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The spatial and temporal distribution of metals in an urban stream: A case study of the Don River in Toronto, Canada

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ABSTRACT

Widespread growth of cities, the association of trace metals with urban runoff, and the potentially deleterious effect of metals on aquatic ecology have made it important to understand the distribution and transport of metals through surface water channel networks. The Don River in Toronto, Canada has been identified as an Area of Concern for pollution to Lake Ontario, with historically high levels of metal contamination. Sampling programs are sparse, therefore a model is needed to understand the spatial and temporal variability of metals in the river network. The objectives of the current study are to: i) describe the sampled spatial and temporal variability of metals in the Don River and ii) develop a modelling strategy to describe within flood metal transport dynamics. A model setup tool is developed that links Storm Water Management Model (SWMM) with the Environmental Fluid Dynamics Code (EFDC) to allow a seamless transition from catchment hydrology to in-stream hydraulic and chemical processes. Results show that lead pollution in the Don River is decreasing, likely as a result of policy changes and sediment dredging in the mouth of the river. However, zinc and copper pollution are increasingly problematic, with copper exceeding recommended lower guidelines, particularly during floods. Model results confirm that most of the sediment and metals are transported in relatively short bursts within longer flood durations and are stored in depositional hotspots within the Lower Don River. A better monitoring strategy is needed to understand and more accurately parametrize these processes in an urban river system.

Introduction

The Don River has been called the ‘most urban river in Canada’ (Ford, 2011) because of its position at the center of the largest metropolitan region (Toronto, Ontario) in the country and its nearly complete (96%) urbanization (Toronto Regional Conservation Authority (TRCA), 2009) (Fig. 1). The river (drainage area 360 km^2) and the harbor into which it flows was identified as one of 53 polluted Areas of Concern in the Great Lakes Basin by the International Joint Commission (MMM, 2012). Pollution is a legacy of development that began in the late 1700s when the town of York was established near the confluence of the river with Lake Ontario. The extent of urban area remained concentrated in the lower watershed up until the middle of the 20th century, when industrialization and waste from combined storm and sanitary sewers severely degraded the quality of the lower river (Boyd and Jaagumagi, 2001). Suburban development rapidly increased the extent of impervious cover throughout the watershed (Reeves and Palassio, 2008); and, while the sanitary sewage from these areas are routed to treatment plants outside of the catchment, only about 20% of the total stormwater flows are routed through management facilities such as ponds (TRCA, 2009a). Previous government reports have highlighted the issue of unsafe levels of metals in the Don River flows and sediment (Boyd, 1988; Dillon and Evans, 1982; Bodo, 1989; Boyd et al., 1999; Boyd and Jaagumagi, 2001). Despite cleanup efforts, the most recent watershed report card still gave the Don River Watershed an ‘F’ for both water quality and stormwater management (TRCA, 2013). There is a need to better understand and model the distribution and transport of metals to guide restoration and mitigation efforts in this urban water course.

Metals such as zinc (Zn), copper (Cu), lead (Pb), and cadmium (Cd) are common in urban rivers as a result of landfills, atmospheric deposition from automobile combustion, and the breakdown of car components such as brake pads and tires (Apeagyei et al., 2011; Estèbe et al., 1998; Foster and Charlesworth, 1996; Landre et al., 2011; Lindström, 2001; Yu et al., 2014). Metals in particulate matter of northeastern North America have been decreasing in the latest years (Husain et al., 2004), although there is increasing evidence of metals in automobile

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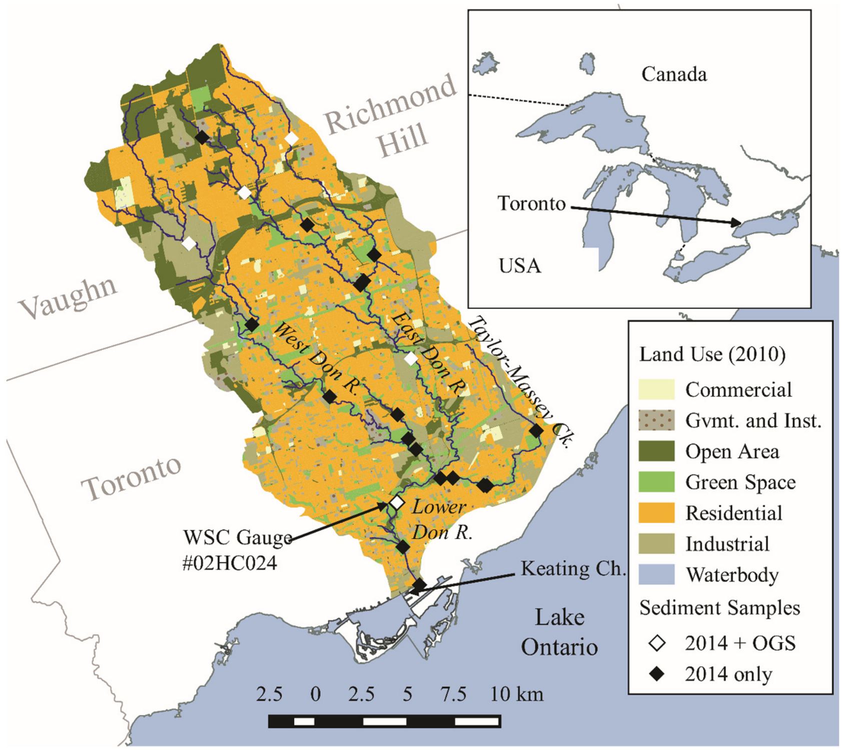

Fig. 1. Location of the Don River watershed showing 2010 land use, Location of the WSC Todmorden gauge used for calibration, and locations of the sediment samples taken as part of the current study (2014) and those where comparisons with the OGS were available. The modelled reach in EFDC is the Lower Don River. On yaxis masl is meters above sea level.

components (Unice et al., 2013). Such trace elements are transported through rivers in association with suspended solids (Meybeck et al., 2007; Walling et al., 2003). A metal budget for the Seine River in France, for example, showed that the basin is gradually storing metals, mostly due to manufactured products used in construction, landfills, soils and floodplain sediments that leach into the environment (Thévenot et al., 2007). Sediment resuspension was found to be a source of metal recontamination during floods, with drivers such as topography, flood frequency, and sediment characteristics (organic content, pH, salinity, iron oxides, etc.) strongly influencing transport and deposition dynamics (Du Laing et al., 2009). Typical ranges have been reported for European rivers (Newman and McIntosh, 1991), but overall there is little information on how metals are being routed through river systems, particularly in urban catchments.

Lake Ontario has a heavy metal legacy from anthropogenic activities around the basin. For example, Boyd (1988) found that the overall flux of suspended solids into Lake Ontario during the spring months of 1985 was in the range of 2500–5600 $kg \cdot km^{-2} \cdot yr^{-1}$ with loadings of 1.8–2 $kg \cdot km^{-2} \cdot yr^{-1}$ of Cu, 2.4–4.9 $kg \cdot km^{-2} \cdot yr^{-1}$ of Pb, and 4–5.9 $kg \cdot km^{-2} \cdot yr^{-1}$ of Zn (Table 1). Bodo (1989) found that deposited sediments in the Don River were significantly enriched with Cu, Pb, and Zn relative to pre-colonial sediments, and that large rainfall events could result in an increase of up to four times the base level loading which is expected from other research (Du Laing et al., 2009). Transport from the river was thought to account for over 90% of the total load to the harbor (Maunder et al., 1995; Boyd et al., 1999). In a later study, Boyd and Jaagumagi (2001) noted that progress had been made towards reducing metal concentrations in sediments through such policy changes as the elimination of lead in gasoline, but overall water quality was still limited by the nutrient and metal loadings from the river. Recommendations led to the creation of surface water quality monitoring programs such as the Provincial Water Quality Monitoring Network (PWQMN) with the goal of increasing the consistency, spatial coverage, and frequency of data.

Despite the investment in sampling programs, there is still a need to model the fluxes of metals to understand spatial and temporal patterns and predict the impact of restoration efforts. Hydrologic models are

Table 1
TSS buildup parameters for various land uses in an urbanized watershed (Hossain et al., 2010).

Land use	Max buildup, C_1 (kg/km^2)	Max buildup, C_1 ($kg\ ha^{-1}$)	Rate constant, k (1/days)
Residential	1000	10	0.12
Commercial	5300	53	0.222
Open area	2600	26	0.382
Government and institutional	5300	53	0.222
Resource and industrial	5300	53	0.222
Parks and recreational	2600	26	0.382

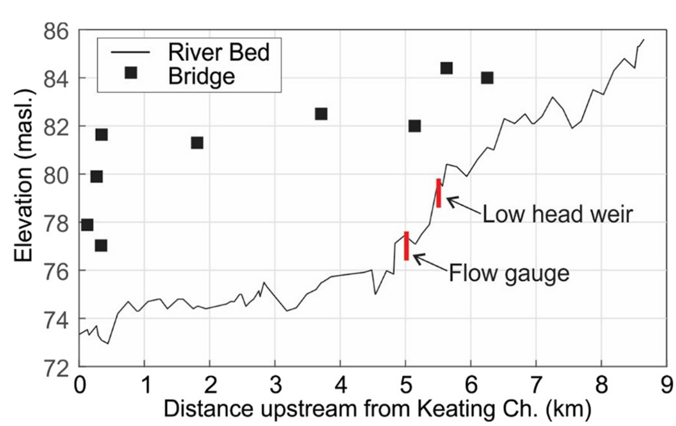

Fig. 2. Longitudinal profile of the Lower Don River from the Keating Channel to the confluence with the West Don River. Note that the EFDC model extends an additional 1 km upstream to the confluence with Taylor Massey Creek and that flow gauge is the Todmorden WSC Gauge 02HC024.

Table 2
TSS wash-off concentrations for various land uses in the Don River watershed (City of Toronto, 2006).

Land use	Concentration (mg/l)
Residential	150
Commercial	120
Open area	200
Government and institutional	120
Resource and industrial	330
Parks and recreational	130

commonly used for predicting discharge and water levels in rivers, but such models are not configured to represent the processes that are important for modelling metal dynamics. For example, the Storm Water Management Model (SWMM) is well adapted for urban watersheds and has the capability to calculate the buildup and washoff of pollutants in parallel with hydrologic calculations and route unsteady flow through river networks using kinematic or dynamic wave assumptions (James et al., 2010). However, this model assumes plug or fully mixed flow for the routing of water quality constituents, and in-stream sediment and contaminant transport processes such as erosion, deposition, diffusion, and sorption to sediments are not considered. The inability to model such processes is a key weakness of many watershed models (Chu and Rediske, 2012; Garneau et al., 2015; Ji et al., 2002; Liu et al., 2012; Massoudieh et al., 2010). Researchers are therefore working on the problem of linking hydrologic models such as SWMM and InfoWorks™ to more comprehensive models of instream processes such as the Environmental Fluid Dynamics Code (EFDC) (Zhu et al., 2016). EFDC solves the Reynolds averaged flow equations in one, two or three dimensions and can model a range of processes related to sediment mobility, pollutant fate, and metals transport (Hamrick, 1992). EFDC has been applied to urban streams including the Blackstone River in Virginia (Ji et al., 2002), the Nansha River in China (Jia et al., 2011), and the Chicago River (Sinha et al., 2012, 2013). More work is needed to link hydrologic and hydraulic models so that they can be used to jointly model metal dynamics in urban systems.

The goal of the current research is to characterize the current distribution and transport of metals through the Don River, with a particular focus on the Lower Don. The Lower Don is a 9 km long reach that extends from Lake Ontario to the confluence of the major branches of the river network (Fig. 1). The river ends at the Keating Channel, where it is turned 90° towards the Toronto Harbor. The bed is relatively deep near the mouth due to regular dredging where sediment tends to accumulate due to low water velocities (Fig. 2). The bed slope is relatively shallow (0.033%) from 0.7 to 4.7 km upstream where the river was straightened to accommodate navigation and highway construction, and relatively steep (0.25%) from 4.7 to 8.6 km upstream. Many bridge crossings and a low head weir constrain the flow and channel morphology. The City of Toronto is implementing a long-term wet-weather flow master plan with the goals of reducing combined sewer overflows into the Lower Don and the harbor in order to improve water quality (Waterfront Toronto, 2016). Other physical changes are being designed for the lower river and the outlet to the lake to reduce flooding, allow for new sustainable city building, and support the re-naturalization of the river mouth (TRCA, personal communication). Specific objectives of the current study are to i) describe the sampled spatial and temporal variability of metals in the Don River and ii) develop a modelling strategy to describe within flood metal transport dynamics. The hope is that such research will help to guide the restoration of the estuary and stimulate studies in other urban rivers.

Table 3
Pollutant co-fractions used in PCSWMM derived from 2008 to 2013 data obtained from TRCA. Unit conversion for the co-fraction values is handled internally by PCSWMM.

Pollutant	Observed mean concentration (μg/l)	Observed TSS mean concentration (mg/l)	Co-fraction
Zn	24.26	55.45	0.438
Cu	7.94	55.45	0.143
Pb	5.06	55.45	0.091

Table 4
Calibrated parameters for cohesive sediments used in EFDC for Lower Don River.

Parameter	Clay(10 μm)	Silt(30 μm)
Settling velocity (m/s)	0.001	0.001
Critical deposition shear stress (N/m^2)	0.16	0.16
Critical erosion shear stress (N/m^2)	0.192	0.192
Reference erosion rate (g/m^2/s)	0.09	0.09

Methods

Available datasets

A number of data sets are available for the Don River watershed to characterize metal concentrations. The Ontario Ministry of Environment and Climate Change maintains the Provincial (Surface) Water Quality Monitoring Network (PWQMN) consisting of 400 sites throughout the province, with one station located on the Lower Don (station 06008501402 - active since 2000, MOECC, 2015). Water quality samples have been collected monthly and analyzed for metal concentration by ICP-OES using ultrasonic nebulization. The Water Survey of Canada maintains a water level gauge at the same location with data stored on an hourly time step and 15 min data available up to 2010 (Todmorden gauge #02HC024, active since 1962, shown on Fig. 1). For bed sediment, one-time sediment grab samples were taken in the winter of 2008 by the Ontario Geological Survey through the southern Ontario Stream Sediment Project (OSSP) to characterize sediment throughout the province. Finally, TRCA has measured metal concentration in sediments dredged from the Keating Channel since 1987. Up to 60 samples per year were available from this sediment, though sample numbers have varied widely over time and generally decreased over the years. Particle size information was also available for the dredged sediment from the Keating Channel.

Table 5
Parameters for non-cohesive sediment used in EFDC for Lower Don River.

Parameter	Sand
Diameter (μm) (calibrated)	410
Critical shield's stress	0.032
Critical stress (N/m^2)	0.21
Critical velocity (m/s)	0.014
Settling velocity (m/s)	0.061

Table 6
Partition coefficients used in EFDC for contaminant modelling in the Lower Don River.

	Clay	Silt	Sand
Partition coefficients, K_d for water column (l/mg)			
Cu	0.001	0.001	0.0003
Pb	0.003	0.003	0
Zn	0.1	0.1	0.0003
Partition coefficients, K_d for sediment bed (l/mg)			
Cu	0.03	0.03	0.03
Pb	0.03	0.03	0.03
Zn	0.013	0.013	0.013

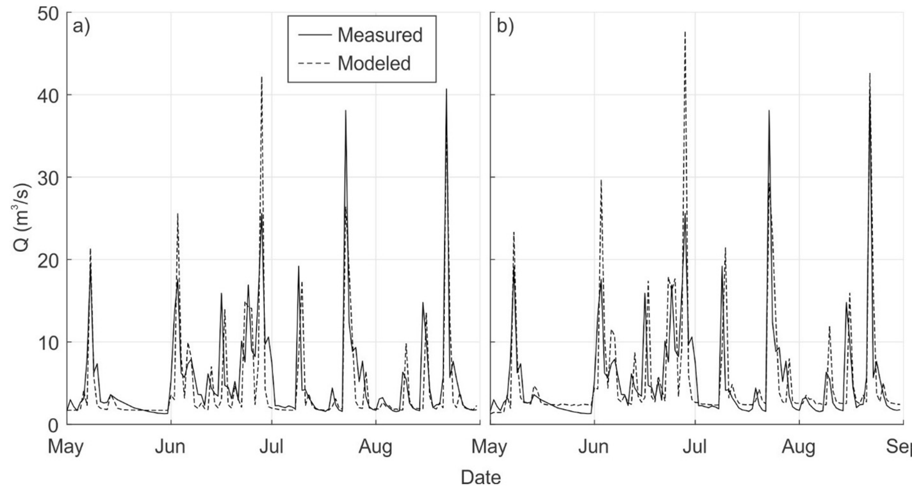

Fig. 3. Daily timestep hydrograph comparison during validation period at the Todmorden monitoring station for (a) SWMM model (RRMSE 10.63%, Nash-Sutcliffe efficiency 0.54) and (b) EFDC model (RRMSE 11.98% Nash Sutcliffe 0.43).

Additional sampling of metal concentration

To improve the spatial coverage of available metals information, river sediment and water samples were collected in April 2014 at locations throughout the Don River and its tributaries (Fig. 1). Locations were chosen to replicate those used for the OSSP study and to sample at least two locations within each of the subwatersheds. Sampling locations were also somewhat dependent on areas with easy access to the river. Seventeen sediment samples were taken from the top 10 cm of the river bed close to the middle of a perpendicular transect to the river bed. The samples were microwave digested using aqua regia (6 mL HCl and 3 mL HNO3), diluted and analyzed with an inductively coupled plasma optical emission spectrometry (Thermo iCAP 6200 Duo ICP-OES) for the total Cu, Pb, and Zn concentrations. Each sample was sieved to remove particles above 2 mm. Approximately 1 g of each sediment sample was weighed and microwave digested with aqua regia. Sediment digestions were performed in triplicate with MilliQ blanks and SRM 8704 reference material with every digestion and extraction cycle, and concentrations were adjusted according to EPA Method 3051A for microwave assisted acid digestions of sediments, sludges, soils, and oils. All glassware, polypropylene tubes, and equipment used for the water and sediment samples were acid washed with 10% HNO_3 overnight, rinsed five times with MilliQ and dried under laminar flow prior to use. More details on the sampling and processing of the samples are described by Louie (2014).

Water and sediment quality guidelines

Sampling and modelling results were compared to regional guidelines. Water quality results were compared with the Canadian Council of Ministers of the Environment guidelines for the protection of aquatic life (CCME, 2008). These guidelines and the methodology therein are widely applied in Canada and around the world (Akkoyunlu and Akiner, 2012; Alexakis et al., 2016; Hurley et al., 2012; Lumb et al., 2006). The guideline thresholds are 2–4 μg L^{-1} (dependent on hardness), 1–7 (dependent on hardness), and 30 μg L^{-1} for Cu, Pb, and Zn, respectively, Metal concentrations in sediments were compared with Ontario sediment quality guidelines (Fletcher et al., 2008). These guidelines were created to protect the environment using a biological effects-based approach and were determined with an aqua-regia sediment digestion and analyzed using spectrometric technique. The Lowest Effect Level (LEL) in sediment reflects the concentration that can be tolerated by most benthic organisms. LEL values in freshwater sediment for Cu, Pb, and Zn are 16, 31, and 120 mg kg^{-1}, respectively, all measured as a dry weight. The Severe Effect Level (SEL) is a threshold beyond which 95% of the benthic organisms could be eliminated. Respective SELs for Cu, Pb, and Zn are 110, 250, and 820 mg kg^{-1}.

Hydrologic model

Watershed hydrology was modelled using a program developed by the U.S. Environmental Protection agency called Storm Water Management Model (SWMM - available for download from https://www.epa.gov/water-research/storm-water-management-model-swmm). TRCA provided a calibrated model for the watershed. SWMM is well adapted for urban watersheds and has the capability to calculate the buildup and washoff of pollutants in parallel with hydrologic calculations and route unsteady flow through river networks using kinematic or dynamic wave assumptions (James et al., 2010). The model was developed using Personal Computer SWMM (PCSWMM™), a proprietary software that offers an advanced user interface with graphical information system (GIS) capabilities for the open source SWMM engine. The spatial resolution of the model for the Don River is relatively high, with a total of 475 subcatchments, 2834 conduits, and 2465 junctions in the domain. Eight rain gauges maintained by the TRCA in the area were used to supply the rainfall data to the model. All rain gauges were tipping bucket type gauges and reported measurements at 5-min intervals. They are considered to be reliable from the spring to the fall where snow accumulation is not a factor. Dry and wet weather time steps of 1 h and 2 min were used for the model, respectively, while a time step of 10 s was used for hydraulic routing through the network. The model reports the output every 5 min, which was used for comparison. Hourly discharge measurements are readily available at this location (WSC Gauge 02HC024 in Fig. 1), with higher frequency (15 min) data available up until 2010. The model calibration was confirmed by checking the Nash-Sutcliffe coefficient (0.873) and the relative root mean square error (RRMSE) (4.59%) for the 40 day calibration period (June 20 to July 30, 2008).

For the current study, the hydrologic model was further validated using a 5-month period from April 1 to August 31, 2010, and select pollution modelling algorithms were activated to simulate sediment and metal routing. A wet time step of 5 min, a dry time step of 30 min, and a hydraulic routing time step of 8 s were used to run the simulation. A smaller hydraulic routing time step was found to increase the numerical stability and computational efficiency of the model as fewer numerical iterations were required to converge to a solution. A reporting timestep of 15 min was used to compare flow rates at the Todmorden gauging station.

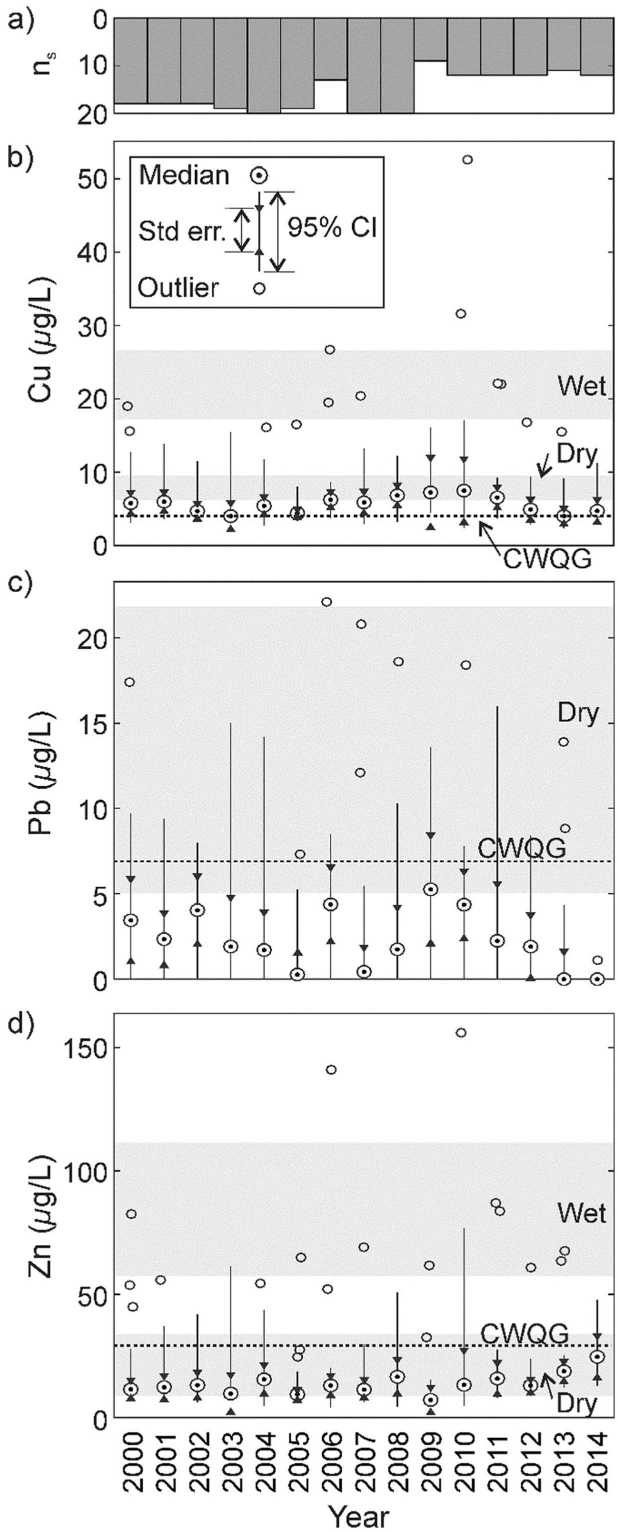

Fig. 4. Surface water PWQMN samples at Todmorden gauging station (2000–2014) including a) number of samples (n_s), b) copper, c) lead, and d) zinc. Shaded areas represent 95% confidence intervals for dry and wet weather concentrations from sampling in 1991 (Boyd et al., 1999). The Canadian Water Quality Guidelines (CWQG) for hard water are also shown for comparison (CCME, 2008).

The pollutant buildup/washoff modules were activated in SWMM to estimate total suspended solids (TSS) and associated metal loads to the study reach. Metals simulated in this study included Cu, Pb, and Zn. The pollutant modules required a land use layer to be added to the project, with classes that included residential, commercial, resource and industrial, government and institutional, parks and recreational and open areas. TRCA (2013) provided a land use layer which was overlain on the subcatchments in PCSWMM™. The area-weighting tool was used to associate each subcatchment with percentages of the various land use classes. Each land use category was then assigned TSS buildup (Table 1) and washoff (Table 2) parameters. An exponential equation (Magill and Sansalone, 2010; Wicke et al., 2012) was used to simulate buildup as:

$$B = C_1\left(1-e^{-kt}\right) \tag{1}$$

where B is the buildup (kg ha^{-1}), C_1 is the maximum buildup possible (kg ha^{-1}), k is the rate constant (1/days) and t is time in dry days. The parameters C_1 and k were derived from an experimental study conducted on a highly urbanized Australian watershed (Hossain et al., 2010). In the absence of data from a watershed with similar soil types and climate, this study was utilized because of similar development patterns and land use classes to those of the current study area. TSS was assumed to wash-off land surfaces following an event-mean-concentration (EMC) model. EMC values were taken from the Toronto Wet Weather Flow Management Guidelines shown in Table 2 (City of Toronto, 2006).

Metal concentrations in surface water runoff were simulated in SWMM using the pollutant co-fraction approach (Bai and Li, 2013). This approach assumes that metals are associated with TSS and requires the definition of co-fractions of the TSS load that represent the metal loads. The co-fraction approach is the simplest way to estimate metal loads using SWMM and is also recommended given the general dearth of pollutant buildup and wash-off parameters for urbanized catchments (James et al., 2010). Co-fractions were calculated for each of the metals (Cu, Pb, Zn) from measured data at the Todmorden station for the years 2008 to 2013. The mean of the observed concentrations was calculated for each of the pollutant and the co-fraction of each metal was calculated by dividing the metal by the TSS concentration (Table 3). Sediment size classes were also modelled by treating them as co-fractions of TSS. A constant size distribution was assumed based on the particle size fractions from material dredged from the Keating Channel (63% sand, 25% silt, and 12% clay).

EFDC model setup

As part of the current study, a software tool was developed to link SWMM to the Environmental Fluid Dynamics Code (EFDC – available for download from https://www.epa.gov/ceam/environmental-fluid-dynamics-code-efdc). EFDC was selected for hydraulic routing based on its suitability for modelling the dynamics of metal transport in rivers (see review by Mansoor, 2015). EFDC was originally developed at the Virginia Institute of Marine Science and is supported by the US Environmental Protection Agency (EPA). The program is free; but, similar to PCSWMM™, proprietary software such as EFDC Explorer™ has been developed to offer an advanced user interface that accelerates pre and post-processing (Craig, 2015). For the current study, a tool called the SWMM to EFDC model setup tool (STEMS) was written in MATLAB™ to initialize the EFDC model using the output files and geospatial layers from PCSWMM™. STEMS is described in more detail in Electronic Supplementary Material (ESM) Appendix S1.

Sediment transport simulations for the Lower Don River were performed with an active sediment bed. There are a total of 105 active cells in the EFDC model of the Lower Don ranging in size from 4.5 to 325.4 m in length and 9.3 to 57.4 m in width. Due to lack of scour data for the study reach, the sediment bed was initialized using a 0.05 m uniform bed thickness, which is consistent with the Blackstone River study (Ji et al., 2002). The sediment size distribution was assumed to match the material dredged from the Keating Channel (TRCA, 12% clay, 25% silt and 63% sand). Sediment transport calculations require the specification of a number of parameters. Various combinations of sediment parameters were tested in EFDC to obtain a reasonable agreement of modelled TSS concentrations with the observed data (Tables 4 and 5). For non-cohesive sediment, such as sand, only the representative grain size is required to determine parameters such as the critical Shields stress, critical velocity, and settling velocity. The calibrated sand size (0.41 mm) is a medium sand within the range of sediments extracted from the Keating Channel. For cohesive sediments such as silt and clay, there is considerably more complexity in the erosion and deposition parameters. In addition to size, parameters include critical deposition stress thresholds, erosion shear stress thresholds, and a reference surface erosion rate when the erosion threshold is exceeded. Representative silt and clay sizes of 30 μm and 10 μm, respectively, are in the middle of the range for silt particles and somewhat high for clay particles. A critical deposition shear stress of 0.16 N m^{-2} was selected to be near the middle of the suggested range from 0.10 to 0.25 N m^{-2} (Ji et al., 2002). Critical erosion shear stress is typically taken to be 1.2 times the critical deposition shear stress (Ji et al., 2002), so a value of 0.192 N m^{-2} was used. A settling velocity of 0.001 m/s was selected because it was consistent with the values reported for cohesive sediments in various case studies (Ji, 2008). A reference erosion rate of 0.09 g m^{-2} s^{-1} for silt and clay provided good agreement of TSS concentrations with the observed data.

Parameterization of the EFDC model was also required to simulate the processes of metal sorption and transport. Initial bed concentrations of metals were assigned based on values from measured metal concentrations in the dredged sediment of the Keating Channel (74, 30, and 148 mg Kg^{-1}, for Cu, Pb and Zn, respectively). As recommended by various researchers, partitioning coefficients were used to model the sorption processes (Allison and Allison, 2005; Ji et al., 2002; Wang et al., 2013). Partitioning coefficients are defined as the ratio of sorbed metal concentration to dissolved metal concentration at equilibrium. The most commonly used models for converting the coefficients to sorption isotherms are the linear (Henry's), Freundlich, and Langmuir isotherms (Allison and Allison, 2005). An EPA report on experimental results for partition coefficients of various metals in water, sediment, and waste was used as a guide to calibrate the partition coefficients in this study (Allison and Allison, 2005). Within the suggested range, partition coefficients were adjusted using to obtain a reasonable agreement of modelled metals with observed data (Table 6).

The model was allowed to 'warm-up' for a period of 43 days prior to the reporting of results. While longer warm-up time periods are preferred for sediments and metals because of their relatively slower response (Bussi et al., 2014; Ji et al., 2002), fast river systems with many external inflows and floods tend to reach steady-state sooner, and relatively shorter warm-up time periods are sufficient (Ji, 2008). The conservative approach of assigning initial sediment bed metal concentrations close to the observed trends also ensured that the system attained equilibrium within the warm-up time period of 43 days, thereby minimizing the impact of such initial conditions. The initial water column concentration of each metal was set at 0 μg L^{-1}.Water column responses tend towards equilibrium relatively quickly, and the warm-up time period of 43 days was deemed sufficient for them to adjust as a result of SWMM model inputs. The diffusion coefficient, which controls the rate at which dissolved contaminant in the pore space of the bed can diffuse to and from the water column was kept at a typical value of 1×10^{-9} m^2 s^{-1} (Ji, 2008).

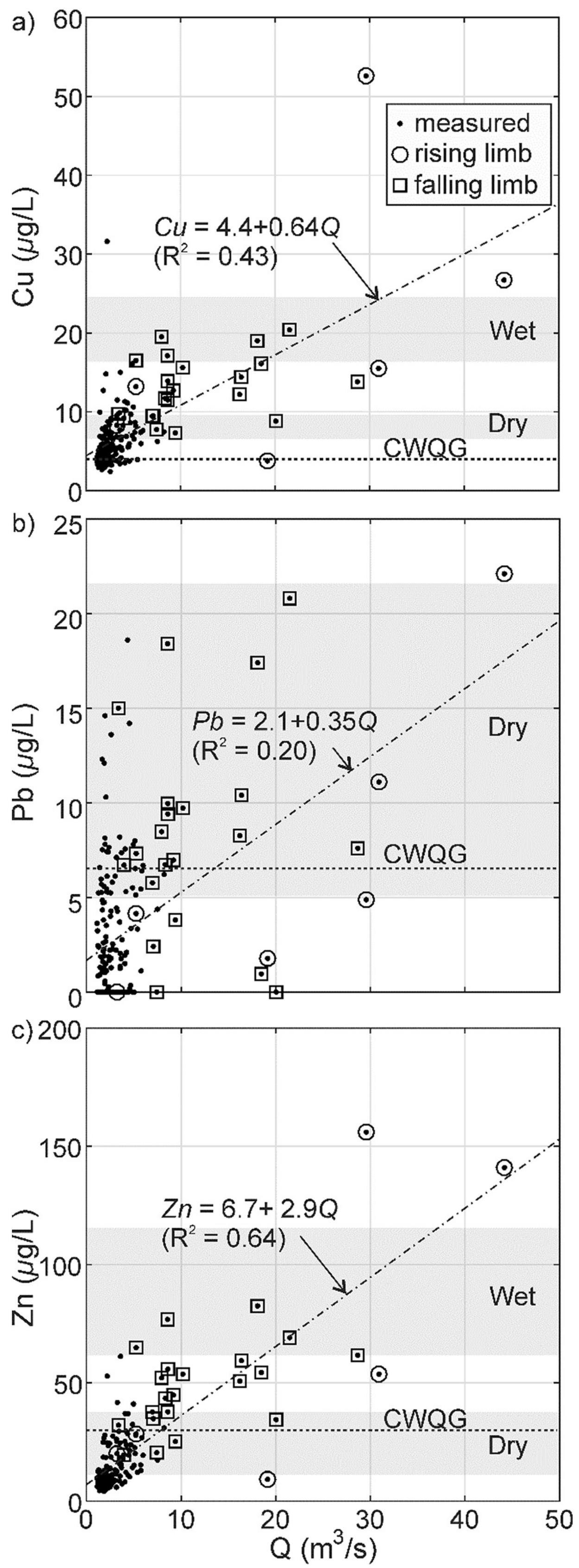

Fig. 5. Effect of discharge (Q) and hydrograph limb on surface water PWQMN samples at Todmorden Mills gauging station (2000–2010) for a) copper, b) lead, and c) zinc. Hydrograph limbs are established based on a flow acceleration thresholds of $+1.0 \times 10^{-4}$ $m^3 \cdot s^{-2}$ for the rising limb and -1.0×10^{-4} $m^3 \cdot s^{-2}$ for the falling limb. Other points represent baseflow conditions. Shaded areas represent 95% confidence intervals for dry and wet weather concentrations from sampling in 1991 (Boyd et al., 1999). The Canadian Water Quality Guidelines (CWQG) for hard water are also shown for comparison (CCME, 2008).

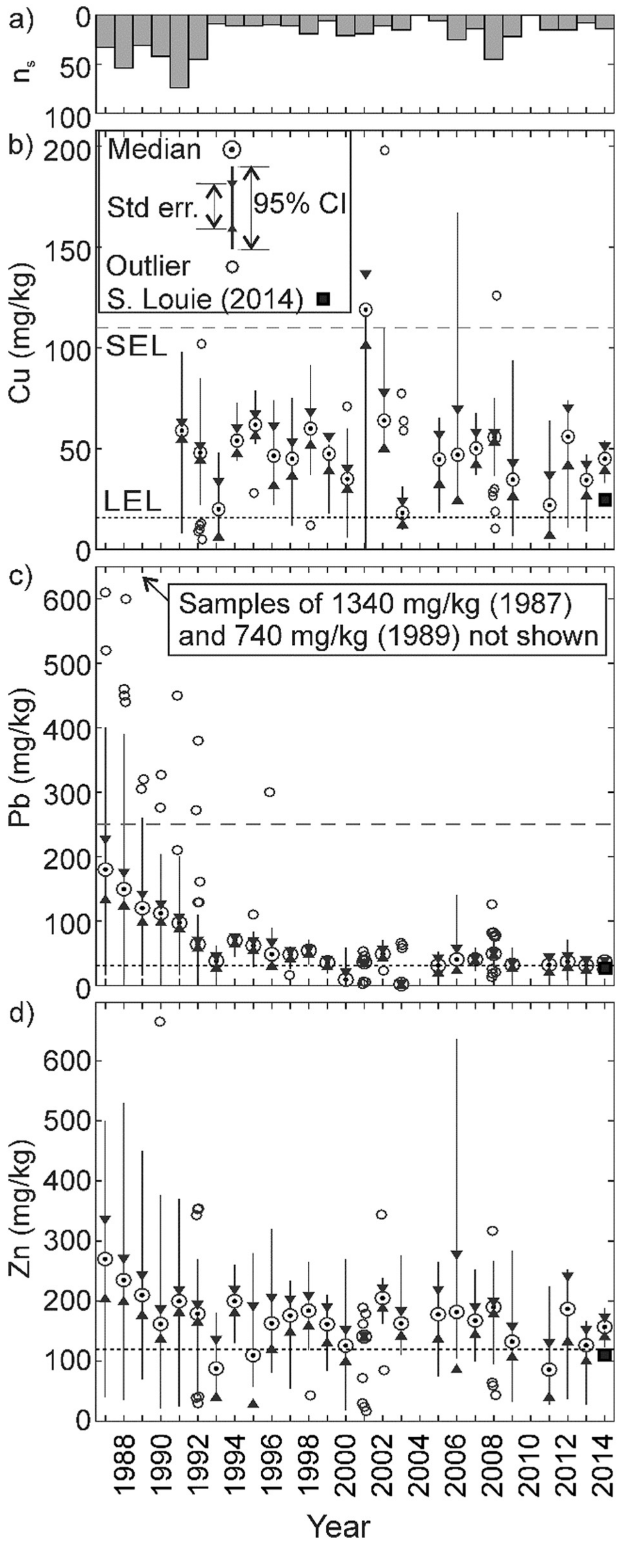

Fig. 6. Sampled metal concentrations in the dredged sediment at Keating Channel including a) number of samples (n_s), b) copper, c) lead, and d) zinc. No measurements of copper were made from 1987 to 1990. The lowest effect level (LEL - dotted line) and the severe effect level (SEL -dashed line) are shown for comparison, as is the sample analyzed for this study (Louie, 2014).

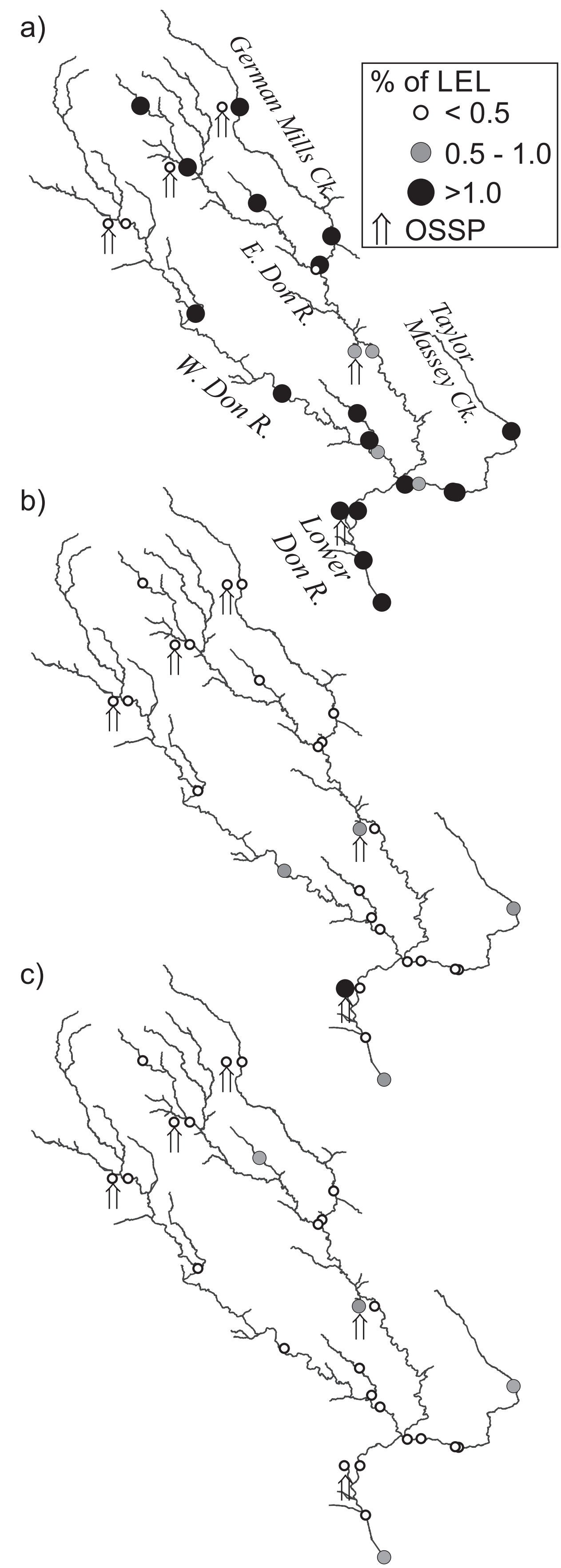

Fig. 7. Sampled concentrations of a) copper, b) lead, and c) zinc from deposited sediment at various locations in the Don River Watershed shown as a percentage of the lowest effect level (LEL) for each metal. For reference the LEL of Cu, Pb and Zn is 16, 31, and 120 mg kg^{-1}, respectively. OSSP (2008) samples are also shown for comparison slightly offset from the channel.

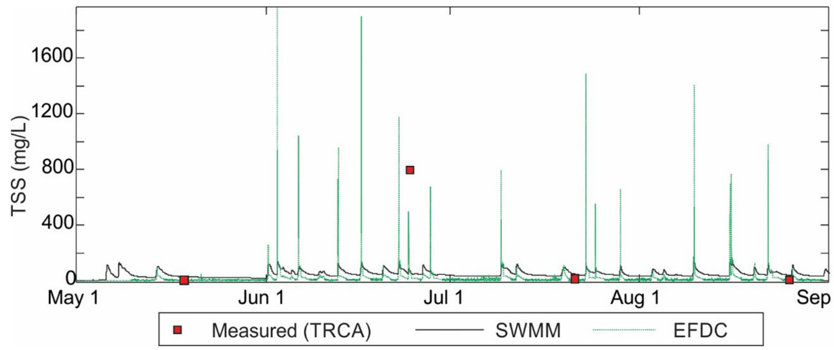

Fig. 8. Comparison between measured and modelled results at the Todmorden monitoring station through the summer months of 2010 for TSS.

Results

Hydrologic modelling

The SWMM model show a good agreement with the observed data for the validation period (Fig. 3a). The SWMM model was developed in 2012. Land use change over the past decade is minor as most of the watershed is now developed. The RRMSE is higher than for the calibration period (10.6% vs 4.6%), as is expected, but peak flow timing and magnitudes are well captured by the model, and the base flow discharge rates agree with measured data. Given that the model was provided as a calibrated model and we did not want to change the calibration parameters of the model in use at the TRCA, it was decided that the model was acceptable for the current study. The results from this validation period were therefore saved in a SWMM binary output file and pulled into EFDC using the STEMS tool for hydraulic routing through the Lower Don River. Hydrologic results from the EFDC model at the Todmorden gauging station match well with the SWMM model results and the measured data (Fig. 3b). The RRMSE is slightly higher for the EFDC model (12.0% vs 10.6%), but the timing and magnitude of the peaks and base flow correspond well with the SWMM results and observed data. The only calibration parameter used to achieve this result was the roughness height, which was given a global value of 0.08 m, which is within the recommended range (Ji, 2008).

Sampled surface water metals concentrations

Surface water metals concentrations from the PWQMN were grouped by year over the 14-year record to understand temporal trends and compare with other information (Fig. 4). Temporal trends were assessed based on the sample means and standard error. The number of samples was approximately halved in 2009, with up to 20 samples per year for 2000–2008, but only 10–12 samples per year since that time. 95% Confidence intervals (95%) from Boyd et al. (1999) are shown for comparison, as are Canadian Water Quality Guidelines (CWQG) for hard water (CCME, 2008). As a note, the wet weather values reported by Boyd et al. (1999) are composite 24-h samples from automatic samplers that were activated at the onset of flood conditions. Though variable, water in the Don River tends to be hard, with a median value of ~300 mgL^{-1} as $CaCO_3$ (Beack Consultants Ltd., 1991), which indicates that the hard water CWQG is more suitable for assessing the risk of ecological impairment.

For Cu (Fig. 4b), most samples exceed the CWQG, with some high outliers exceeding it as much as 10-fold. Medians from the PWQMN data are frequently below the confidence intervals for dry weather given by Boyd et al. (1999), though outliers were of a similar magnitude to earlier wet weather flow. No temporal trend is evident in the data. For Pb (Fig. 4c) the median of PWQMN samples was significantly less than the CWQG in all years except 2009; however, 95% confidence intervals frequently exceeded the guideline. The median of PWQMN samples was also typically less than the dry weather confidence intervals given by Boyd et al. (1999) and, with the exception of one measurement in 2006, the earlier confidence intervals also encompass the statistical outliers (>95% CI) from the 2000–2014 sampling. Similar to the results for Cu, no significant temporal trend was observed. As a note, significant variability is expected in the Pb results due to the low precision of the analysis (the measurement error was reported as ≥11 μg L^{-1}for all tests by MOECC, 2015). For Zn (Fig. 4d), the sample medians were generally below the CWQG, although the standard error of the mean exceeded the guideline in 2014. Outliers were generally above the guideline, sometimes reaching as high as 150 μg L^{-1}. The medians were generally within the dry weather confidence intervals given by Boyd et al. (1999) and the outliers are close to the range reported for wet weather flows. As with the other metals, no significant temporal trends were found for the 2000 to 2014 period.

Fifteen minute flow data from the hydrometric gauge on the Lower Don for the period of 2000–2010 was used to assess the effect of flow on metal concentrations. The time derivative of the discharge (i.e. the flow acceleration) was also calculated to assess whether the flows were on the rising or falling limbs at the time of sampling. An arbitrary flow acceleration threshold of 1.0×10^{-4} m^3 s^{-2} was found to reliably classify the hydrograph limbs. The results confirm that all three metals are positively correlated with discharge (Fig. 5). The relationship is strongest for Zn, which has a coefficient of determination (R^2) of 0.64, and the weakest for Pb ($R^2 = 0.20$). The CWQGs are routinely exceeded for the Don, particularly in wet weather, though Cu is again notable because the guideline is exceeded at all discharges. The comparison with the sampling results of Boyd et al. (1999), indicate that the dry and wet weather concentrations have decreased over time for Pb but are relatively unchanged for the Cu and Zn. When classified by hydrograph limb, the concentrations for the rising limb frequently plot to the right of the concentrations for the falling limb, which would indicate that there is less metal on the rising limb. Such a result is unexpected based on the assumption that metals accumulate on the land surface during dry weather and then are flushed into the surface water channels during wet weather. However, only four points were measured on the rising limbs at $Q > 10$ m^3 s^{-1} between 2000 and 2010, and no statistical comparison of the rising and falling limbs was attempted.

Sampled sediment metal concentrations

The dredged sediment in and near Keating Channel provides the best available record of the temporal trends of metal concentration in sediment (Fig. 6). The record is most accurate for the late 1980s and into the early 1990s when the number of samples exceeded 35 per year (Fig. 6a). After 1993, the number of samples decreased and in some cases (2004 and 2010), no samples were collected. Samples of Cu were not available until 1991 (Fig. 6a). The median concentration for Cu exceeded the LEL at this time, but few samples exceeded the SEL. No significant temporal trends are apparent in the Cu

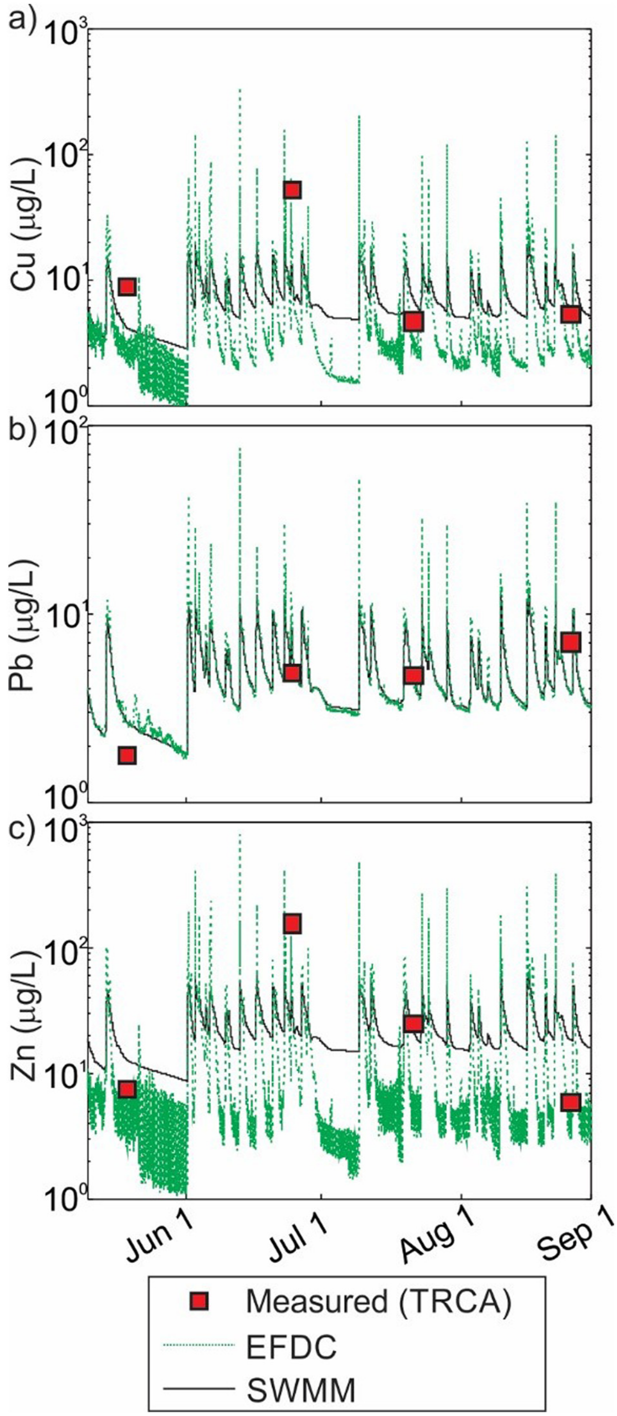

Fig. 9. Comparison between measured and modelled results at the Todmorden monitoring station through the summer months of 2010 for: a) copper; b) lead; and c) zinc.

concentrations, although a number of samples exceeding the SEL is apparent between 2000 and 2008. A significant decrease in Pb concentrations occurred between 1987 and 1993. During this period, the sample medians exceeded the LEL and many Pb samples exceeded the SEL in the dredged sediment (Fig. 6b). The most extreme sample was approximately 5 times the SEL, indicating that the sediment quality was very poor during this period. After 1993 it appears that metal concentrations have continued to decrease, albeit at a lower rate than before, but all samples have been close to the LEL since 2010. However, over 50 samples were taken in the year 2008, making it the best single year to assess changes, and a comparison with 1992 shows no significant difference for any of the metals. Samples taken as part of the current study in 2014 were at or slightly lower than the TRCA results and were close to the LEL for the three metals.

Table 7
Sensitivity analysis for metal sorption coefficients using changes in median concentration for each metal. Scenario A represents variation in sorption coefficients of each metal associated with clay size class, scenario B for silt size class, and scenario C for sand size class. Scenario C shows highest sensitivity of sorption coefficient associated with Cu.

	Sorption coefficient (K_d) variation	Median concentration change (%)		
		Cu	Pb	Zn
Scenario A (clay)	20% increase	0.0%	−0.5%	−2.2%
	20% decrease	−0.3%	0.3%	2.4%
Scenario B (silt)	20% increase	0.3%	−0.5%	−1.7%
	20% decrease	−0.6%	0.3%	1.7%
Scenario C (sand)	20% increase	−10.6%	−3.6%	−7.4%
	20% decrease	12.9%	0.5%	8.9%

Analysis of the sediment samples taken from various locations in the Don River watershed in 2014 show that Cu concentrations are elevated throughout the watershed but that Pb and Zn are generally low in comparison with the LEL (Fig. 7). For Cu the total concentrations were above the LEL in 17 of the sediment samples and included all subwatersheds, with the possible exception of the Upper West Don River. The OSSP (2008) results offer some temporal information and indicate that Cu concentrations are increasing in the Upper East Don River and German Mills Creek. The highest concentrations of Pb and Zn are found in the Lower Don and Taylor Massey Creek, but most samples showed that concentrations of these metals were less than half of the respective LEL concentrations. A temporal comparison with the OSSP (2008) data shows that metal concentrations may be decreasing in the East Don and the Lower Don River, which fits with the temporal trends observed in the Keating Channel (Fig. 6).

Modelled results

The range of total suspended solids (TSS) concentration is better captured in the EFDC model than the SWMM model (Fig. 8). The PCSWMM results have lower peak concentrations than the observed data, while the base flow concentrations over-estimate the measured values. In contrast, the observed TSS peak of ~800 mg L^{-1} during a storm event on June 26 was reasonably captured by the EFDC model, and the baseflow concentrations for the other samples were more accurately represented. Largely as a result of the improved sensitivity of TSS, metals concentrations were also more sensitive to flow in EFDC (Fig. 9). The peak concentrations of Cu and Zn, for instance, were underestimated with the SWMM model during the storm and overestimated during base flow conditions (Fig. 9a, c). Pb concentrations are somewhat different than the other metals as the concentration did not go up appreciably during the June storm in the sampled data (Fig. 9b). As a result, the peak appears to be overestimated with the EFDC model. This result is consistent with the low correlation between discharge and Pb concentration that was found for the sampling period (Fig. 5b) and suggests that Pb does not follow the same model of build-up and flushing off of land-surfaces (primarily roads) that the other metals do. Calibrated sorption partition coefficients (K_d) for the three metals are shown in Table 6.

A sensitivity check was carried out for each of the calibrated K_d values against each sediment size class (Table 7). Three scenarios were established for testing based on size class with scenarios A, B, and C testing the sensitivity of the overall results to K_d values for clay, silt, and sand particles, respectively. Each scenario represents a 20% variation in the K_d value for each metal. As shown, Cu is most sensitive to the K_d value for sand particles (scenario C). Zn also shows relatively higher variations in median concentration for each of the scenarios. Based on this analysis, it appears that Cu and Zn concentrations are

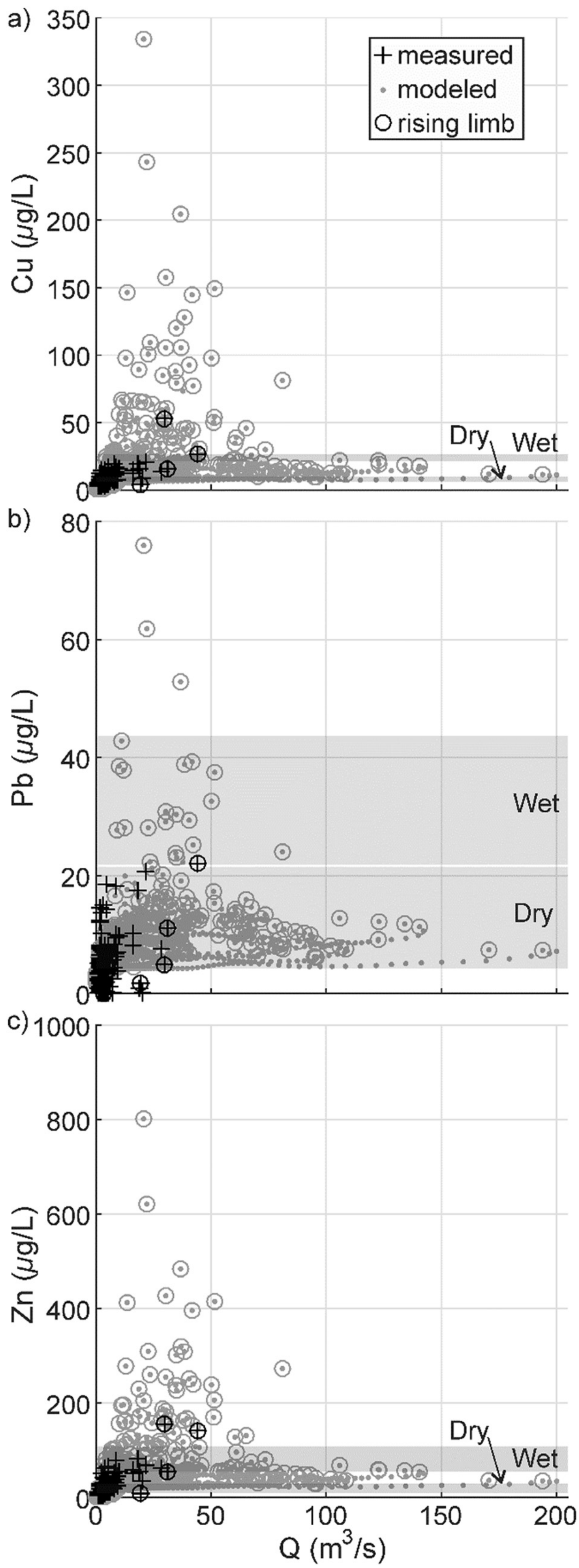

Fig. 10. Comparison of discharge and metal concentration for a) copper, b) lead, and c) zinc at Todmorden site for measured and modelled results. Shaded areas represent 95% confidence intervals for dry and wet weather concentrations from sampling in 1991 (Boyd et al., 1999).

sensitive to the sand calibration parameters, likely due to the high proportion of sand in the system.

Despite the years of sampling for the PWQMN, floods are underrepresented in the existing database. Plotted versus discharge and the modelled data from the summer of 2010, all of the measured concentration data between 2000 and 2010 tend to cluster on the lower left where flow rates and concentrations are low. The highest flows during sampling are all at $Q < 50\ m^3\ s^{-1}$, which is one quarter of the range in the summer of 2010. Measured concentrations are relatively low, but it is not clear whether this reflects the conditions of the water or simply a product of the sampling strategy. Sampling from 1985 was used to establish wet weather flow concentrations based on 24 h composite samples (Boyd and Jaagumagi, 2001), but these values are not suitable for comparison with models that simulate build-up and wash-off. Within storm sampling is particularly limited on the rising limb of the floods. Only four measurements on hydrograph rising limbs were made between 2000 and 2010, and these events tend to plot to the right of the other flow measurements, meaning that the metal concentrations were not particularly high. However, the modelled results suggest that the rising limb concentrations can be much higher. For the highest floods, the pattern of concentrations was to rise quickly along with the rising limb, peaking somewhere between $Q = 0–50\ m^3\ s^{-1}$, and then decaying exponentially towards the discharge peaks, whereupon the modelled concentrations are indistinguishable from the dry weather concentrations. On the falling limb of the floods, concentrations are essentially insensitive to discharge. This pattern is a product of the modelling strategy of build-up and wash off, with the largest floods resulting in a flushing of metals from most of the basin and so leading to peaks in concentration.

The spatial distributions of the metal concentrations in the sediment bed at the end of the summer 2010 modelling period are shown using a conceptual depiction of the Lower Don River in Fig. 11. Metal concentrations are relatively higher in the sediment bed at two locations that appear to be deposition "hot spots". These locations are in the kilometer upstream of the mouth of the study reach where it enters into the Keating Channel and upstream of the Todmorden monitoring site where flow is restricted by a low flow weir and two railway crossings (Fig. 3). The LEL is exceeded for Cu in both of these zones (Fig. 11a) and in Zn for the upstream zone (Fig. 11c). The LEL for Pb is not exceeded anywhere in the Lower Don according to these simulations. The Keating Channel and the area upstream is known as a hotspot based on the dredging requirements in the area, which is one of the motivations for the proposed modification of the Don River estuary (Waterfront Toronto, 2016). The other deposition hotspot is interesting because it is located upstream of the stream gauging and main water quality sampling location (Fig. 3). In this location it is thought that the flow restrictions due to the weir and the bridges are resulting in the deposition of contaminated sediments. The accumulation of metals in this area could be critical for understanding the within flood variability that has been measured at the downstream gauge.

Discussion

The current study shows that metals pollution in the Don River in Toronto, Canada is improving in some respects while remaining flat or even getting worse for some components. Pb in particular seems to be a success story whereby sediments were highly polluted in the late 1980s and early 1990s, but more recently dredged sediment in the Keating Channel shows that the channel has progressively been cleaned up to the point where Pb concentrations most samples are now at or below the LEL for invertebrates (Fig. 6b). Water concentrations are typically below the CWQG (Fig. 4) and are relatively insensitive to flooding (Fig. 5b), which indicates that the sources of Pb in the catchment are not strongly correlated with overland flow. Clearly, the policy measures that required Pb to be removed from gasoline production (Macdonald et al., 2000) are having a positive impact, and the overall picture is one of

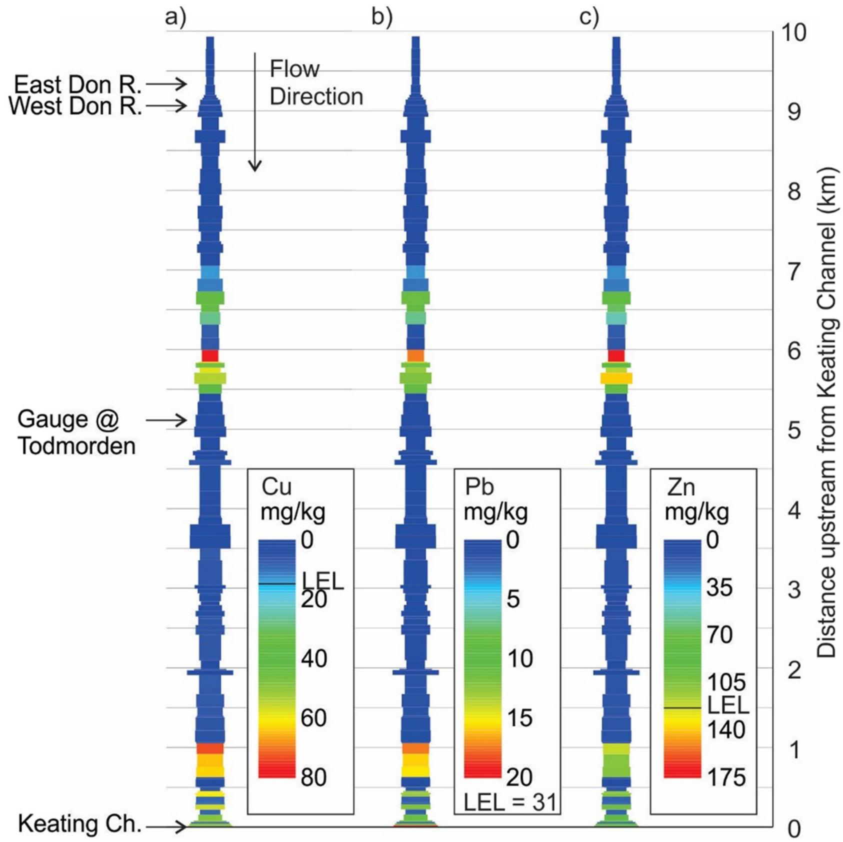

Fig. 11. Spatial distribution of modelled metal concentration in the bed of the Lower Don R. at the end of the simulation (Aug 31, 2010) for a) copper, b) lead, and c) zinc.

gradual flushing and physical removal of this pollutant out of the system. The story for Zn similarly shows a reduced concentration in sediment, though the reduction is less significant than for Pb and sample medians remain above LEL thresholds (Fig. 6c), and the concentrations in most water samples are below the CWQG (Fig. 4c). Of the three metals, however, Zn has the highest correlation with flow (Fig. 5c), which indicates that it is being added to the system from overland flow or through resuspension within channels. The hypothesis of overland flow seems reasonable given that Zn is actively used in car tires (Councell et al., 2004) and brakepads (Lough et al., 2005). Of the three studied metals, Cu most clearly remains a problem. Concentrations in sediment samples at the mouth of the river sometimes exhibit severe impairment levels (Fig. 6a), meaning that this single pollutant will affect most of the invertebrate community; and median concentrations in the water typically exceed the CWQ guidelines (Fig. 4a). The distribution of the metal in all of the main channels (Fig. 7a) means that the problem is widespread in the watershed, and the comparison with the OGGS data indicates that the problem has become worse over the last decade in the upper watershed. Development has been the most recent in the upper watershed, which indicates that Cu is being added to the system as a result of urbanization, likely because of flow off roads and parking lots where Cu is known to accumulate due to its use in car brakepads (Lough et al., 2005).

The sample data were used to develop a simulation approach for instream metal dynamics. The STEMS tool allows uses of SWMM, a hydrologic model that is well adapted for urban watersheds, to access EFDC, a much more representative hydraulic model of river flow. Using the same boundary conditions as the SWMM model, which simulates baseflow TSS concentrations of ~55 mg L^{-1}, the EFDC model resulted in baseflow concentrations of only ~4 mg L^{-1} (Fig. 8), which are much more in line with sampled field data. During floods, the observed peak concentration value of TSS (~800 mg L^{-1}) could not be captured with the SWMM model, even after calibration of the build-up and wash-off parameters, but were well represented with EFDC. In EFDC, overland runoff during floods is supplemented by the resuspension of previously deposited sediment and adsorbed metals. Diffusion processes between sediment bed and water column interface are also represented in EFDC, which allows a more physically representative model of the relevant processes. The STEMS tool allows a user to transition between the hydrologic and hydraulic routing at a location of their choosing. In steep upland catchments, for instance, it may not be necessary to simulate instream processes of smaller sediments because they are

Table 8
Comparison of Cu, Pb and Zn loadings of the Don river, normalized by area, between different sampling years. Loadings of the Seine are also given as a parallel.

Location	Measured/modelled	Description	Years	Metal load ($kg \cdot km^{-2} \cdot yr^{-1}$)			Reference
				Cu	Pb	Zn	
Seine River	Measured	Total reservoir retention		26	14	15	Thévenot et al., 2007
Seine River	Measured	Floodplain		46	61	108	Thévenot et al., 2007
Don River	Measured	Suspended particulate matter	1985	1.8–2	2.4–4.9	4–5.9	Boyd, 1988
Don River	Measured	Suspended particulate matter	1992	4.5	7.8	12.8	Boyd and Jaagumagi, 2001
Don River	Modelled	Suspended particulate matter	2010	5.0	3.2	14.2	This study

likely to wash through to the lower reaches. In the lower reaches like the lower Don River, however, the sediments and metals are likely to spend much longer times in the channel, making it important to more accurately represent processes of deposition, sorption and diffusion.

The main challenge with the simulation of metal dynamics is that the current sampling strategies are poorly adapted to parameterize the process level equations. The build-up and wash-off parameters, the co-fraction method for linking metals with TSS, and the sediment size parameters used in EFDC are all uncertain. Data for calibration are extremely limited, with only four samples on the rising limb of floods over 10 years of record (Fig. 5), four samples over the fourth month simulation period in 2010 (Fig. 9), and no samples with Q > 50 $m^3\ s^{-1}$, which is approximately one-third of the 2 year return period flow of 142 $m^3\ s^{-1}$ (TRCA, 2009a). Plotted against modelled flows for the summer of 2010 (Fig. 10), it is apparent that the sampling strategy has captured few of either the potentially high concentrations on the rising limb or the highest flow events. Sediment transport in flashy urban rivers is intermittent, meaning that most of the transport will occur in a relatively short period of time. Metals associated with sediment are likely to be transported in short bursts, both as they are flushed off of land surfaces and re-suspended in the stream. Targeted monitoring programs are needed to accurately capture and model such dynamics in an urban river system.

To calculate areal loading rates to Lake Ontario and compare with previous results and other watersheds, total suspended sediment and metal loadings were integrated for the model simulation period at the mouth of the river. The total exported suspended sediment load was estimated to be 29.4 t $km^{-2}\ yr^{-1}$, with metal loads of 5.0, 3.2, and 14.2 kg $km^{-2}\ yr^{-1}$ for Cu, Pb and Zn, respectively (Table 8). As a comparison, the Seine possesses average river suspended particulate matter of 10.8 t $km^{-2}\ yr^{-1}$ (Meybeck et al., 2007), or one third of the Don River export, with higher metal loads thought to be the legacy of significant sources of metals pollution buried in the floodplain (Table 8). Data from other systems around the world would help to put these results in context, but information in other urban catchments is rare. A comparison with earlier estimates for the Don River indicate that Cu and Zn are higher while Pb is lower than in previous decades, which supports the idea that the policy change to remove Pb from gasoline is having a positive effect, while the expansion of the urban area has continued to exacerbate problems as a result of high Cu and Zn concentrations in the water and sediment.

Conclusions

The Don River watershed faces significant environmental challenges due to urbanization and the associated flooding, erosion, and degradation of water quality. This research, focused on the metal dynamics in the lower Don River supports the following conclusions:

1. Lead pollution in the Don River is less of a problem than it was in past decades. Policy changes and sediment dredging in the mouth of the river have reduced lead concentrations in the water and sediment to the point where they no longer exceed recommended guidelines except occasionally during floods;
2. Zinc and copper pollution are increasingly a problem in the Don River, with copper in particular exceeding recommended lower guidelines throughout the watershed and severe effect guidelines during floods and at hotspots within the watershed.
3. The STEMS tool successfully integrates the EFDC hydrodynamic model with the SWMM hydrologic model. STEMS provides an efficient setup process for the EFDC model based on the results of the SWMM model and can be applied on any river network where a SWMM model is available. This approach is recommended to take advantage of the more accurate representation of instream hydraulic and chemical processes in EFDC.
4. Most of the sediment and metals are transported in relatively shorter bursts within longer flood durations and are stored in depositional hotspots in the lower river. High frequency surface water quality monitoring and modelling of sediment and metals transport is needed to understand and more accurately parametrize these processes in an urban river system.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jglr.2018.08.010.

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