urbanized catchment in this study (Sheridan Creek; 92% urban). Agriculture is the predominant form of human activity at the 13 watersheds where NO_3-N increased, accounting for 51–71% of total land cover. Both the total area of agricultural land and the type of agriculture have changed dramatically in southern Ontario; and these shifts could alter nutrient transfer to waterways. Specifically, shifts in agriculture towards more N-demanding annual row crops like corn could result in higher NO_3-N leakage to streams, and the impact of this form of land use change on nutrient export requires further investigation. Overall, these results suggest that changes in tributary loading may have contributed to recent observations of increasing NO_3-N levels in offshore waters of Lake Ontario.

Introduction

Spring nitrate (NO_3-N) concentrations increased by approximately 60% in the offshore waters of Lake Ontario between the 1970s and 2000s (Dove and Chapra, 2015) and long-term increases in Lake Superior NO_3-N have been the subject of study and debate over the past four decades (e.g. Weiler, 1978; Bennett, 1986; Finlay et al., 2007). The driver(s) of increasing NO_3-N levels in the North American Great Lakes remain uncertain, but have been attributed to a variety of causes including increases in N input *via* atmospheric deposition (Ostrom et al., 1998; Dove and Chapra, 2015) or tributary loading (McDonald et al., 2010), changes in N processing within lakes *via* increases in in-lake nitrification (Finlay et al., 2007), or decreased loss of N from the water column *via* N burial in sediment or denitrification (Sterner et al., 2007). Modeling efforts suggest that in-lake processes alone cannot explain rising NO_3-N in Lake Superior, and instead watershed sources including increases in atmospheric N deposition and/or increased tributary input must be responsible (McDonald et al., 2010).

Recent observations of declining total phosphorus concentrations in streams within the Lake Ontario watershed (Raney and Eimers, 2014), which match declines observed in offshore lake waters (Dove and Chapra, 2015) suggest that tributary loading is an important driver of lake nutrient levels, and could similarly explain increases in lake NO_3-N. However, there are few reports of patterns or trends in stream NO_3-N concentrations across Lake Ontario tributaries to test this. There are a number of potential watershed-processes that could contribute to increases in tributary NO_3-N. For example, an increase in N input to the watershed *via* atmospheric deposition or surface amendments (e.g. inorganic fertilizer, manure) could augment stream NO_3-N levels. Changes in the delivery of NO_3-N to streams *via* runoff could also contribute to higher stream NO_3-N. Baseflow NO_3-N concentrations, for example, are often higher compared with surface runoff (e.g. Schilling and Zhang, 2004) and so a shift in the relative proportion of baseflow to surface flow could contribute. A loss of natural land cover or a decline in vegetation health is another factor to consider, as a decrease in the area of land that is available to assimilate NO_3-N (e.g. healthy forest cover or riparian vegetation) or remove NO_3-N *via* denitrification (e.g. wetlands; riparian zones) could lead to higher stream NO_3-N concentrations (Groffman et al., 2003). In addition, shifts in land use within a particular land cover type could influence stream NO_3-N. For example, a change in agricultural practice from pasture to fertilized cropland or from perennial to annual crops or from one type of livestock to another could influence the form and magnitude of N input and loss to streams (e.g. Randall and Mulla, 2000; Schilling and Spooner, 2006).

Southern Ontario is the most populated region in Canada, with the majority of the population residing in urban centres within the 'Greater Golden Horseshoe', which is one of the most rapidly growing areas in Canada (Statistics Canada, 2013). Southern Ontario also contains the majority of prime agricultural land in the province, has more farms than any other province and ranks 4th in Canada for total area of farmland (Statistics Canada, 2011). This intersection of a large and growing urban population within a productive agricultural landscape means

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that land cover is dynamic and the predominant direction of land cover change in Southern Ontario over the past four decades has been the conversion of agricultural to urban land (Hofmann, 2001). In our discussion of drivers of declining total phosphorus (TP) in Southern Ontario streams we speculated that changes in land cover could be a contributing factor, as replacement of fertilized agricultural lands with impervious urban cover could result in lower TP export (e.g. Roberts et al., 2009) and increasing stream chloride (Cl), which was also observed at the majority of sites.

Conversion of agricultural to urban land may similarly influence stream NO_3-N, by enhancing nitrogen (N) input to the watershed in atmospheric deposition due to greater transportation-related emissions and by altering the effectiveness of NO_3-N removal in stream riparian zones (e.g. Groffman et al., 2003). Changes in hydrology resulting from land cover change can also affect nutrient export from watersheds and should be considered. However, there have been few studies that have specifically addressed this form of land use change on N levels in waterways, and most of these have been modelling simulations (e.g. Tang et al., 2005; Roberts et al., 2009). In addition, there have been dramatic shifts in the types of agriculture (i.e. land use) practiced within southern Ontario over the past three decades (Ontario Ministry of Agriculture Food and Rural Affairs, OMAFRA, 2014; Statistics Canada, 2011) with substantial declines between 1981 and 2014 in the production of perennial cereal grains, including rye, oats and barley as well as hay and dramatic increases in grain corn and soybean production (both annual plants) over the same time period (45% and 525%, respectively; OMAFRA, 2014). Most studies suggest that annual crops take up only about 50% of applied N, leaving the remainder available to be leached to waterways (reviewed in Syswerda et al., 2012), and thus a shift in crop type without any change in total agricultural land area could influence NO_3-N leakage to streams (e.g. Randall et al., 1997; Schilling and Spooner, 2006). Schilling and Spooner (2006), for example, found that stream NO_3-N levels increased in agricultural streams when perennial grasses were converted to row crops, and Randall et al., (1997) found that row crops like corn and soybeans were associated with substantially higher NO_3-N levels in drainage waters compared with perennial crops like hay.

Given the importance of NO_3-N as a nutrient in aquatic systems and its unexplained rise in the Great Lakes, the objective of this study was to evaluate long-term trends in NO_3-N concentrations in tributaries draining into Lake Ontario to determine whether tributaries have increased in NO_3-N similar to the lake. Seasonal averages and trends were calculated to evaluate within-year variability and patterns over time. Tributaries were selected across the Greater Golden Horseshoe region of southern Ontario, where land cover varies greatly from predominantly agricultural to almost entirely urban. Through this, we evaluated whether there is any correspondence between land cover and stream NO_3-N and to identify potential causal factors.

Methods

Fifteen large streams (8.4–2779 km^2) that drain directly into Lake Ontario (Fig. 1) and span the 'Greater Golden Horseshoe' (GGH) were selected for this study. The GGH had a population of 8.7 million people in 2011, and is home to two thirds of Ontarians and one quarter of Canada's total population (Statistics Canada, 2013). The population of the GGH is also rapidly increasing with a growth rate of 8.4% per annum (Statistics Canada, 2013). All streams are part of the Ontario Provincial Water Quality Monitoring Network (PWQMN) which was initiated by the Ontario Ministry of the Environment and Climate Change (OMECC) in 1964 and is carried out in collaboration with local Conservation Authorities. The PWQMN network spans an area of approximately 330,000 km^2 and includes streams that ultimately drain into Lakes Erie, Ontario, Huron and Simcoe as well as the St. Lawrence River which discharges to the Atlantic Ocean. In 2010 there were 257 active stream monitoring stations that had record lengths of 20 years or longer and 30 of the monitored tributaries drain directly into Lake Ontario. Of these, 15 have no known upstream wastewater treatment plant (WWTP) influence or reservoirs and so were selected for this study (Table 1).

The Conservation Authorities sample streams following a standardized protocol, and submit samples to a central OMECC laboratory located in Etobicoke (Laboratory Services Branch) for chemical analysis. This ensures consistency in field and analytical methods across sites. The Laboratory Services Branch analyses PWQMN water samples for a total of 37 parameters, including NO_3-N and nitrite (NO_2-N), as described in the Handbook of Analytical Methods for Environmental Samples (Ontario Ministry of the Environment, 1983). Consistent sampling protocol and laboratory methods ensure that results are comparable across the province; however, there have been some changes in the method of NO_3-N analysis over time. Specifically, during the 1970s through early 1990s, stream samples were first filtered and then analyzed separately for NO_3-N and NO_2-N. For the purpose of this study, these NO_3-N and NO_2-N concentrations were summed to provide an indication of 'total' nitrates. Subsequent to 1997, samples were analyzed unfiltered for 'total nitrates' (i.e. NO_3-N + NO_2-N) and separately for NO_2-N, which allows calculation of NO_3-N alone by subtraction. For this study we evaluate patterns and trends in 'total nitrate' (which includes NO_2-N) only, and do not evaluate trends in nitrite separately, as NO_2-N concentrations are typically low (<10% of total nitrates). For simplicity, we hereafter use 'NO_3-N′ to refer to 'total nitrates'.

Sampling frequency has varied through the history of the PWQMN, with the total number of samples analyzed annually ranging from a low of six samples per year to as high as 24 per year, but eight samples per year were common post 1993 (i.e. the ice-free months). The number of sites monitored through the PWQMN has also varied greatly over time and five of our 15 study sites ceased to be monitored between 1993 and 1996, and the majority of streams have at least one year with no measurements, with some streams having gaps in monitoring for as long as eight consecutive years (see 'n' values in Table 1). In order to address changes in sampling frequency over time, and to ensure that these changes did not impact the detection or magnitude of trends, we 'collapsed' the dataset, by first averaging values for each month (i.e. when there was more than 1 measurement per month) and then averaging monthly measurements to calculate seasonal concentrations, where summer = June, July, August; fall = September, October, November; winter = December, January, February and spring = March, April, May. Seasons were based on the hydrological year, which is June 1 to May 31. Annual averages were not calculated, since most streams were not sampled during the winter post 1993. Instead, trends in each season were evaluated. We also present decadal averages in order to minimize the impact of gaps in monitoring on the visual interpretation of temporal and spatial patterns in stream nutrient concentrations. Although volume-weighted mean concentrations would have been preferable for this analysis, flow data from the same stream locations where water quality is measured and over the same time period of water quality records are not available.

Streamflow

Although streamflow is not measured at the PWQMN locations where water is sampled for nutrient analysis, the Water Survey of Canada (WSC) operates gauges on several of the study tributaries at locations generally upstream of human settlements and where chemistry is monitored (Fig. 1). Daily streamflow data (1970–2009) from Wilmot (02HD009), Oshawa (02HD008), Mimico (02HC033) and Grindstone Creeks (02HB012), which span the study area were obtained from the WSC website (http://wateroffice.ec.gc.ca/) in order to evaluate whether seasonal stream runoff (mm) has changed over the same time period as nutrients. It should be noted that WSC monitoring stations are generally located well upstream of areas of urban development in these watersheds, whereas PWQMN stations tend to be located