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# Calculating discharge of phosphorus and nitrogen with groundwater base flow to a small urban stream reach



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## SUMMARY

Elevated levels of nutrients, especially phosphorus, in urban streams can lead to eutrophication and general degradation of stream water quality. Contributions of phosphorus from groundwater have typically been assumed minor, though elevated concentrations have been associated with riparian areas and urban settings. The objective of this study was to investigate the importance of groundwater as a pathway for phosphorus and nitrogen input to a gaining urban stream. The stream at the 28-m study reach was 3–5 m wide and straight, flowing generally eastward, with a relatively smooth bottom of predominantly sand, with some areas of finer sediments and a few boulders. Temperature-based methods were used to estimate the groundwater flux distribution. Detailed concentration distributions in discharging groundwater were mapped using in-stream piezometers and diffusion-based peepers, and showed elevated levels of soluble reactive phosphorus (SRP) and ammonium compared to the stream (while nitrate levels were lower), especially along the south bank, where groundwater fluxes were lower and geochemically reducing conditions dominated. Field evidence suggests the ammonium may originate from nearby landfills, but that local sediments likely contribute the SRP. Ammonium and SRP mass discharges with groundwater were then estimated as the product of the respective concentration distributions and the groundwater flux distribution. These were determined as approximately 9 and 200 g d<sup>-1</sup> for SRP and ammonium, respectively, which compares to stream mass discharges over the observed range of base flows of 20–1100 and 270–7600 g d<sup>-1</sup>, respectively. This suggests that groundwater from this small reach, and any similar areas along Dymment's Creek, has the potential to contribute substantially to the stream nutrient concentrations.

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## 1. Introduction

Inputs of phosphorus (P) and other nutrients to streams may lead to eutrophication, which can harm aquatic life via reduced dissolved oxygen levels, increase the chance of toxic algal blooms, and impair drinking water quality (Chambers et al., 2001). Commonly-recognized sources of these nutrients include treated wastewater discharges and urban or agricultural runoff. However, groundwater may also contain elevated levels of nutrients (see Dubrovsky et al. (2010) for review), from both natural and anthropogenic sources, meaning that groundwater may act as a source of these nutrients to streams or sections of streams that are receiving groundwater discharge (i.e. gaining streams) (e.g. Banaszuk and Wysocka-Czubaszek, 2005; Carlyle and Hill, 2001;

Jarvie et al., 2008; Palmer-Felgate et al., 2010; Pretty et al., 2006; Schilling and Jacobson, 2008).

There is a long-held belief that the levels of phosphorus in discharging groundwater will usually be low. This likely originates from the fact that adsorption and metal-complex formation tend to restrict the subsurface migration of potentially mobile P species (Holman et al., 2008). Indeed, the large-scale study on nutrients in groundwater of Dubrovsky et al. (2010) reported low P levels as the norm. And yet many studies (see Table 1 in Roy and Malenica, 2013) indicate that groundwater can have high dissolved P. Many of these studies reported maximum concentrations >0.5 mg L<sup>-1</sup> as soluble reactive phosphorus (SRP), whereas surface water bodies with SRP > 0.1 mg L<sup>-1</sup> are commonly considered hyper-eutrophic (Canadian Council of Ministers of the Environment, 2004). Qian et al. (2011) reported groundwater SRP values up to 11.6 mg L<sup>-1</sup> from boreholes in an urban area of China. Common anthropogenic sources of P to groundwater include wastewater (Palmer-Felgate et al., 2010; Ptacek, 1998) and fertilizer (Banaszuk et al., 2005).

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**Table 1**

Comparison of studies with measured phosphorus mass flux from groundwater or sediment porewater to a surface water body. Phosphorus measured as: SRP – Soluble reactive phosphorus, TP – Total phosphorus, TDP – Total dissolved phosphorus, PO<sub>4</sub> – Orthophosphate. Note that the methods used generally combine separate measures of groundwater flux and phosphorus concentration.

Study	Phosphorus flux (mg m <sup>-2</sup> d <sup>-1</sup> )	Possible source	Methods used	Scale (m <sup>2</sup> ) [water body]
This study	Mean: 75 (SRP)	Organic-rich sediments, maybe landfills	Heat tracer methods combined with piezometers and peepers	1.2 * 10 <sup>2</sup> [stream]
Belanger and Mikutel (1985)	Mean: 0.13 (TP)	Unknown	Seepage meters combined with piezometer data	4.7 * 10 <sup>7</sup> [lake]
Shaw et al. (1990)	Mean: 0.06–0.16, depending on method (SRP, TDP)	Unknown	Water balance, seepage meters and Darcy's law combined with piezometer concentrations	1.1 * 10 <sup>6</sup> [lake]
McCobb et al. (2003)	Mean: 142 (P)	Sewage treatment plant	Groundwater flow model combined with groundwater concentrations	6.1 * 10 <sup>3</sup> [pond shoreline]
Jarvie et al. (2008)	Mean values of 0.03–0.84, depending on location (SRP)	Sewage, agriculture	DET probes, measures diffusive flux	3 stream sites, catchment areas up to 5.6 * 10 <sup>8</sup>
Spruill and Bratton (2008)	Range of 0–86, mean value of 19 (PO <sub>4</sub> )	Organic-rich sediments	Mass balance, seepage meters and Darcy's law combined with piezometer concentrations	4.6 * 10 <sup>8</sup> [estuary]
Rivett et al. (2011)	Mean values of 323–933 (PO <sub>4</sub> ), depending on method	Urban and industrial	Combining base flow values with piezometer concentrations	8.9 * 10 <sup>4</sup> [river]

Groundwater may also acquire P from natural organic or inorganic sediment materials (e.g., Banaszuk and Wysocka-Czubaszek, 2005; Carlyle and Hill, 2001; Jarvie et al., 2008; Palmer-Felgate et al., 2010; Spruill et al., 1998). Of note, Holman et al. (2010) and Qian et al. (2011) determined that groundwater P levels were highest in urban areas compared to agricultural and natural areas. In addition, there is growing evidence that the contribution of nutrients, including phosphorus, to urban streams from groundwater may have been previously underappreciated (Holman et al., 2008; Kannel et al., 2008; Mayer et al., 2010; Roy and Bickerton, 2012, 2014; Shepherd et al., 2006).

The input of nitrogen with groundwater to streams has received more attention than the input of P (see Dubrovsky et al., 2010). Nitrate tends to be the more mobile of the nitrogen species in groundwater, with ammonium more commonly sorbed to sediments (Dubrovsky et al., 2010). Both species can be sourced from wastewater, synthetic fertilizers and atmospheric deposition (Dubrovsky et al., 2010). Also, ammonium can be generated through the mineralization of organic matter under reducing (anaerobic) conditions, with nitrate produced via nitrification of ammonium by autotrophic bacteria (Brady and Weil, 2004).

The objective of this study was to investigate the importance of groundwater as a pathway for nutrient input to a short reach of Dymont's Creek, an urban stream located in the city of Barrie within the Lake Simcoe watershed. The nutrient of primary focus was P because it is considered the most significant for water quality in Lake Simcoe (Ministry of the Environment, Ontario, 2009). Low dissolved oxygen (DO) levels in this lake have impaired the year-round sport fishery and have largely been attributed to eutrophication caused by elevated lake P concentrations (Young et al., 2011). Information on sources of P to the lake and the streams feeding into it is required to facilitate effective nutrient management strategies. One possible source that has not received much attention to date is urban groundwater. A previous study on a ~1-km section of Dymont's Creek (Roy and Bickerton, 2012) found that 42 of the 99 shallow groundwater samples (0.3–1.2 m below the stream bed) had SRP concentrations > 0.1 mg L<sup>-1</sup> (hyper-eutrophic water) while 51 of them had ammonium levels above its aquatic life guideline (~1 mg L<sup>-1</sup> for the site conditions; Canadian Council of Ministers of the Environment (CCME), 2010). These groundwater concentrations were routinely above that of the stream. There were only a few groundwater samples with elevated nitrate. A secondary objective of the work was to investigate the source of the nutrients and the factors affecting their discharge in groundwater to this stream reach.

In this study the groundwater mass discharges of relevant soluble forms of P and N to this small reach were calculated from nutrient concentrations measured in groundwater (a.k.a sediment porewater) samples collected within the stream sediments, and temperature-based groundwater flux measurements (using VFLUX, Gordon et al., 2012). We focused on base flow periods because rain events involved complex changes in flow patterns that were beyond the scope of this work. Both flux and concentration data sets involved spatially-distributed measurements (m scale) taken over ~1 yr. This method limits issues of nutrient transformations that can affect calculations from seepage meters (Belanger and Mikutel, 1985), from groundwater models based on observations from land-based wells, and from differences in stream nutrient mass discharge between two locations along a stream. A similar approach (but not identical methodology) was used by Milosevic et al. (2012) to measure the mass flux of contaminants from a landfill to a nearby stream, and by Kalbus et al. (2007) to determine the spatial pattern and magnitude of mass fluxes of organic compounds to a stream in an industrial area of Germany. To the best of our knowledge, this approach has not been reported for groundwater P discharge to a stream. In addition, there have been few studies that report direct nutrient mass discharge in groundwater to streams and rivers (Table 1), especially at the sub-reach scale.

## 2. Study site

This study was performed in Barrie, Ontario, Canada (population: 135 000), on Dymont's Creek, which is about 5 km long and flows into Lake Simcoe's Kempenfelt Bay. The study area (44.378180N, 79.69440W) was a 28-m reach with a streambed area of ~115 m<sup>2</sup>; it is in a residential-commercial area and is directly adjacent to historic buried landfill from the early 1960s (Fig. 1). A previous study found elevated levels of nutrients (SRP and ammonium), various organic contaminants, metals and the artificial sweetener saccharin, in the shallow groundwater at the upstream end of this reach (Roy and Bickerton, 2012). This reach of stream is 3–5 m wide and straight, with a relatively smooth bottom of at least partially calcareous shallow sediments, which are predominantly sand, with some areas of finer sediments and a few boulders. Garbage is present in the stream, along the shore, and buried in the streambed. The stream is tree-lined at the study site (Fig. S1) and supports various fish, amphibians, birds, and invertebrates. On the northwest bank (hereafter north bank), there is a steep 5-m rise about 5–10 m from the stream; groundwater

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