Metal loads in an urban stream catchment (Don River, Ontario)

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

The Don River watershed has been called the most urbanized watershed in Canada. Trace metals are common contaminants in urban areas that may threaten ecosystems at high concentrations. Major urban sources of trace metal include stormwater and wastewater discharges, buried landfills, and automobile combustion. Establishing geochemical baselines for urban contaminants supports environmental assessments and improved management practices. This study focuses on copper, lead, and zinc concentrations in surface water and sediment samples within the Don River. Data collected by multiple agencies are synthesized and complemented with new measurements, including sequential extractions of sediments. Spatial and temporal trends are analyzed to identify enrichment areas and improvements or shortcomings in current monitoring efforts.

Samples collected in this study from the Don River include 22 water and sediment grab samples and two sediment cores. Unfiltered surface water, sediment, and sediment core material (sliced in 1cm intervals) were microwave digested with aqua regia and analyzed by ICP-OES for total copper, lead, and zinc concentrations. Thirteen of the sediment grab samples were also used for sequential extraction by the Tessier (1979) method before analysis by ICP-OES. Monitoring data were provided by the Ministry of Environment (MOE), Environment Canada, Toronto and Region Conservation Authority (TRCA), and the Ontario Geological Survey (OGS).

Water monitoring data show exceedances of provincial guideline levels for all three metals. The highest concentrations are found in the Lower Don River, Lower East River, and Taylor Massey Creek. This is expected as the downstream portion of the watershed is the most urbanized. The trace metals are strongly associated with suspended solids and increase in the river system after rain events. Without the contribution of runoffs, suspended solid concentrations are low and trace metals are near or below detection. Trace metals in bottom sediments show similar spatial trends as surface water. Particularly high concentrations are found in areas with lower discharge rates.

Long-term monitoring data for the Lower Don suggest unchanged copper and zinc concentrations from 2000 to 2012. Sediment samples exhibit the highest concentrations of the three metals within the Lower Don and Taylor Massey Creek. However, the sediment samples only exceed the Lowest Effects Level (LEL) for copper. The annually dredged sediments near the river mouth provides an

accurate measure of temporal trends: they show a decrease in total copper concentrations while lead concentrations have stabilized, and zinc concentrations increased. Sequential extractions show that copper concentration preferentially sorb to organic matter, while lead and zinc are preferentially associated with oxides. The exchangeable fractions of the three trace metals are highest in the upper watershed.

Acknowledgements

Dedication

For Vince.

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Chapter 1
Introduction

1.1 Background

Urbanization is a major land use change that is likely to rapidly continue with the increase in population. In Canada, the population growth from 2000 to 2100 is projected to almost double according to the United Nations (UN Population Division, 2011). With an increase in worldwide population, there is added pressure for the use of resources as well as for waste disposal. In 2030, the urban population is expected to grow to 4.9 billion while the rural population decreases by 28 million (Lahariya, 2008). As the world's population increasingly shifts to urban settings, the understanding of important biogeochemical processes in urban systems becomes more necessary to establish baseline data as different stressors are added to the system. These processes on urban environments are a global issue.

Trace metals that are often enriched in urban areas include copper, lead, and zinc and are chosen as the focus for this study. While all three metals have natural sources in the environment, their anthropogenic sources in urban areas make up the majority of the concentrations found in water and sediment. Copper uses include household water pipes, metal alloys, wiring, insecticides and fungicides. Due to copper's conductive properties, it is also commonly found in electronics (Duncan Boyd, Todd, & Jaagumagi, 2001; Bradl, 2005). Lead was heavily used in fuel additives and in paints but was mostly phased out of these products in the 90s (Bradl, 2005). Zinc is commonly used for metal galvanizing and plating as well as in dyes and paints and commonly released in automobile tire ware (Boyd et al., 2001; Bradl, 2005). All three metals are emitted as automobile combustion products, which is especially prevalent in urban centers. Other major sources in urban areas include wastewater treatment plants, industrial emissions, runoffs, and leachates. It is estimated that global atmospheric emissions of Cu, Pb, and Zn increased from the 1850s to mid-1990s by 20 370 tonnes/year, 252 350 tonnes/year, and 121 880 tonnes/year respectively (Nriagu, 1996; Pacyna & Pacyna, 2001).

The Don River Watershed has an area of 358 km^2 with a population of 1.2 million, making it the most densely populated and urbanized watershed in Canada (TRCA, 2007). The area incorporates portions of Downtown Toronto, Thornhill, Vaughan, Markham and Richmond Hill shown in Figure 1. The watershed can also be broken up into seven subwatersheds; the Upper West Don, Upper East Don, German Mills, Lower West Don, Lower East Don, Taylor Massey Creek, and the Lower Don subwatershed as shown in

Figure A1. The main river is composed of two branches (Don East and Don West) that start at the Oak Ridges Moraine and flows southward to converge into a 5th order stream before further flowing southward and draining into Lake Ontario. The river flows from the Oak Ridges Moraine approximately 35 km before reaching the mouth with a mean discharge of 125 million m^3/year (TRCA, 2009b).
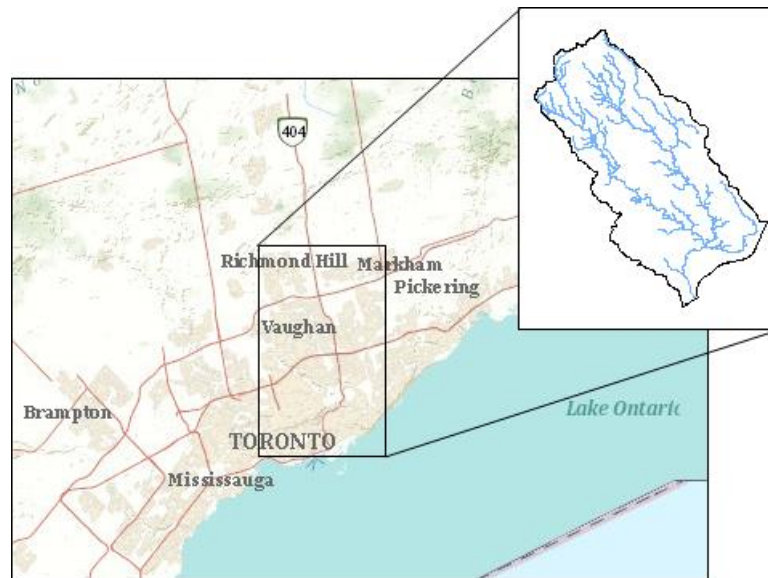
Figure 1 Location of the Don River watershed in Southern Ontario

The Don River Watershed has gone through drastic changes in landscape and land use over the last two centuries. The drainage area remained pristine up until the mid-19th century when intense urbanization and industrialization began (Palassio, 2008). Runoff and effluents resulted in the deposition of large silt quantities that severely polluted the river downstream (Desfor & Keil, 2000). By the end of the 19th century, the last 3 km of the river were so polluted that plans to widen, deepen, and dredge this section developed (Desfor & Keil, 2000). The watershed continued to change with its influx of people through the reduction of wetlands, burying of tributaries, and increase in paved surfaces (Desfor & Keil, 2000). The contamination of the river was at its worse by the 1950s and rehabilitation efforts of the Don started by 1970 (Palassio, 2008). Comparison of land use within the watershed from 1966 to 2002 can be seen in Figure 2.
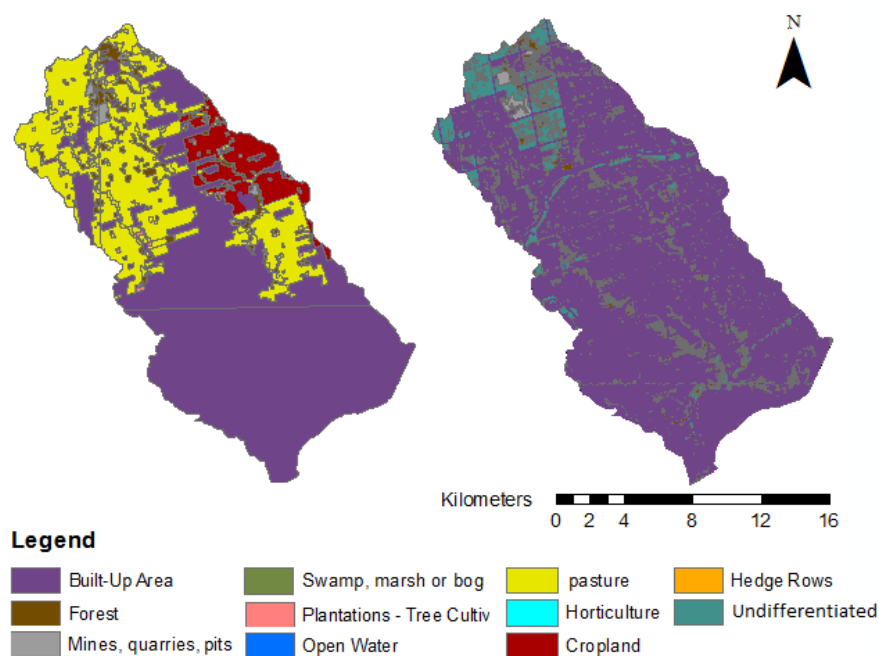
Figure 2 Land use map of the Don River watershed 1966 (left) to 2002 (right) showing the increase of Built-up Area from 58% to 80% over 36 years. Data based on Southern Ontario Land use Resource Information System and mapped using ArcMap 10.1

The Don River was listed as an area of concern by the International Joint Commission in their 1985 report and considered the main contributor of metal pollutants into the Toronto Harbour (Nriagu, Wong, & Snodgrass, 1983). The highly urbanized watershed experiences extremely flashy hydrology characterized by flooding and large inputs of suspended solids into the system. The majority of trace elements are transported through rivers in association with suspended solids (Meybeck et al., 2007; Walling et al., 2003). Bodo (1989) found that large rainfall resulted in an increase to baseflow of up to four times, bringing in large amounts of trace metal contaminants. A 1985 study found that the spring flux of suspended solid into Lake Ontario was in the range of 2500 – 5562 kg/day with 1.8 – 2 kg/day of copper, 2.4 – 4.8 kg/day of lead, and 4 – 5.8 kg/day of zinc (Boyd, 1988). Studies done in the 1990s estimated that the total annual loading of copper, lead, and zinc in all forms from the Don River into the Toronto Harbor were 1.6×10^3 kg, 2.8×10^3 kg, and 4.6×10^3 kg respectively (Boyd et al., 2001).

Surface water monitoring of the Don River has been conducted by agencies, including the Provincial Water Quality Monitoring Network (PWQMN), Environment Canada, and most recently the Toronto and Regional Conservation Authority (TRCA). Prior to the formation of the TRCA, the data sets were

incomplete, used different analytical methods, and were often unshared between agencies (Moore, Normand, Smith, Vandenberg, & Tam, 2008). The TRCA started monitoring the surface water in 2002 using their own monitoring stations along with the provincial monitoring station as shown in Figure 5. The monitoring is the most recent and consistent data available but still likely misrepresent metal concentrations due to their limited sampling coverage and frequency.

Don River sediment quality is generally unmonitored throughout the watershed. The most recent analysis for total trace metals was conducted by the Ontario Geological Survey (OGS) in 2008 using one sample at several locations. The only other total metal data in sediment collected consist of the analysis of the yearly dredged sediment at the mouth of the Don River from the TRCA. The only fractionation study in the area was done by Warren and Zimmerman (1994) who examined trace metal partitioning in suspended particulate matter at four locations within the Don River. The Tessier (1979) method was used to quantify the metal concentrations in the sediment in the following fractions; leachable, reducible, oxidizable, and residual. There is very limited data examining the Don River sediment for copper, lead, and zinc.

The purpose of this thesis was to investigate the concentrations and speciation of copper, lead, and zinc in surface water and sediment within the Don River. My own data were complemented by datasets provided by various agencies. There have been few and limited past studied conducted in the area despite the drastic changes within the watershed. This study adds to the existing data and knowledge on trace metal concentrations in the Don River. The objectives of this thesis are as follows:

1. Consolidate existing monitoring data in the Don River;

2. Identify spatial and temporal trends for Cu, Pb, Zn concentrations in the water and sediment of the Don River;

3. Investigate the Cu, Pb and Zn geochemical associations in the Don River sediments.

The testable hypotheses proposed from the objectives are that trace metal concentrations are higher in the southern, more urbanized portion of the watershed compared to the northern headwaters in surface water and sediment; growing population density has increased Cu, Pb, and Zn concentrations in surface water and sediment from 2000 – 2014; and Cu is predominantly associated with organics while Pb and Zn are predominantly associated with oxides in the watershed.

Chapter 2
Metal sources in the Don

Copper, lead, and zinc concentrations naturally occur in the environment in rocks and soil. Metals are naturally found in the earth's crust and can surface as igneous rocks. These forms can change and be distributed through sedimentary and metamorphic processes. The environmental conditions that occur at the time of these processes dictate the form they take in different rock and soil types. The bedrock within the Don River watershed is largely made up of shale and limestone that likely represent the largest natural source for the trace metals. The average content of shale is estimated to be 35 ppm Cu, 20 ppm Pb, and 97 ppm Zn (Bradl, 2005). The average content of limestone in turn is estimated to have concentrations of 6 ppm Cu, 9 ppm Pb, and 20 ppm of Zn (Bradl, 2005). While shale and limestone are likely large natural sources, the concentrations released highly depend on erosional processes. The average dissolved concentration found in freshwater stream samples is reported as 7 ppb Cu, 1 ppb Pb, and 20 ppb Zn (Bradl, 2005). These values reflect dissolved metal concentrations in water samples filtered by 45μm pore size filters, while the majority of metal concentrations in river systems are sorbed to suspended particulate matter and surface sediment. The partitioning of the dissolved concentration on solid surfaces in the Don River is likely influenced by temperature, redox potential, sorption processes, suspended matter and bottom sediments type, cation exchange, and organisms (Bradl, 2005).

2.1 Stormwater and sewage flow

Urban watersheds such as the Don have large impervious surface areas. Heavy metals sorbed to particulates settle on these surfaces and get flushed into waterways during rain events through the storm drainage system. Separate storm sewers (SS) and sanitary drainage systems are used in most of the watershed except in older Toronto areas that still use Combined Sewage Outflows (CSO). CSOs collect both the sanitary sewage and the stormwater runoff in the same pipes to be treated in pollution control plants and then discharged into the river. The Don trunk sewershed has an area of 191 km^2, 10% is used for combined sewer area serving 739 583 people (MMM Group Limited, 2012). The Don River has approximately 30 CSO and 872 SS outfalls (Duncan Boyd et al., 2001). The CSOs and SSs contribute large quantities of suspended solids and trace metals that discharge into the river and eventually flush out to Toronto Harbour.

The North Toronto wastewater treatment plant (NTTP) located at Pottery Road along the Don River was commissioned in 1929. The plant serves approximately 55 000 people and discharges effluent continuously into the river at about 0.41 m^3/s (Bodo, 1989). The discharge from the treatment plant makes up 8-10% of the mean annual flow but 25-50% of the summer baseflow measured in the lower Don (Bodo, 1989). The area of the sewershed that serves the NTTP is 31 km^2 and 70% uses CSOs (MMM Group Limited, 2012). Waste flow bypassing the NTTP is diverted outside the Don River watershed to the much larger Ashbridges Bay Treatment Plant. The inflow rate for the NTTP is 0.4 - 0.5 m^3/s but during large runoff events the CSO can reach its storage tank volume of 5 800 m^3 and discharges directly into the river (Bodo, 1989; MMM Group Limited, 2012). Based on NTTP annual reports from 2007 - 2013, there was an average of 13 overflow events a year. The plant discharges about 34 ML a day with an average suspended solid concentration of 6.8 mg/L. The average dissolved trace metal concentration was 18.43 ppb Cu, 14.8 ppb Pb, and 50.6 ppb Zn (City of Toronto, 2008, 2009, 2010, 2011, 2012, 2013).

2.2 Landfills

Groundwater contaminants are not well known because of the lack of provincial groundwater monitoring stations within the watershed. Based on MOE data of former landfills, there are about 50 closed landfills identified within the watershed shown in Figure A8. Contaminants from landfill leachates have the potential to travel with groundwater flows and either discharge into surface water rivers, or directly into Lake Ontario. Most of the landfills identified were small (below 0.1 km^2 and less than 25 m deep) and active from 1940s to 1970s (Howard & Livingstone, 2001). These sites contained domestic waste, incinerator ashes, construction debris, and occasionally liquid waste but quantities are unknown because landfills were unregulated until 1971 (Howard & Livingstone, 2001).

The largest landfill within the watershed was Keele Valley, located in the Upper West subwatershed. The landfill was built in 1982 and was the last to shut down in 2002. Using data from Keele Valley, the quantity of waste in the unregulated sites could be predicted. Without taking into account degradation or precipitation effects, the estimated total mass of potential leachable waste was 1.8 x 10^{10} kg (Howard & Livingstone, 2001). Data from 11 monitored landfills near the watershed were used to estimate contaminant concentrations in the leachate. The mean concentrations were 0.045 ppm Cu, 0.068 ppm Pb, and 1.41 ppm Zn (Howard, Eyles, & Livingstone, 1996).

Howard and Livingstone (1994) use the groundwater flow model FLOWPATH to determine the travel time and potential reach of contaminants. Their findings showed that chemically conservative contaminants released a few kilometers away from the Don River would discharge within 50 years and those released in more central locations would be released in several hundred years (Howard et al., 1996). The leachates have likely already begun entering Lake Ontario each year and may still be a contributing source as the majority of sites were estimated to start releasing within 10 years.

2.3 Automobiles

The watershed contains a large area of paved roads and highways that see hundreds of thousands of cars go through every day. The average road density within the Don River watershed is 9.4 km/km^2 (TRCA, 2011). Major highways that go through the watershed include the 400, 401, 404, 407, 427 and the Don Valley Parkway (DVP) (TRCA, 2007). The 400 and 404 go through the Oak Ridges Moraine which is a recharge area for groundwater (TRCA, 2007). The Don Valley Parkway (DVP) runs through the watershed and often right next to the river itself. It is designed for a capacity of 60 000 vehicles per day but sections often carry close to 100 000 per day (Nazzal, Rosen, & Al-Rawabdeh, 2013). The average daily traffic in the downtown area was 70 000 cars in 2009 (City of Toronto Transportation services, 2010).

Vehicular emissions are a significant source of trace metals in the watershed. The metals that get emitted likely deposit onto the roads and eventually get washed into the waterway during rain events and either accumulate in sediment or get washed down with the river into Lake Ontario. A study conducted by Nazzal et al. (2013) examined the 400, 401, 404 and DVP for trace metals. The study used 42 samples in total and 14 samples on the DVP, the <2 μm fractions were digested using HNO_3, HF, and $HClO_4$ and analyzed with an atomic absorption spectrometer. In terms of the DVP they concluded that there was strong trace metal contamination with average concentrations of 154.1 ppm copper, 196 ppm lead, and 183.7 ppm zinc (Nazzal et al., 2013).

Both copper and zinc are still commonly added to petroleum products and released during combustion into the atmosphere. The concentrations released vary depending on the type of petroleum and the vehicle. The average concentration released with premium petroleum emits 19.2 ppb Cu, 13.5 ppb Pb, and 1.06 ppm Zn (Ozaki, Watanabe, & Kuno, 2004). Zinc is added to tires to aid in vulcanization and they contain 1.3 – 1.7% zinc that is released with tire wear (Ozaki et al., 2004). Lead was commonly added to fuels in the form of tetraethyl lead as an antiknock agent and released into the environment during

combustion. Due to concerns over the toxicity of the lead concentrations emitted, the Environmental Protection Agency (EPA) started to phased the lead out in the 1970s and eventually banned it entirely after 1995 (United States Environment, 2007). For this reason the lead concentrations in the area likely see the most drastic temporal change in concentrations. Globally, anthropogenic emissions are estimated to be 260 x 10^3 tonne/yr copper, 400 x 10^3 tonne/yr for lead, and 840 x 10^3 tonne/yr for zinc (Bradl, 2005).

Chapter 3
Materials and Methods

3.1 Sediment and water collection

River sediment and water samples were collected in April of 2014 at 22 locations in the Don River and its tributaries shown in Figure A9. Locations were chosen in an effort to sample at least two locations within each of the seven subwatersheds and dependent on areas with river accessibility. Sediment samples were taken from the top 10 cm of the river floor as close to the middle of a perpendicular transect to the river bed as possible. Water samples were taken in the same locations as the sediment samples. Shuttle core samples were taken in two locations within the Don River in May of 2013 (Pallud, Meile, Laverman, Abell, & Van Cappellen, 2007). One of the cores were taken as close to the mouth of the river as possible and the other one was taken near the head of the river. All samples were stored in acid washed 125ml polyethylene bottles and polypropylene bags.

3.2 Analysis

Samples were transported and refrigerated at $4^{\circ}C$ within 72 hours of collection. Water pH and conductivity were measured using a Thermo Scientific Orion Versa Star Advanced Electrochemistry meter. Water samples were agitated and pipetted into 45 mL portions and digested with an Anton Paar Multiwave 3000 microwave using the EPA method 3015A (microwave assisted acid digestion of aqueous samples and extracts). Water samples were digested in duplicate with MilliQ blanks and Buffalo River sediment certified reference material (SRM 8704) with every digestion cycle. Sample values reported were adjusted to the blank.

Sediment cores were first sliced into 1 cm intervals. Core sediment and sediment grab samples were prepared by initially air drying followed by freeze drying for 24 hours and homogenized using a mortar and pestle. Each sample was sieved to remove particles above 2 mm. Approximately 1g of each sediment sample was weighed and microwave digested with aqua regia (6 mL HCl and 3 mL HNO_3). Sediment grab samples were also separated into 1 g aliquots to be used for sequential extractions to determine the geochemical speciation of the metals in order to understand their availability. A modified Tessier (1979) method was used for the extraction using the steps shown in Appendix B. The Tessier (1979) method was chosen for comparability to previous sequential extractions conducted using suspended particulates within the Don River by Warren and Zimmerman (1994). All sediment microwave digestions and sequential

extractions were performed in triplicate with MilliQ blanks and SRM 8704 reference material with every digestion and extraction cycle. Sample values for all sediment concentrations were blank adjusted.

Water samples, sediment samples, core samples were filtered with 0.45 μm pore size Millipore filter paper directly after each digestion and sequential extraction. Samples were diluted and analyzed with an Inductively Coupled Plasma Optical Emission Spectrometry (Thermo iCAP 6200 Duo ICP-OES) for copper, lead, zinc, calcium, magnesium, and sodium. 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.

Using Thermogravimetric Analysis (TGA) approximately 100 mg of sediment was placed in platinum baskets and heated at 10°C/min up to 800°C and held until stable. This allowed the determination of the organic matter and carbonate content. Sediment grab samples also underwent Particle Size Analysis (PSA) using a Frittsch Analysette 22 wet dispersion unit in order to determine the proportion of the size ranges within the sediment.

3.3 Data sources

Total metal data were obtained through the Ministry of Environment Provincial Water Quality Monitoring Network (PWQMN). The data are freely available online and provide continuous stream data from 2000 to 2012. The PWQMN includes 400 sites in Ontario and only one site is currently located in the Don River watershed at the intersection to Pottery road (site 06008501402). Historical stream flow data were obtained from the Water Survey of Canada (WSC), operating through Environment Canada. The WSC operates over 2800 hydrometric gauges throughout Canada and three of them are located in the Don (02HC005 – West Don, 02HC024 – Lower Don, 02HC029 – East Don) shown in Figure A4. Additional stream monitoring data were obtained from the Toronto and Region Conservation Authority (TRCA) through their Regional Water Monitoring Network (RWMN) that includes 6 stations within the Don shown in Figure 5. The RWMN data reflect three years (2008 – 2010) of stream concentrations and flow gauging. Rain data within the watershed were obtained from Environment Canada weather stations. The stations chosen in Buttonville, Nork York, and East York were chosen to reflect the upper, middle, and lower sections of the watershed. Metal concentrations in sediment grab samples from the Don River were also obtained from the Ontario Geological Survey through the southern Ontario stream sediment project. The sediment was sampled in the winter of 2008 and several points were within the Don River watershed.

Geospatial data were available through multiple sources were provided by the University of Waterloo Geospatial library. The raster and vector data obtained were used in ArcMap 10.1 in order to create the maps included.

Chapter 4

Results

4.1 Water

The watershed has a calcium carbonate bedrock which makes the river a well buffered system. This causes the narrow pH range of the water samples of 7.7 – 8.2. The underlying geology of the area also contributes to the very hard water in the river. The water hardness was calculated with the concentration of calcium and magnesium and ranged from 277 mg/L to 579 mg/L. Hardness was calculated using the following equation:

Water Hardness (mg/L) = Ca(mg/L) x (MWt of Ca) + Mg(mg/L)*(MWt of Mg)
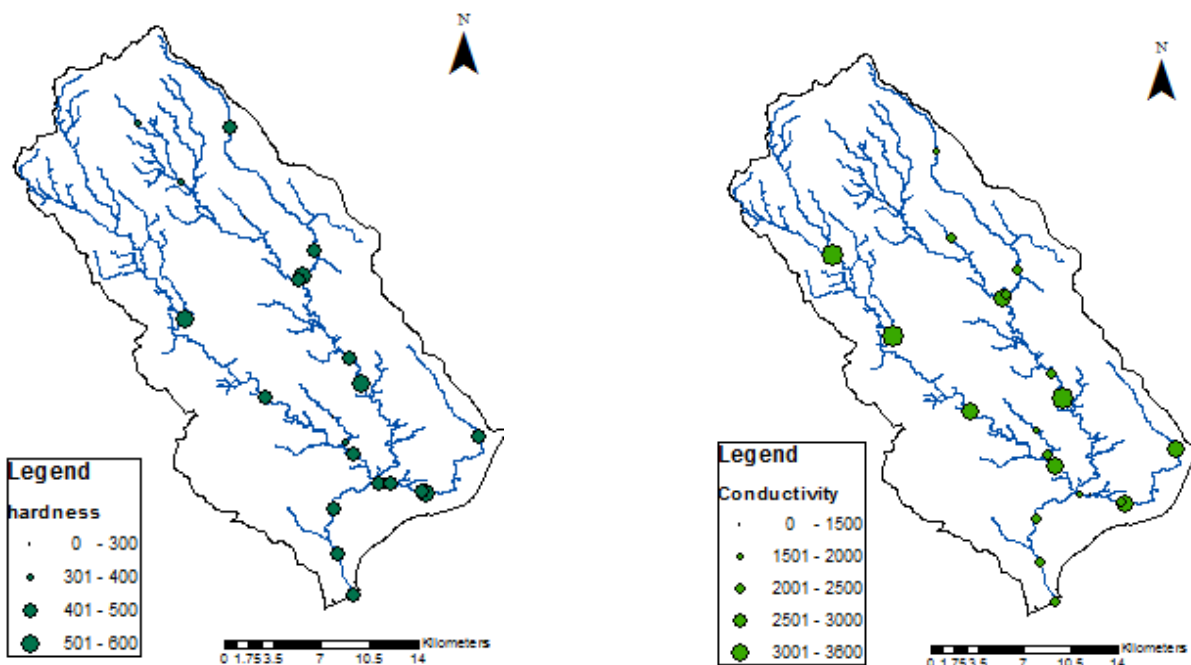
Figure 3 Water hardness (mg/L) and conductivity (µS/cm) measurements on the 23 water samples collected on April 18th and 26th 2014 in the Don River. Results mapped using ArcMap 10.1.

The limit of quantification is the lowest concentration that can be determined with 98% confidence and the limit of detection is the lowest concentration within the sample that can be detected but not quantified. Using the standard deviation of the blank to calculate the Limit of Detection (LOD) and Limit of Quantification (LOQ), the follow equation evaluated by Apostol et al. (2009) was used to calculate the values.

LOQ =(10 x SD)/gA

LOD =(3.3 x SD)/gA

The calculated LOD and LOQ for copper was 0.033 mg/L and 0.099 mg/L. The LOD and LOQ for lead was 0.030 mg/L and 0.092 mg/L and zinc was 0.0036 mg/L and 0.011 mg/L. The copper and lead concentrations in the water samples collected were below the limit of detection and their values were not included. The zinc concentrations in the digested water samples collected were plotted below in Figure 4 with values included in Table A3. Reference material (CRM 8704) was run with each microwave digestion and compared to the total certified values as well as values obtained from the aqua regia digestions from Chand & Prasad (2013) and Divrikli, Kartal, Soylak, & Elci (2007). The analysis of the reference material revealed an average recovery of 89% for lead and 79% for zinc compared to the certified total concentrations. Certified copper concentrations were not provided. The recovery compared to the average values obtained from the two studies also using aqua regia were 86% for copper, 94% for lead, and 82% for zinc.
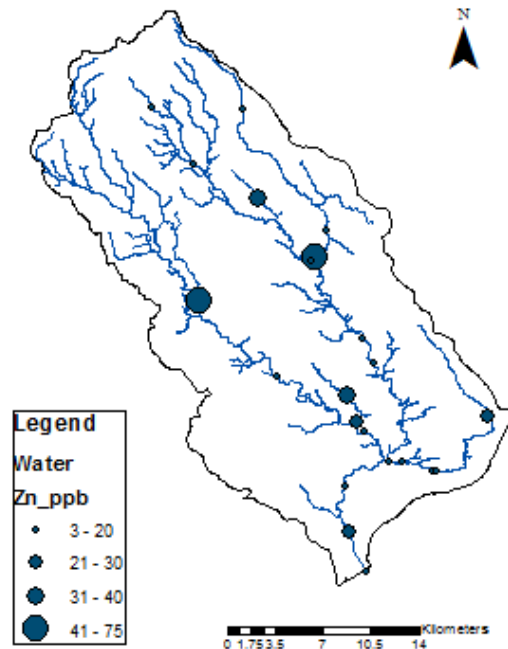
Figure 4 Zinc concentrations (ppb) of the 22 water samples collected on April 18th and 26th 2014 in the Don River using microwave assisted acid digestion and ICP-OES. Results show highest zinc concentrations in the midsection of the watershed. Mapped using ArcMap 10.1.

The Regional Watershed Monitoring Program (RWMP) provides long-term monitoring to watersheds in the Toronto region. There are currently six stations located in the Don River watershed (Figure 5) that monitor various aquatic parameters including stream water quality and quantity. The monitoring began in

2001 with partnership with various agencies in order to reduce the overlap of monitoring, reduce the number of data gaps, and establish a network for data sharing and reporting that could be used for informed environmental management decisions (Moore et al., 2008). The monitoring also compensates for the reduced provincial funding in the 90s that closed all but one Provincial Water Quality Monitoring Network (PWQMN) station in the Don River watershed that provided long term baseline data.
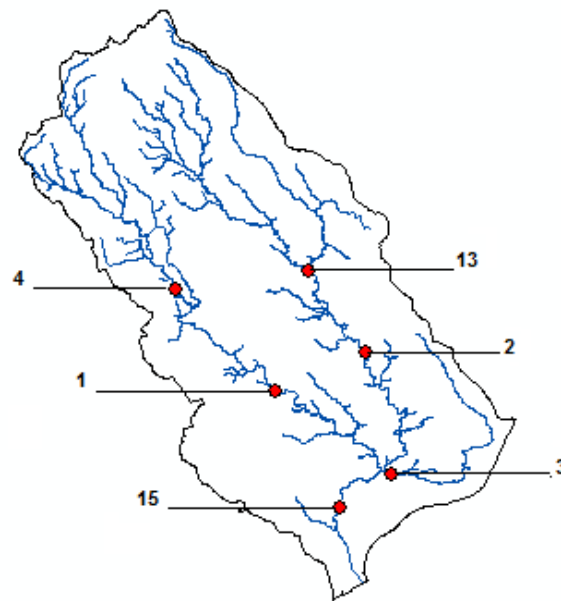
Figure 5 Regional Water Monitoring Program (RWMP) sites within the Don River Watershed. Results mapped using ArcMap 10.1.

The RWMP data provided by the TRCA include the monitoring done from 2008-2010 with unfiltered water sampling occurring approximately 1 – 2 times a month. The data are approximately 45 sampling points taken at all the stations on the same days. The range of copper, lead, and zinc concentrations are chosen as the focus and plotted in Figure 6. The sampling stations used by the RWMP also measure the daily discharge rate at each monitoring station that allow the analysis of the range of metal flux at each location (Figure 6).
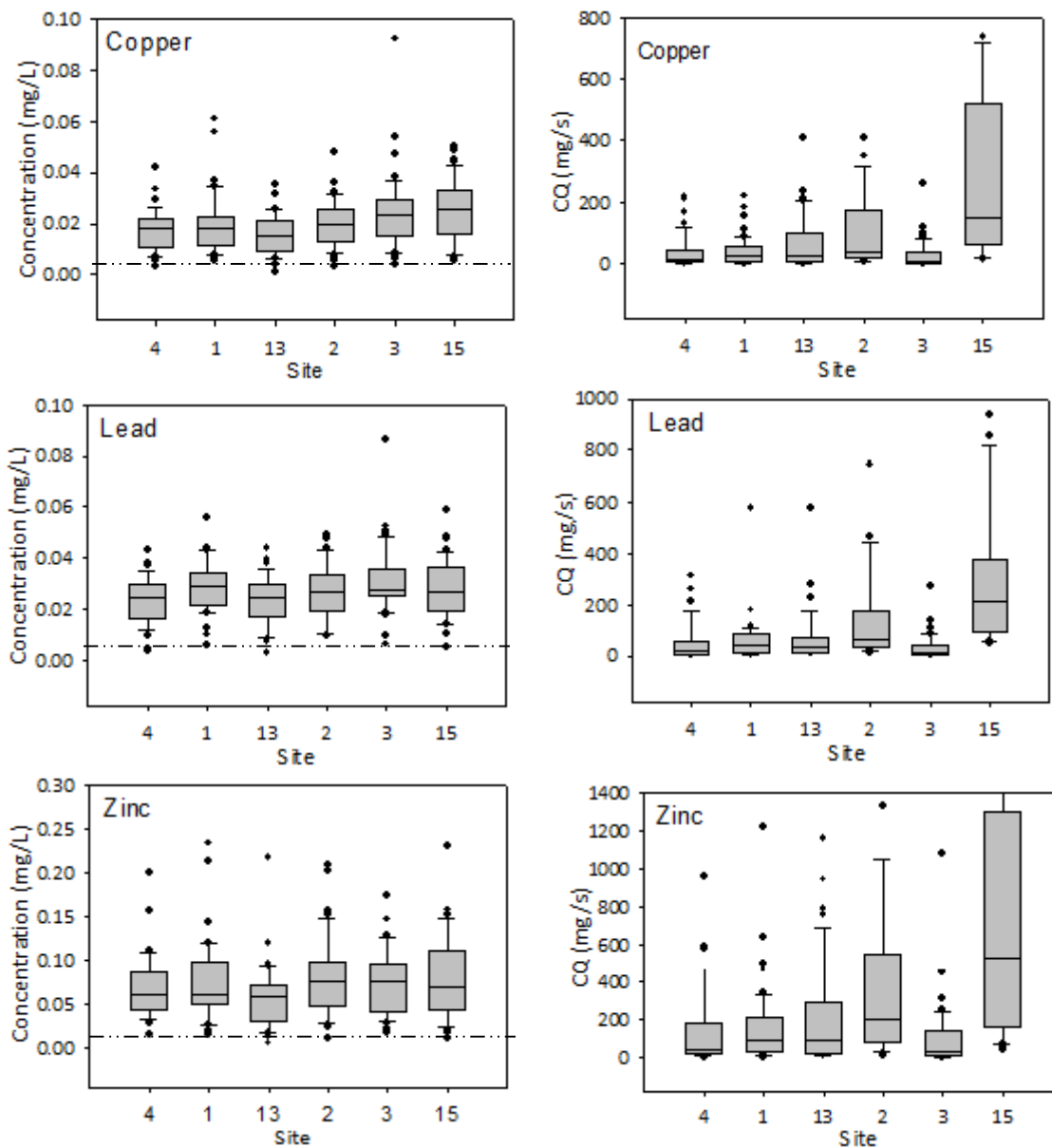
Figure 6 Copper, Lead, and Zinc concentrations (mg/L) and fluxes (mg/s) from 2008-2010 from the RWMP sites in the Don River. Boxplot data include 43 – 49 values at each site. The interquartile range of concentrations for each Cu, Pb, and Zn are above the Provincial Water Quality Objectives indicated by the dashed line (---). The highest concentrations of each metal appear to be in site 3 (Taylor Massey Creek) and site 15 (Lower Don River). The flux of metals is highest and most variable in site 15.

The Provincial Water Quality Monitoring Network (PWQMN) was created by the Ministry of Ontario in order to collect long term water quality data in Ontario. There are approximately 400 stations across

Ontario and currently one station located at Pottery Road along the Don River, the RWMP site 15 in Figure 5. The data represent samples that were collected at the site approximately 1 – 2 times a month from 2000 to 2012. Each year represents 9 – 20 sampling points. The water grab samples were unfiltered and analyzed for metals by ICP-OES using ultrasonic nebulization. Lead concentrations were below the limit of detection and omitted. Copper and zinc concentrations were plotted per year and shown in Figure 7 and Figure 8 respectively.
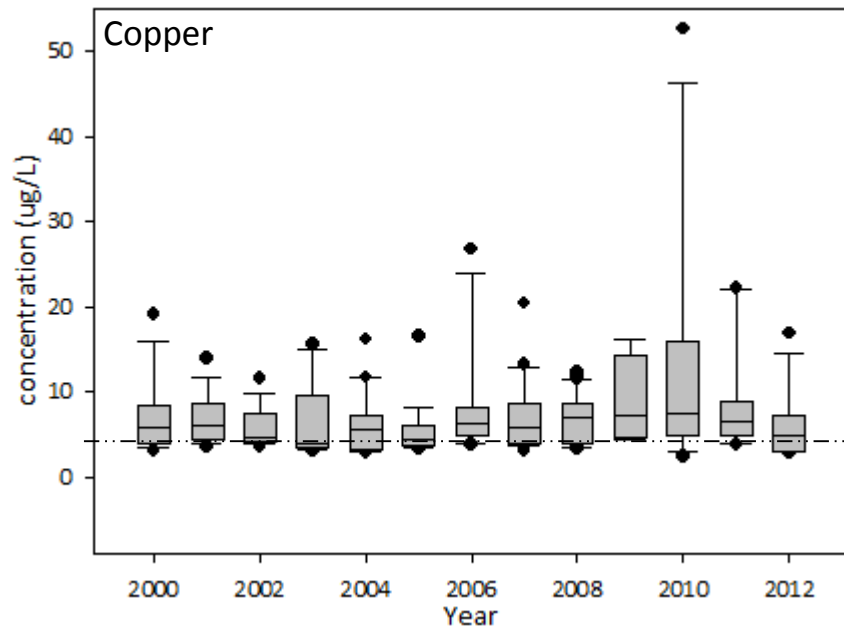
Figure 7 Copper concentration (ppb) in the Lower Don River (Todmorden) monitoring site. Data include 9-20 values per year from 2000 – 2012 monitored by the Provincial Water Quality Monitoring Network (PWQMN). The dashed line (⊢---⊣) indicate the Provincial Water Quality Objectives (PWQO) level. Boxplot data show stable copper concentrations in the 12 year period.
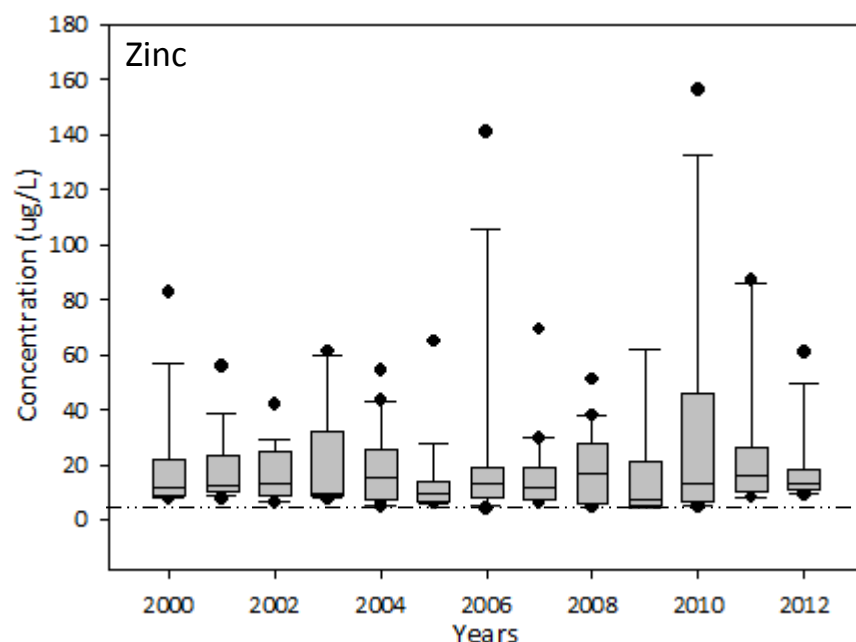
Figure 8 Zinc concentration (ppb) in the Lower Don River (Todmorden) monitoring site. Data include 9-20 values per year from 2000 – 2012 monitored by the Provincial Water Quality Monitoring Network (PWQMN). The dashed line (─ ─ ─) indicate the Provincial Water Quality Objectives (PWQO) level. Boxplot data show stable zinc concentrations in the 12 year period.

4.2 Sediment

The 23 sediment grab samples collected were microwave digested using aqua regia, diluted and analyzed with the ICP-OES for the total copper, lead, and zinc concentrations. Values for the samples, blanks and CRM are shown in Table A4. The total copper, lead, and zinc recoveries were 73%, 77%, and 76% based on the reported CRM values. However, the reported CRM values were determined by a lithium metaborate fusion procedure followed by analysis by ICP-MS and ICP-OES (National Institute of Standards and Technology, 2008). Chand and Prasad (2013) and Divrikli et al. (2007) analyzed CRM 8704 using aqua regia in a microwave digestion and ICP-OES. The recovery compared to the average values obtained from the CRM studies were 76%, 80%, and 77% for copper, lead, and zinc. The total copper, lead, and zinc concentrations within the sampled areas were adjusted to the blank and shown in Figure 9, Figure 10 and Figure 11.
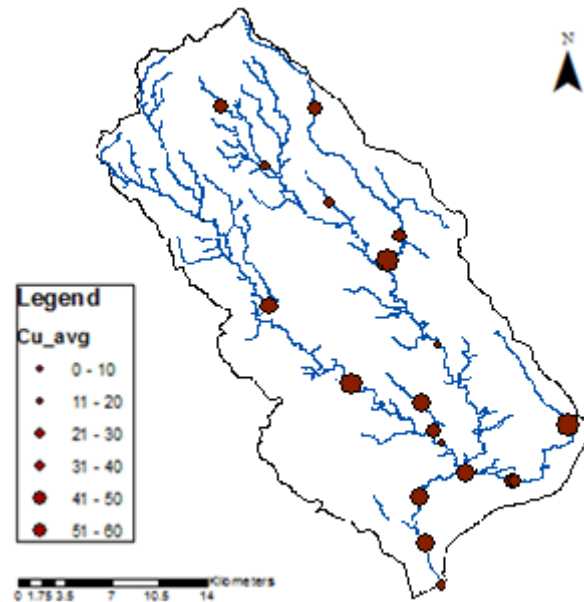
Figure 9 Total copper concentrations (mg/kg) in 22 sediment samples collected on April 18th and 26th 2014 within the Don River. Samples were microwave digested in triplicate using aqua regia and analyzed by ICP-OES. Results show the distribution of the averages with the lowest values in the upper watershed and the highest values in the lower watershed. Mapped using ArcMap 10.1.
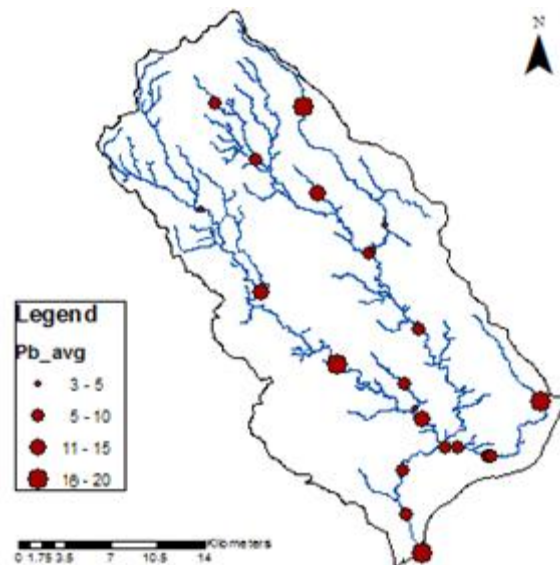
Figure 10 Total lead concentrations (mg/kg) in 22 sediment samples collected on April 18th and 26th 2014 within the Don River. Samples were microwave digested in triplicate using aqua regia and analyzed by ICP-OES. Results show the distribution of the averages with fairly even concentrations throughout the river. Mapped using ArcMap 10.1.

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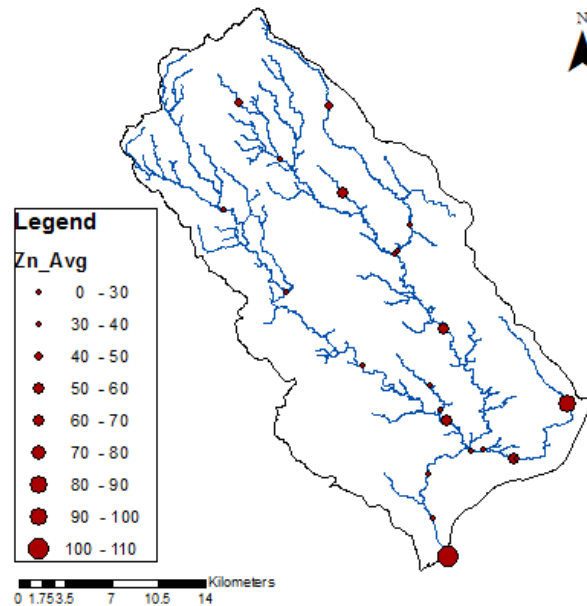
Figure 11 Total zinc concentrations (mg/kg) in 22 sediment samples collected on April 18th and 26th 2014 within the Don River. Samples were microwave digested in triplicate using aqua regia and analyzed by ICP-OES. Results show the distribution of the averages with the highest concentrations near the mouth of the Don River and within Taylor Massey Creek. Mapped using ArcMap 10.1

Using hand cores, two core samples were collected on August 3rd 2013. One was located in the Upper East subwatershed near the headwater and the other was collected close to the mouth of the river in the Lower Don subwatershed. The upper core had a depth of 9 cm and the lower core had a depth of 18 cm. Both cores were sliced in 1 cm intervals, microwave digested with aqua regia, diluted and analyzed by ICP-OES. The interval from 12-13 cm in the Lower Don core was not included in the study due to analysis error.

 The results are illustrated in the depth profiles shown in Figure 12.
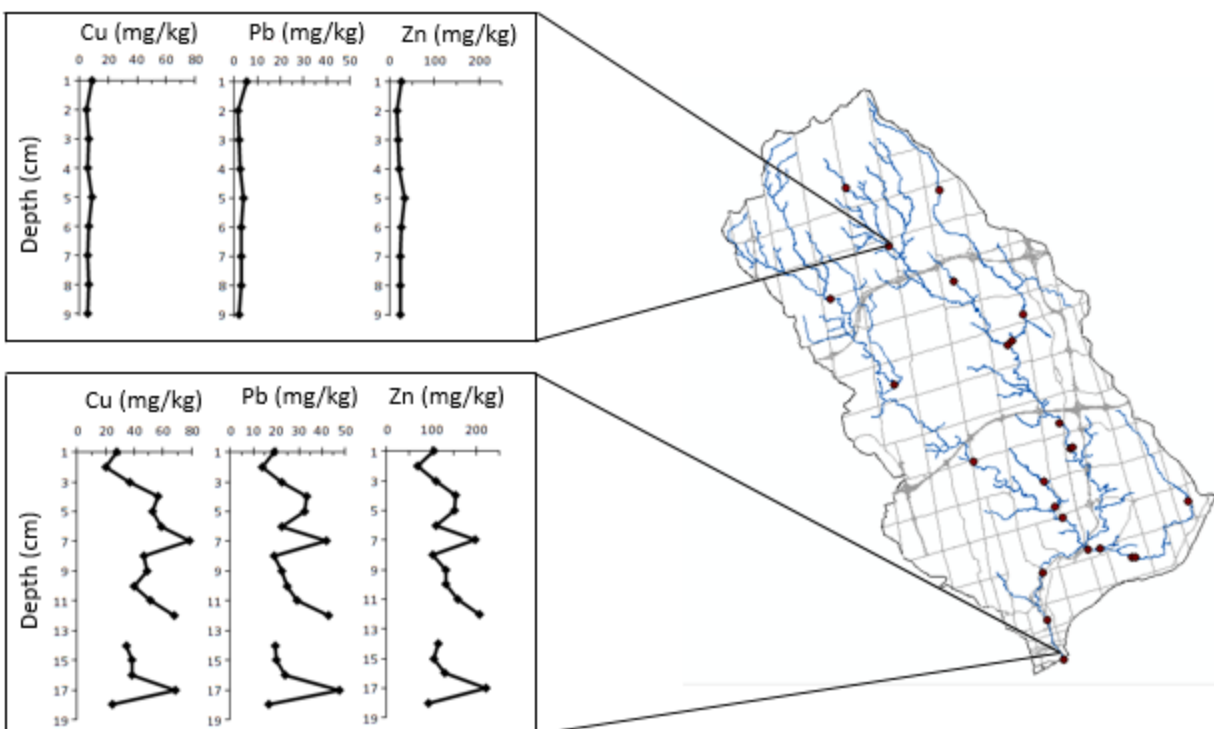
Figure 12 Total copper, lead, and zinc concentrations (mg/kg) in two sediment cores taken in the Upper East Don and Lower Don River subwatersheds. Samples were microwave digested in triplicate at 1 cm intervals and analyzed by ICP-OES. The depth profile of the upper core show a low and stable concentration of copper between 5 - 9 mg/kg, lead between 2 – 5 mg/kg, and zinc between 17 – 33 mg/kg. The lower core show concentrations that are at least four times higher and more unpredictable between intervals. Copper range from 20 – 80 mg/kg, lead range from 15 – 47 mg/kg, and zinc range from 70 – 220 mg/kg.

The 1 cm intervals of each core were also individually analyzed by TGA in order to reveal any trends due to the physical contents of the sediment samples. Each interval of the upper core was plotted against the samples organic matter content and calcium carbonate content and shown in Figure 13. The core slices of the lower core was also analyzed and plotted against the organic matter and carbonate content and the relationships are shown in Figure 14.
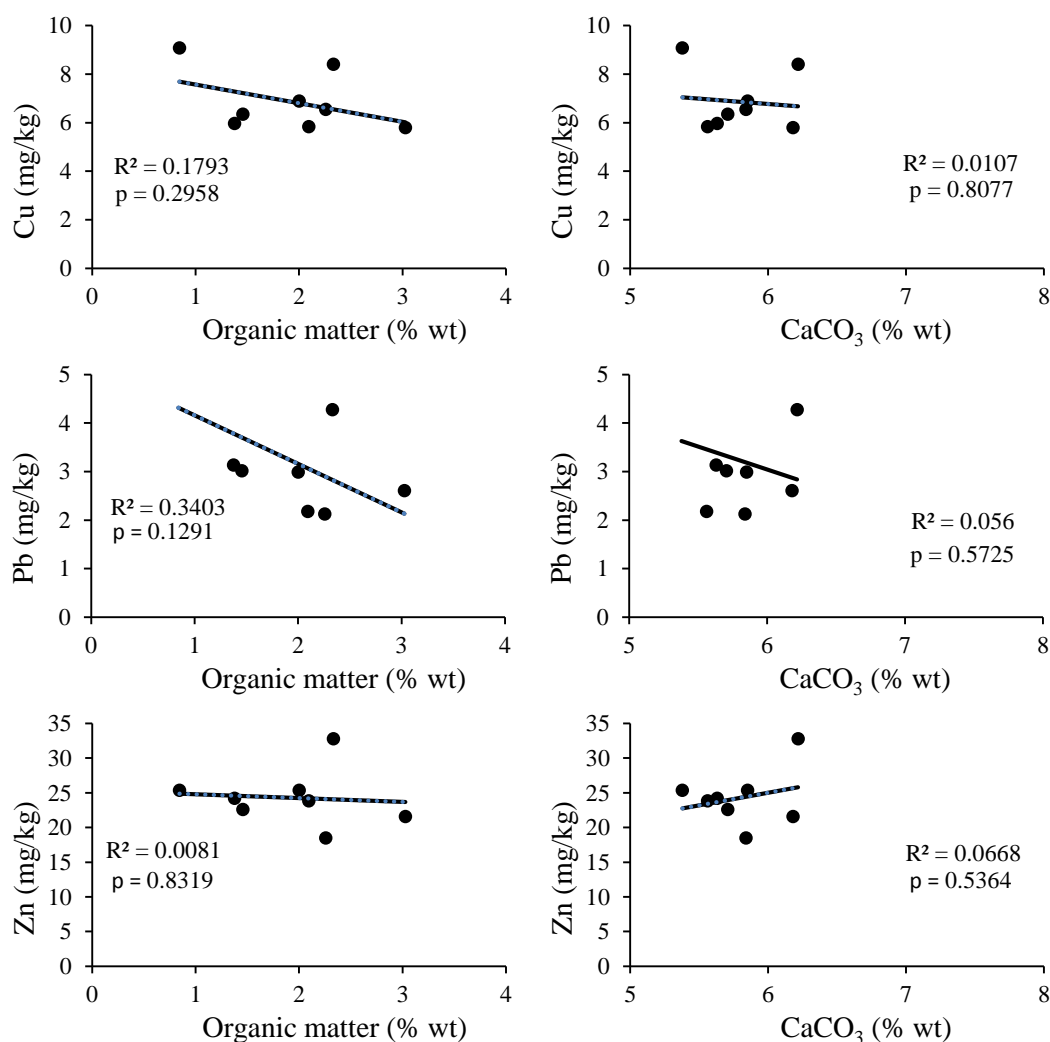
Figure 13 Copper, lead, zinc concentrations (mg/kg) correlated to organic matter (% wt) and calcium carbonate (% wt) based on the Upper Don River sediment core. Metal concentrations analyzed by aqua regia microwave digestion and ICP-OES. Organic and calcium carbonate content analyzed by TGA. The seven points of data don't show a strong correlation between the metals and organic matter or calcium carbonate.
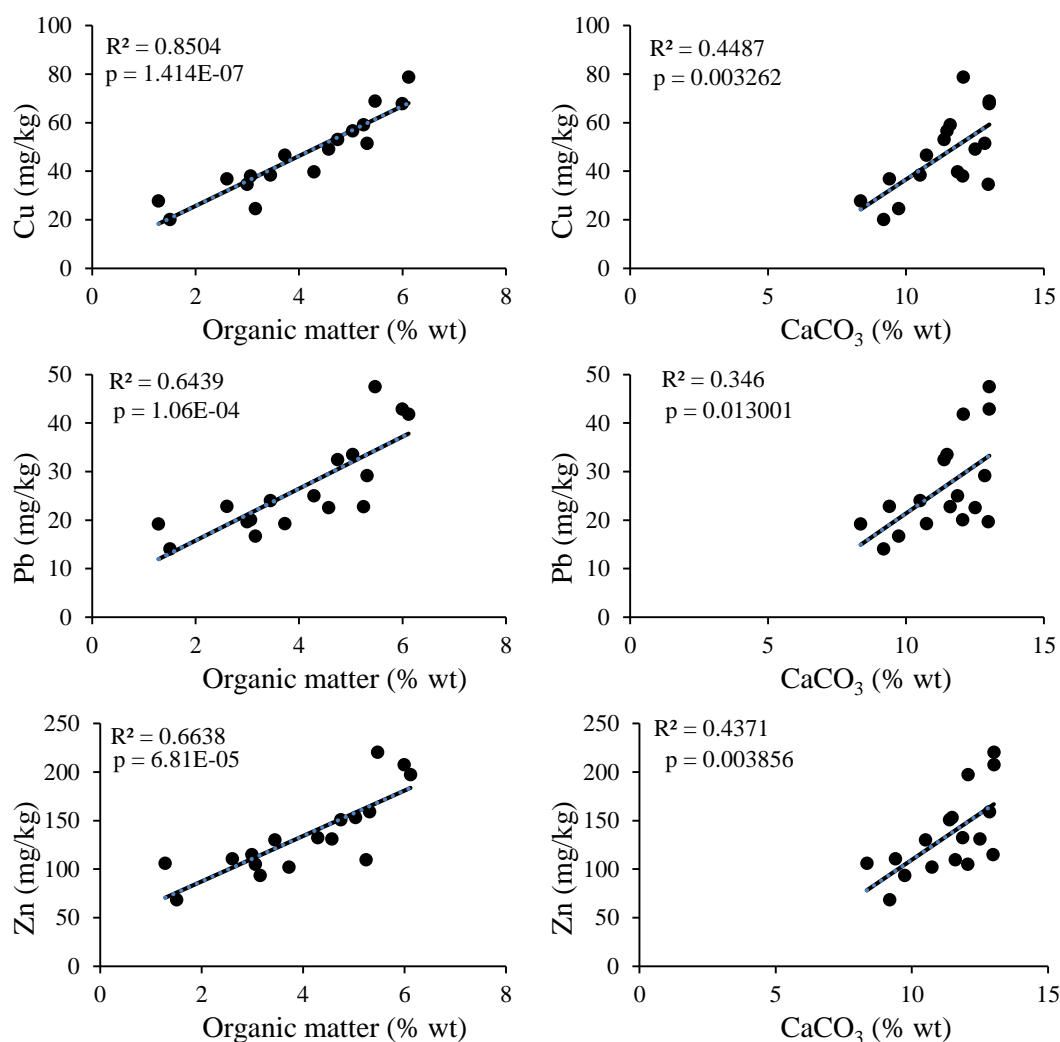
Figure 14 Copper, lead, zinc concentrations (mg/kg) correlated to organic matter (% wt) and calcium carbonate (% wt) in the Lower Don River sediment core. Metal concentrations were analyzed by aqua regia microwave digestion and ICP-OES. Organic and calcium carbonate content analyzed by TGA. The data represent sixteen data points and show a positive correlation between the metal concentrations and organic matter content in the sediment. Copper showed the best linear correlation. A poor correlation was seen with the metals and calcium carbonate.

4.3 Sequential Extraction

Using a modified Tessier method, a sequential extraction was performed on 13 of the grab samples collected from the upper 10 cm of the river bed. Samples were chosen in an attempt to include 1 or 2 points from each subwatershed. The extraction separated the metal concentrations into five geochemical phases; exchangeable, carbonates, oxides, organics, and residuals. Each sequential extraction sample was corrected with the blanks. The sum of the phases showed a copper, lead, and zinc recovery of 69%, 78%, and 93% compared to the reported CRM values. The sum of the phases of the extraction compared to the total concentrations of the same sediment analyzed by microwave digestion in section 4.2 showed a copper, lead, and zinc recovery of 94%, 102%, and 123%. Samples that underwent a sequential extraction with a recovery lower than 75% and greater than 125% compared to the total concentrations were omitted. The portion of the total copper concentration found sorbed to each phase is shown in Figure 15.
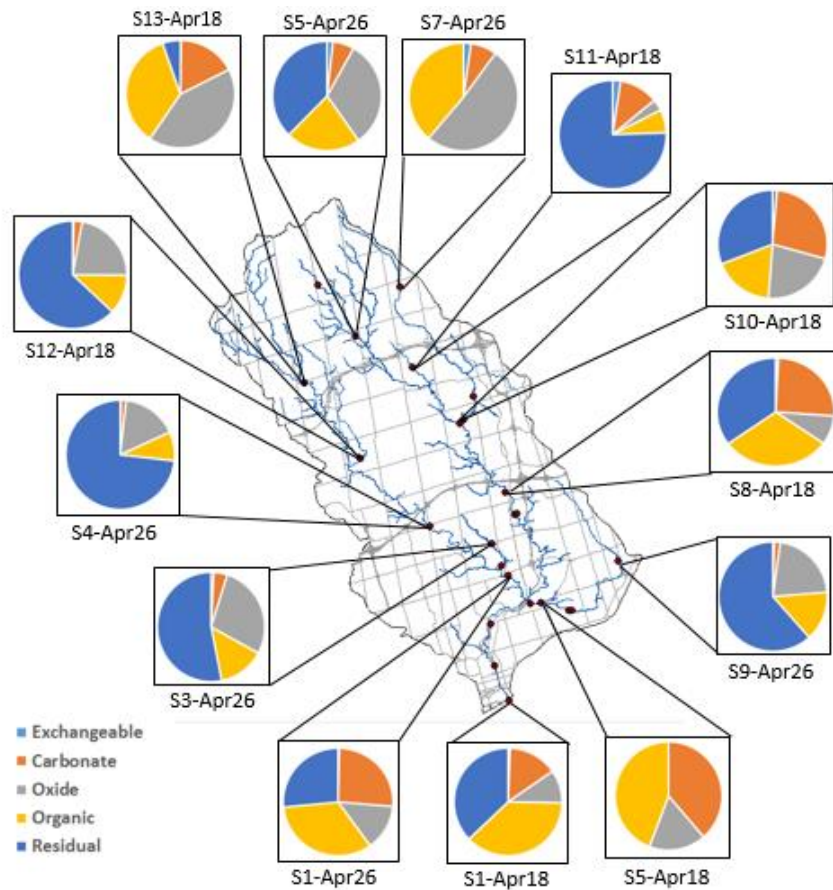
Figure 15 Copper sequential extraction associations into five phases; exchangeable (light blue), carbonates (orange), iron and manganese oxides (grey), organics (yellow), and residual (dark blue). Sediment samples were taken within the Don River on April 18th and 26th 2014 and thirteen were chosen for fractionation. Samples underwent sequential extraction in triplicate using the method outlined by Tessier, Campbell, & Bisson (1979). Samples that had a recovery within 75% - 125% of the total sediment concentrations are shown. Copper appear to only be associated to the most loosely bound exchangeable phase in the upper watershed. The West Don shows more copper in the residual phase. The East Don show a fairly distribution in the carbonate, organics and residual phase. Sediment in the Lower Don show strong associates with organics.

Values for the copper sequential extraction in Figure 15 are shown in Table 1.

Table 1 Copper sequential extraction values from sampled sites in the Don

Cu	Total mg/kg	Exchangeable (mg/kg)	Carbonate (mg/kg)	Oxide (mg/kg)	Organic (mg/kg)	Residual (mg/kg)
S13-Apr18	2.61	0.00	0.44	1.10	0.91	0.16
S5-Apr26	29.00	0.00	0.44	1.10	0.91	0.16
S7-Apr26	31.31	0.58	1.74	9.28	6.38	11.02
S11-Apr18	27.07	0.63	2.50	15.97	12.21	0.00
S10-Apr18	3.75	0.54	3.25	0.81	1.89	20.57
S8-Apr18	11.99	0.04	1.05	0.83	0.68	1.16
S9-Apr26	61.55	0.12	3.00	1.08	3.60	4.20
S5-Apr18	9.08	0.00	1.23	12.93	9.23	38.16
S12-Apr18	47.94	0.00	3.54	1.54	4.00	0.00
S4-Apr26	57.52	0.00	1.44	10.55	5.75	30.20
S3-Apr26	47.13	0.00	1.15	9.20	5.18	41.99
S1-Apr26	11.19	0.47	1.89	13.20	6.60	24.98
S1-Apr18	27.74	0.00	2.91	1.57	3.69	3.02

The same sediment samples were also analyzed on the ICP-OES for lead. Five of the sediment samples run had samples that reported results below the detection limit and were omitted. This was likely due to the low sensitivity of lead analysis on the ICP-OES. The percentage of the total lead concentration sorbed to each phase is shown in Figure 16.

Figure 16 Lead sequential extraction associations into five phases; exchangeable (light blue), carbonates (orange), iron and manganese oxides (grey), organics (yellow), and residual (dark blue). Sediment samples were taken within the Don River on April 18th and 26th 2014 and thirteen were chosen for fractionation. Samples underwent sequential extraction in triplicate using the method outlined by Tessier, Campbell, & Bisson (1979). Samples that had a recovery within 75% - 125% of the total sediment concentrations are shown. Lead associated to the exchangeable phase is most evident in the upper watershed. Lead appears to be most strongly associated to the oxide and residual phase of the sediment throughout the samples.

Lead values represented in Figure 16 are shown in Table 2.

Table 2 Lead sequential extraction values from sampled sites in the Don

Pb	Total mg/kg	Exchangeable (mg/kg)	Carbonate (mg/kg)	Oxide (mg/kg)	Organic (mg/kg)	Residual (mg/kg)
S13-Apr18	4.70	0.09	0.56	0.56	0.19	3.29
S5-Apr26	7.97	0.56	1.59	0.00	0.48	5.34
S7-Apr26	15.06	0.45	2.26	5.12	1.36	5.87
S11-Apr18	12.08	0.12	0.24	3.50	0.48	7.73
S10-Apr18	7.41	0.15	0.52	2.59	0.15	4.00
S8-Apr18	9.93	0.20	1.09	3.57	0.30	4.77
S9-Apr26	17.36	0.17	2.60	7.99	0.35	6.25
S5-Apr18	5.59	0.00	0.28	0.50	0.22	4.58
S12-Apr18	11.76	0.47	2.23	5.41	1.41	2.23
S4-Apr26	18.03	0.36	6.85	7.39	0.90	2.52
S3-Apr26	5.09	0.31	2.19	0.05	0.36	2.19
S1-Apr26	10.27	0.10	1.95	3.70	0.41	4.11
S1-Apr18	19.21	0.19	2.31	8.07	0.77	7.88

Zinc concentrations were run on all 13 sediment samples selected for sequential extraction. Values are shown in Figure 17.
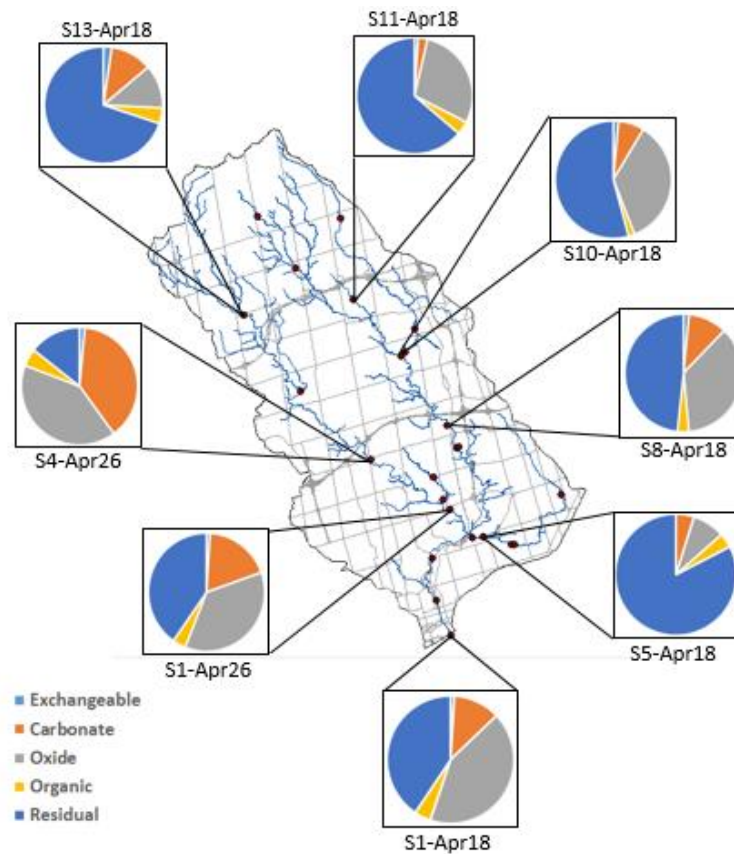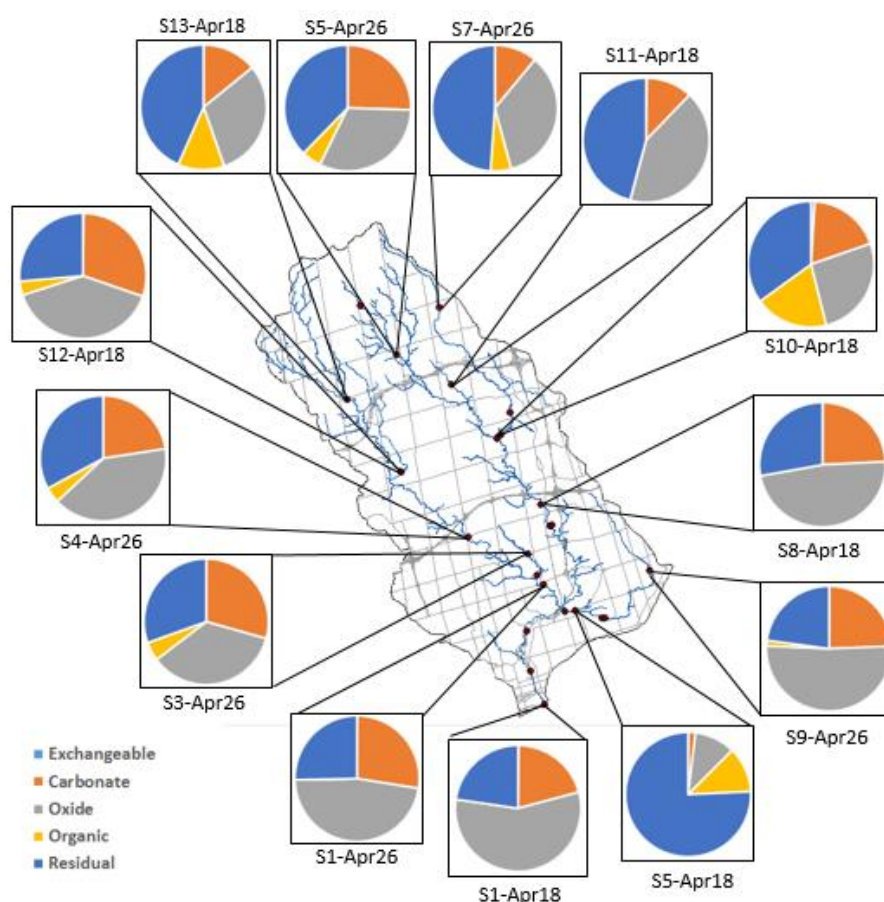
Figure 17 Zinc sequential extraction associations into five phases; exchangeable (light blue), carbonates (orange), iron and manganese oxides (grey), organics (yellow), and residual (dark blue). Sediment samples were taken within the Don River on April 18th and 26th 2014 and thirteen were chosen for fractionation. Samples underwent sequential extraction in triplicate using the method outlined by Tessier, Campbell, & Bisson (1979). Samples that had a recovery within 75% - 125% of the total sediment concentrations are shown. Zinc was not associated with the exchangeable phase in the sediment samples. Overall zinc was mostly associated to the oxide phase throughout the watershed.

Values of Zinc to each phase is shown in Table 3.

Table 3 Zinc sequential extraction values from sampled sites in the Don

Zn	Total mg/kg	Exchangeable (mg/kg)	Carbonate (mg/kg)	Oxide (mg/kg)	Organic (mg/kg)	Residual (mg/kg)
S13-Apr18	24.09	0.00	3.37	7.47	2.89	10.36
S5-Apr26	36.97	0.00	9.24	11.83	1.85	14.05
S7-Apr26	40.16	0.00	4.42	14.06	2.01	19.68
S11-Apr18	67.17	0.00	8.06	28.21	0.00	30.90
S10-Apr18	30.42	0.30	5.78	7.91	5.78	10.65
S8-Apr18	59.08	0.00	14.18	28.36	0.00	16.54
S9-Apr26	87.33	0.00	20.96	44.54	1.75	20.09
S5-Apr18	25.35	0.00	0.51	2.54	3.04	19.27
S12-Apr18	39.07	0.00	11.72	15.63	1.56	10.16
S4-Apr26	33.42	0.00	7.69	13.37	1.34	11.03
S3-Apr26	28.01	0.00	8.12	9.80	1.40	8.68
S1-Apr26	54.81	0.00	15.35	25.76	0.00	13.70
S1-Apr18	106.01	0.00	22.26	59.37	0.00	24.38

Chapter 5
Discussion

5.1 Surface Water Quality

The Don River watershed is a hardwater, high alkalinity, high pH, oxidizing pE system (Warren & Zimmerman, 1994). This is corroborated by current analysis (see Section 4.1) and in conformity to the geological background, since the watershed is largely comprised of limestone. All the hardness values are well above 400 mg/L $CaCO_3$ with the exception of two values at the very top of the Upper East subwatershed and two points at the bottom of the Lower West subwatershed with values between 200 and 350 mg/L CaCO3 (see Figure 3). The samples also show high electrical conductivity that measure up to 3600 µS/cm, indicating a high amount of dissolved ions within the river. Possibly as a result of high salt concentrations from the snowmelt. These parameters agree with the values reported by Warren and Zimmerman (1994) and the TRCA (2013).

The results for all three trace metals are below the detection limit in the dissolved water samples and are not used. This is expected given the measured high pH in the river at the time of sampling. The pH measurements taken from 2000 – 2012 data provided by the provincial monitoring showed a range from 7.7 to 8.6 with a median of 8.13. The pH value is often the controlling variable that determine the trace metal dissolution or precipitation behavior. The pH range of the Don River is above the point where absorbance is near 100% for copper, lead, and zinc. The lack of studies or datasets measuring dissolved trace metals is likely due to their low concentration. The majority of the trace metals found in the freshwater system are likely in a particulate form rather than in a dissolved one.

To confirm this, the unfiltered water with suspended particulate matter (SPM) is microwave digested. The Canadian standards for unfiltered total copper, lead, and zinc is 5 ppb, 7 ppb, and 30 ppb while the provincial standards are 4 ppb, 5 ppb, and 20 ppb respectively. The analyzed metal contents are still low and only zinc concentrations are above the detection limit and used for comparison (Figure 4). Seven of the sampling locations exceed the provincial standard and four of the seven exceed the Canadian standard as shown in Table A3. These samples are in the Upper West subwatershed with a measurement of 74 ppb (S12-Apr18), near the confluence of the German Mills Creek with a value of 48 ppb (S10-Apr26), in the Upper east watershed with 32 ppb (S11-Apr18), and in the Lower West subwatershed with a value of 35 ppb (S3-Apr26). The three other points that exceed the provincial but not the Canadian standards include the, Lower Don with 22 ppb (S2-Apr18), Wilket creek in the Lower West subwatershed with 26 ppb (S2-

Apr26), and a point in Taylor Massey Creek with 24 ppb (S9-Apr26). The distribution of these samples are even throughout the watershed. The highest of the samples are found in the Upper West subwatershed and the German Mills subwatershed.

The unfiltered zinc concentrations that were above the provincial guidelines did not appear to be clustered in one area of the watershed. However, the two exceptionally high values were found in the Upper West subwatershed and in the German Mills Creek subwatershed. Sources for zinc that could explain the elevated concentrations in these may be industrial. Both subwatersheds have the highest percentage of industrial area with 29.4% in the Upper West and 17.4% in the German Mills Creek subwatershed (TRCA, 2009a). These areas are characterized by warehouses, buildings, storage yards, train stations, and parking lots that may release zinc from fossil fuel combustion and wear of galvanized surfaces and zinc alloys (TRCA, 2009a).

The RWMP data use unfiltered water samples as well, at six locations from 2008 – 2010 with approximately 45 samples at each site (Figure 5). The interquartile range for copper, lead, and zinc at all six locations shown in Figure 6 are all above the provincial water quality objectives concentration. The dataset have missing values resulting in unequal sample sizes for each site. A one-way ANOVA on ranks ($p < 0.05$), indicates a significant difference between site 15 and 13, 3 and 4, and 3 and 13 for copper concentrations. Site 15 and 3 have higher concentrations overall and site 13 has the lowest concentrations for all three metals. The same test was applied to the concentration of lead and zinc and the difference between the six sites were not statistically significant (P=0.052 and P=0.0867). The RWMP data show that statistically, any difference between sites throughout the watershed for lead and zinc may be caused by sample variability.

The RWMP results reflect a larger sample size that includes samples from multiple years and every season which better represents the river. The data show a statistically significant increase in copper concentration between the upstream site 4 and the downstream site 15 near the mouth of the river. This implies that the lower Don is richer in Cu, probably due to accumulation effects – as expected. The highest copper concentrations are found in Taylor Massey Creek, the Lower Don River, and the Lower East Don as indicated in Figure 6. These subwatersheds are mostly located within the city of Toronto and are subject to urban sources. The Taylor Massey creek, East Don, and Lower Don subwatersheds have the highest percentage of dense residential area with 55%, 57% and 65.9% by land use (TRCA, 2009a). These subwatersheds also have the highest road densities with 8.92 km/km^2, 9.63 km/km^2 and 8.92

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km/km^2 respectively (TRCA, 2013). This suggests increased vehicle metal sources and a higher degree of runoff from the paved surfaces to stormwater outfalls. Other sources of metal to Taylor Massey Creek is also the former landfills shown in Figure A8 that surround the creek. These buried landfills (discussed in section 2.2) likely contribute to the high metal concentrations within the creek despite its small size and discharge rate. The data supports the hypothesis that higher copper concentrations are found in the southern, more urbanized portion of the watershed but is rejected for lead and zinc.

The difference between the results of the grab samples taken in this study and the RWMP data underlines the importance of representative samples. While the RWMP data better represents the data over the one set of grab samples taken in this study, it may still underrepresent metal concentrations. The inclusion of precipitation events is necessary to accurately estimate annual SPM concentrations and the metals sorbed to them. This is especially important due to the increasing trend in annual precipitation shown in Figure A10 that enter as runoffs and increase river discharge rates shown in Figures A5, A6, and A7. The frequency and severity of precipitation events change each season, and so SPM and metals entering the river is likely to change by season as well. The SPM concentrations were measured by Environment Canada at the Todmorden (site 15) location from 1986 – 1988, the relationship between these concentrations and the recorded discharge during each season are shown in Figure 18.
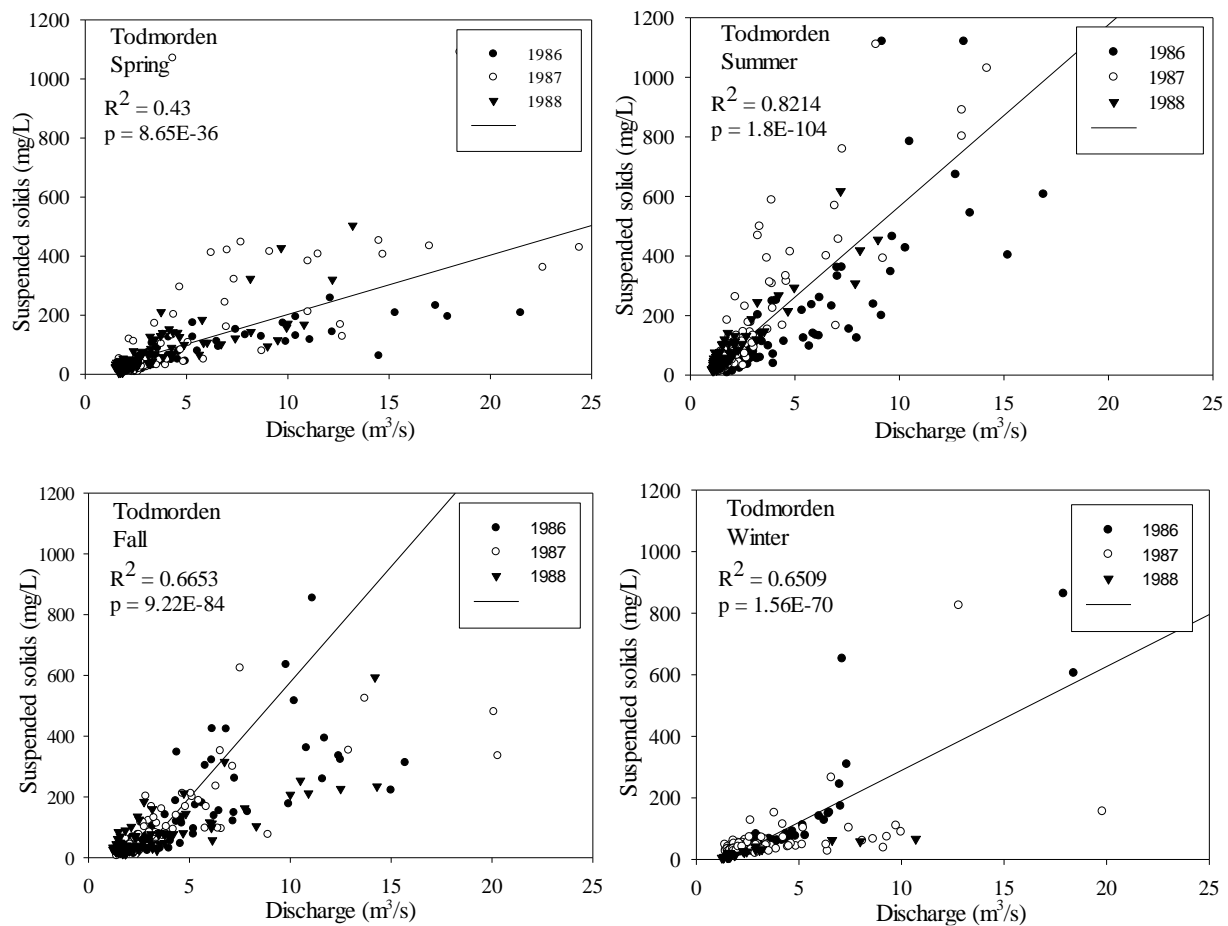
Figure 18 Seasonal trends of Todmorden river flow (m³/s) vs suspended solids concentration (mg/L) from 1985 to 1988. Three year data taken daily and separated into spring (March-May), summer (June-August), fall (September-November), winter (December-February). Highest suspended solids concentration found in summer and lowest suspended solids concentration found in winter. Trend in spring start levelling off at 10 m³/s.

Spring has more frequent precipitation events that bring in SPM and metals into the river at a lower consistent rate but begins to level out as the precipitation begins to dilute the SPM concentration in the river. Summer has the highest concentration of suspended solids flushed into the river with a given precipitation event. This is likely due to the first flush effect, which is described as the highest load of contaminants being carried by runoffs during the early stages of a rain event (Sansalone, Buchberger, & ASCE, 1997). Summer rain events are less frequent which provides more time for contaminants to accumulate on urban surfaces which provide a higher concentration once it rains. Suspended solids were

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only measured from 1986 to 1988 and the corresponding metal concentrations were not analyzed. So the direct correlation between SPM and metals could not be established.

The average discharge rate at each RWMP monitoring site based on data from 2009 to 2011 are 0.87 m^3/s, 1.25 m^3/s, 1.29 m^3/s, 2.25 m^3/s, 0.39 m^3/s, and 6.38 m^3/s for sites 4, 1, 13, 2, 3, and 15 respectively. Using the corresponding daily discharge rates, the flux of copper, lead and zinc are plotted and compared per site as shown in Figure 6. The results determine the possible movement and settling of metal concentrations throughout the river that eventually get flushed through the Toronto Harbour and into Lake Ontario. A one way ANOVA on ranks was used to compare flux values between sites. The flux of all three metals show significant (P<0.05) differences between site 2 and 4, site 2 and 3, as well as site 15 compared to all other sites.

The metal fluxes shown in Figure 6 depend on the discharge rates in the area as anticipated. Copper, lead and zinc fluxes appear to increase going from upstream to downstream in both the west and east branch of the river but could not be statistically proven. Both the west and east branch of the river have similar metal fluxes going from upstream to downstream. The East Don has higher discharge rates compared to the West Don and in turn contributes higher metal loads. Site 2 found on the east branch has a large interquartile range, suggesting large variability in the discharge rate. The flux of copper, lead and zinc at site 3 in Taylor Massey Creek is low despite having high metal concentrations. This can result in an accumulation of metal sorbed SPM onto the river floor. Site 15 located in the Lower Don River have significantly higher metal concentrations but also a high discharge rate. Less accumulation of metal sorbed SPM onto the sediment floor is expected because the particulates likely don't have the chance to settle in this channelized portion of the river. The large interquartile range within the Lower Don River is a result of the large flux variability caused by periodic high discharge rates. This is expected as it is composed of the convergence of the other segments as well as addition outflows from stormwater outfalls and the sewage treatment plant.

The data provided by the MOE include a total of 210 samples from 2000 to 2012 shown in Figure 7 and Figure 8. The dataset does not show normal distribute and a Kruskal-Wallis one way analysis of variance on ranks is used to compare the 12 years of water sampling. Statistically, the difference in yearly values are not enough to exclude the possibility of random sampling variability (P = 0.530 for zinc and P = 0.090 for copper). The metal concentration and discharge data are also plotted seasonally in Figure 19 and Figure 20.
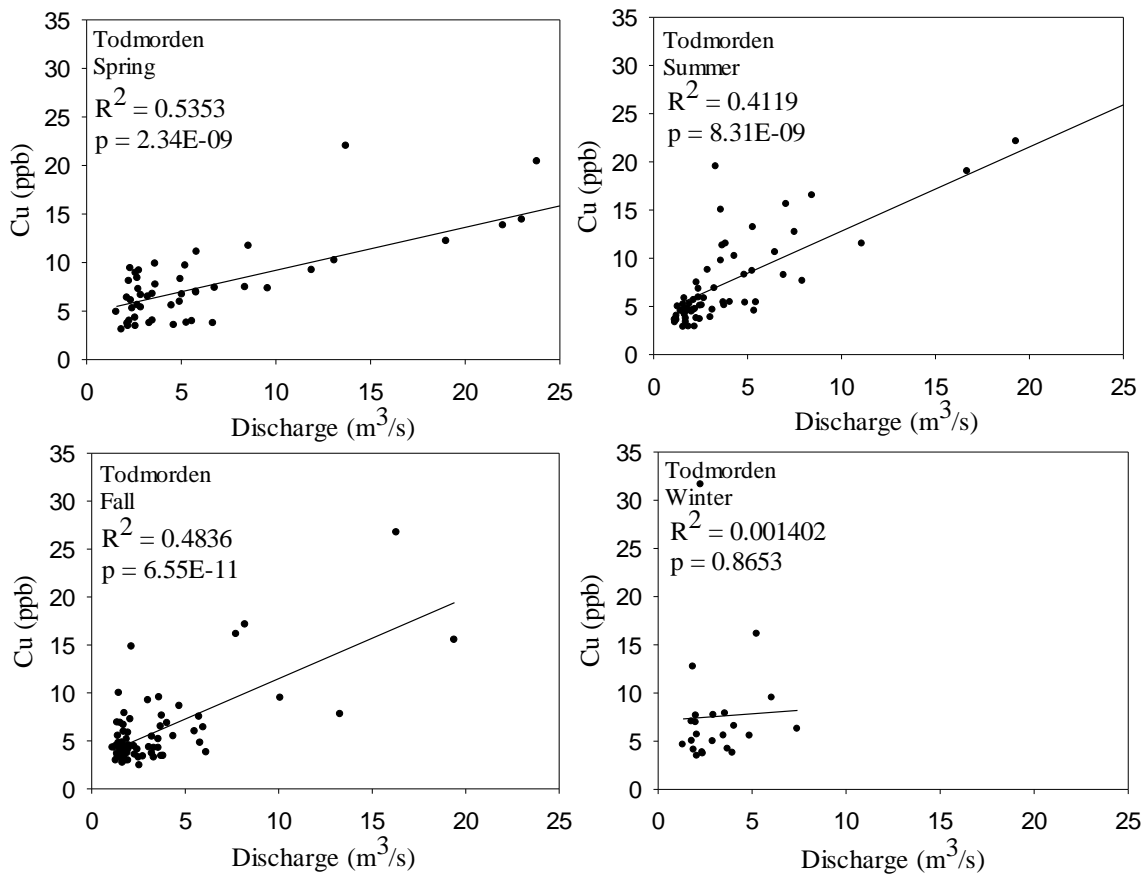
Figure 19 Copper concentration (ppb) vs discharge (m³/s) in the Lower Don River Todmorden site using the Provincial Water Quality Monitoring Network Data from 2000 – 2012. Winter (December – February) have the lowest concentrations. Summer (June – August) show higher copper concentrations with lower discharge rates. Spring (March – May) show overall higher copper concentrations.
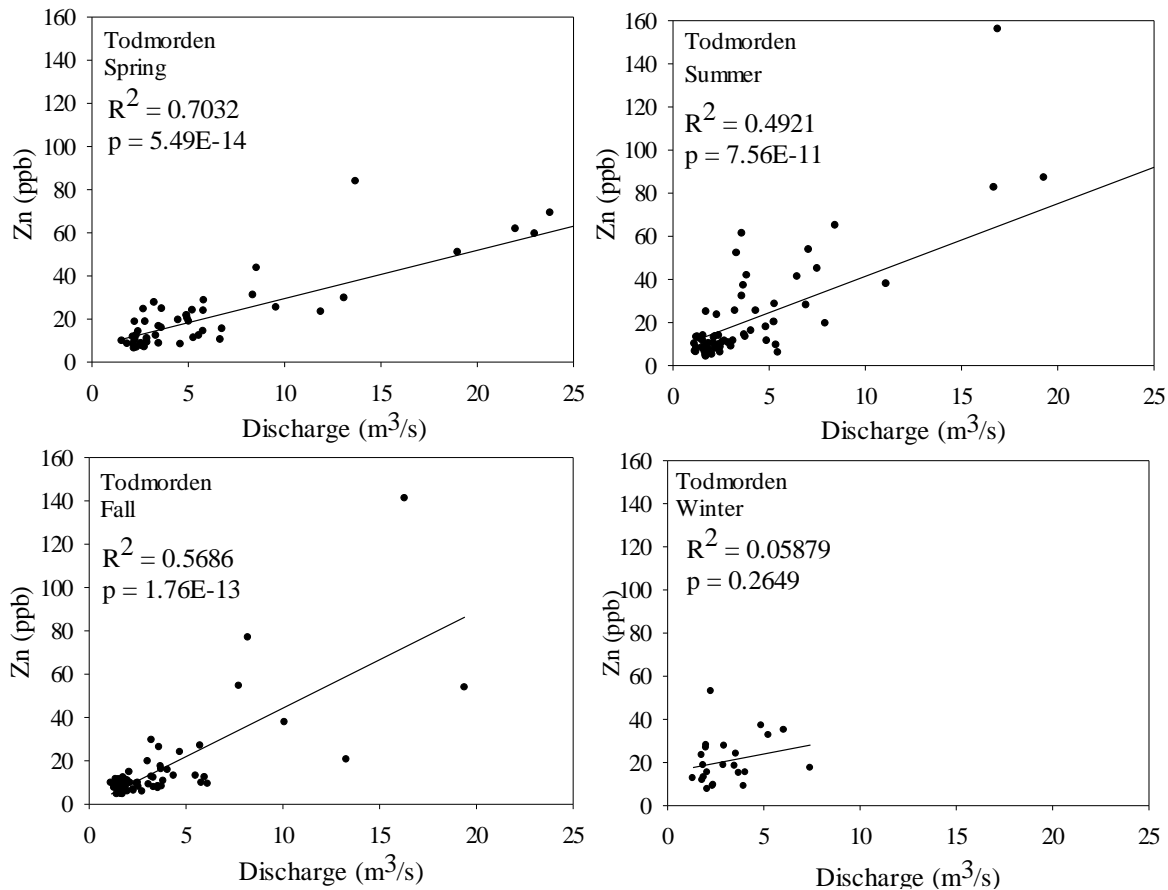
Figure 20 Zinc concentration (ppb) vs discharge (m³/s) in the Lower Don River Todmorden site using the Provincial Water Quality Monitoring Network Data from 2000 – 2012. Winter (December – February) show the lowest concentrations. Summer (June – August) show higher zinc concentrations with lower discharge rates. Spring (March – May) show higher zinc concentrations overall.

Using a Pearson product moment correlation on the entire data set, the correlation coefficient between copper and discharge is 0.574 with p<0.050. The correlation coefficient for zinc and the discharge is 0.688 with p< 0.050. This shows a positive correlation between Cu and discharge as well as Zn and discharge. The seasonal patterns for copper and zinc are similar to the suspended solids data shown in Figure 18. Summer shows the highest concentrations in a few points but spring likely has higher concentrations overall. A TRCA report summarizing their own data from 2006 – 2010 suggests that the highest copper and zinc concentrations are generally found in spring and winter months (TRCA, 2011). Spring brings in higher concentrations of suspended solids while winter months have higher salt

concentrations from deicing agents that release metals sorbed to sediment in the river (TRCA, 2011). The high winter concentrations concluded by the TRCA (2011) are not reflected in Figure 19 and Figure 20.

The findings in this study show that trace metal concentrations in surface water is mostly found sorbed to suspended particulate matter. Based on the RWMP data, higher concentrations of all three metals are found in the lower portion of the watershed. Specifically, within the Lower Don River, Taylor Massey Creek and Lower East Don. These subwatersheds are highly urbanized and sources include the wastewater treatment plant in the Lower Don, buried landfills in Taylor Massey Creek, and most importantly the runoffs that discharge into the river from the many stormwater outfalls. The important role of runoffs is confirmed through the positive correlation of suspended solids and metal concentrations with river discharge. Incorporating discharge data with the metal concentrations also suggests high metal accumulation within Taylor Massey Creek.

The positive correlation with the suspended solids and metal concentrations with discharge shown in Figure 18, Figure 19, and Figure 20 are in agreement with Bodo (1989). The study compares baseflow data from PWQMN between 1983 – 1986 to peak rainfall data from the Toronto Area Watershed Management Strategy (TAWMNS) in 1984 and 1986. During normal baseflow, the suspended solid concentration was 1 – 2059 mg/L with a median of 21 mg/L. Measured peak runoffs had suspended solid concentrations from 59 – 2380 mg/L and a median of 1672 mg/L in 1984 and 361 to 1610 mg/L with a median of 740 mg/L in 1986 Bodo (1989). Copper, lead and zinc concentrations increased with suspended solid concentrations from the runoff. Another study conducted using MOE data from 1990 to 1992 at site 15 compared 22 dry weather samples to 24 wet weather samples (D Boyd, D'Andrea, & Anderson, 1999). Copper and lead concentrations doubled and zinc concentrations increased by a factor of 10 during wet weather events (D Boyd et al., 1999).

Temporally, copper and zinc concentrations have not statistically changed based on the 12 year PWQMN data and the hypothesis that growing population density has increased trace metal concentrations in surface water from 2000 to 2014 is rejected. The undetected concentration change in surface water may be due to sampling error. The Don has a history of having extremely flashy hydrology from rain events that brings in urban particulates into the river. The annual rain data for the last five decades show an increasing trend that may increase the concentration of particulates and metals. The lack of variability over the years is likely a result of the changing sample sizes, disproportionate seasonal sampling, and a

lack of representation of rain events. Using season as a control could increase the comparability between years if more samples are taken during the particular season chosen.

Currently the RWMP dataset is the only one available for spatial comparisons of surface water. Sampling occurs approximately once a month and likely misses important weather events that influence the contaminants being flushed into the river. Similarly, the PWQMN site in the Lower Don River is the only station with long term data. However, the sampling size of each year changes from 18 – 20 surface water samples from 2000 to 2008 to 9 – 12 samples from 2009 – 2012. January and February samples weren't taken prior to 2009, limiting winter data and likely underrepresenting yearly data. Further studies and data are needed to confirm any trends spatially or temporally.

There are many data gaps in the data provided, often associated with detection limits. Further method development to lower the method of detection using the instruments would improve the results of the surface water grab samples particularly for copper and lead. Error could also be reduced through possible improved trace metal recovery, as Chand & Prasad (2013) and Divrikli et al. (2007) had trace metal recoveries over 95%. The trace metals concentrations found in freshwater are very low and any sampling variability in the field may have skewed the data.

5.2 Don river Sediment quality

The provincial sediment quality guideline was created to protect the environment using a biological effects-based approach. Guideline values were determined with an aqua regia sediment digestion and analyzed using spectrometric technique (Ministry of Environment, 2004). The Lowest Effect Level (LEL) in sediment reflects the concentration to which harmful effects are not expected to be observed in biota. These concentrations are tolerated by most biota and are considered clean to slightly polluted. The Severe Effect Level (SEL) is the level to which the majority of biota is likely adversely effected. Concentrations above guideline values result in reduced benthic communities and biodiversity.

The copper LEL in freshwater sediment is approximately 16 mg/kg DW while the SEL is approximately 110 mg/kg DW (Fletcher, Welsh, & Fletcher, 2008). Based on the 22 samples collected (Figure 9), 17 exceed the LEL and all the samples are below the SEL. The 17 samples represent sites to which severe effects aren't likely observed but chronic effects may be taking place. The highest concentration is 62 mg/kg DW located in Taylor Massey Creek. The majority of the copper concentrations above 45 mg/kg are located throughout the Lower Don segment, within Taylor Massey Creek, and the Lower West Don.

The lead LEL reported is 31 mg/kg DW and the SEL is 250 mg/kg DW while the zinc LEL is 120 mg/kg DW and SEL is 820 mg/kg (Fletcher et al., 2008). All the sampling points are below the LEL and SEL for lead and zinc (Figure 10 and Figure 11). These values indicate that the levels in all the sampling locations are acceptable and are likely below the threshold to which any type of effect could be observed. The highest lead and zinc concentrations are found in Taylor Massey Creek and closest to the mouth of the river before entering into Lake Ontario. The zinc concentrations in the sediment samples do not follow the same distribution as the water samples, likely due to their dynamic nature.

The high concentrations of all three metals near the river mouth is likely a result of both an accumulation of metals from the upper river segments and additional metal sources from urban areas. This supports the hypothesis that higher trace metals are found in the southern more urbanized portion of the watershed within sediments. Copper, lead, and zinc also show high concentrations at certain points along Taylor Massey Creek. The high metal concentrations within the small creek agree with the concentrations found in the water samples shown in Figure 6, reinforcing the indication of potentially significant trace metal source in the area. As previously stated, the subwatershed have large amount of dense residential space contributing to the stormwater outfalls in the creek that is a source of metal concentration (TRCA, 2009a). Additionally the buried landfills described in section 2.2 is likely a major source of metal contamination in the area.

A similar study was conducted by the Southern Ontario stream sediment project, undertaken by the Ontario Geological Survey (OGS) in partnership with the Ministry of Environment (MOE) and Conservation Ontario. Part of the project was to sample stream sediment across Ontario and measure for inorganics such as metals. The objective of the study was to create an environmental geochemical baseline for southern Ontario and to gather more information for better environmental management. Samples were collected in the winter of 2008, digested with aqua regia, and analyzed by ICP-MS and ICP-OES for metals. There were approximately 6500 samples in southern Ontario and seven within the Don River watershed. Five of the seven sites within the Don are in similar locations as the sediment grab samples taken. A comparison of the OGS data and the grab samples concentrations taken in this study are shown in Table A5, A6, A7.

Based on the five OGS data points, copper and lead concentrations have a similar spatial distribution in the watershed. The highest concentrations of both metals are found in the southern portion of the Don (10

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and 18 mg Cu/kg; 16 and 35 mg Pb/kg) while the lowest concentrations are found in the northern portion (2-4 mg Cu/kg; 2-8 mg Pb/kg), particularly in the Upper West subwatershed. The highest zinc concentration is within the Lower East (73 mg/kg) and the other sites are within a range of 44-58 mg/kg. The distribution of metals suggested by the OGS data are not followed by the samples collected in this study for the same locations. The OGS copper concentrations are 2 – 6 times lower than the values determined in this study at the same locations. The lead values analyzed by the OGS are approximately 3 times higher in the Lower Don and Lower East locations and slightly lower in the upper watershed samples. All the OGS zinc values are higher than the concentrations determined in this study.

The OGS samples and the sediment samples taken in the same locations don't show conformity in pattern or range. Differences in analyzed values may be due to sample size, sample time, analysis method, and sediment size. The main area for improvement in both the sediment grab samples and the OGS samples are increasing replicates. The sampling done in both studies involved one surficial sediment grab sample at each location. Sample replicates need to be taken to adequately determine reliable baseline concentrations. The OGS samples were sampled in the winter of 2008 and the sediment sampled in this study were sampled in the spring of 2014. This makes the values less comparable and may explain some of the differences seen. Both studies were digested in the same way but the analysis for lead in the OGS samples used an ICP-MS rather than an ICP-OES. The ICP-MS is more sensitive for lead concentrations and better suited for lead analysis. The use of the ICP-OES for lead concentrations in this study have reduced sensitivity and may explain the sporadic distribution of lead concentrations.

The physical characteristics of the sediment may also influence the spatial distribution of the concentrations found. It is expected that smaller particles have a larger surface area for metals to sorb and differences in the particles of the sampled sediment may skew spatial trends (Bradl, 2005). The sediment particle sizes are shown in Table A11. The sediment samples taken throughout the watershed show physically different proportions of sediment sizes at each location that likely effect the total metal concentration found. In future studies it may be beneficial to also sieve sediment samples prior to digestion for a better comparison.

5.2.1 Up and downstream cores

The upper core taken in the Upper East subwatershed represents the short term change in trace metal concentrations near the headwaters of the Don River shown in Figure 12. The area surrounding the core

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include dense residential area, agricultural land, forest, and the Oak Ridges Moraine (TRCA, 2009a). The range of metal concentrations within the 9 cm core are 4 to 9 mg/kg DW of copper, 1.8 to 5.6 mg/kg DW of lead, and 17.3 to 32.8 mg/kg DW of zinc. Concentrations for copper, lead, and zinc show a stable trend that is consistent with depth.

The lower core taken in the Lower Don subwatershed represent the sediment concentrations near the mouth of the Don River (Figure 12). The surrounding area of the core is composed of urban space such as industrial land, high residential area, and major roads (TRCA, 2009a). The lower core has a 19 cm depth with concentration ranges of 20 to 79 mg/kg DW of copper, 14 to 17 mg/kg DW of lead, and 68.4 to 220.5 mg/kg DW of zinc. Concentrations found in the lower core are up to 8 times higher than the concentrations found in the upper core and don't show a clear increasing or decreasing trend. The values for all three metals change with depth in a similar pattern.

The top 7 cm of the lower core show a possible decreasing trend in copper, lead and zinc concentrations. A study conducted in 1983 examined a core near the mouth of the Don in the Keating Channel and determined a sedimentation rate of 1 520 g/m^2/year which was approximately 3.8 mm/year (J. O. Nriagu et al., 1983). Assuming the same rate of sedimentation, the lower core would represent about 47 years of data and the decreasing trend in the top 7 cm represent 1996 to 2014. This decrease is plausible given the restoration efforts put forth since the 1970s but a larger core would need to be taken to confirm any real trends. This is especially true because the sedimentation rate has likely changed since 1983 from the drastic land use changes within the watershed. Lead and zinc show identical trends within the core, possibly indicating a correlation to the same sediment parameter.

Each interval on both cores underwent Thermogravimetric Analysis. The percentage of organic matter and carbonates are determined and their correlation between copper, lead, and zinc are shown in Figure 13 and Figure 14. In the upper core, trends with increased organic content and calcium carbonate content are not seen. This may be due to the smaller sample size as well as lower metal concentrations available in the area. The correlation seen in the Lower Don core is more apparent. There is no clear correlation with the calcium carbonate but the organics revealed a linear trend particularly for copper. Copper concentration in the lower core seem highly dependent on the organic content in the sediment while lead and zinc are likely dependent on another parameter.

Nriagu et al. (1983) sectioned the core into 1 cm intervals, digested the samples using a bomb technique and analyzed for trace metals by atomic absorption spectrometry. Based on the isotope dating, the 70 – 100 cm layer was determined to be pre-colonial and the average sample concentration was 26 mg/kg for copper, 27 mg/kg for lead, and 34 mg/kg for zinc (Nriagu et al., 1983). These values compared to those in the lower core in this study (shown in Figure 12) suggest a large increase in concentration from pre-colonial time in copper and zinc. Copper often showing values two times higher and zinc often showing values five times higher. The lead concentrations show values that are both below and over the reported pre-colonial values. This may be due to overestimation of lead concentration in the pre-colonial sediment.

Since the beginning of the development of Toronto, large amounts of sediment have been released into the river that eventually discharges into Toronto Harbour. The contents of the Don River were eventually first diverted into Keating Channel in 1909 which also acted as a settling pond. The sediment in the Keating Channel required dredging of 5×10^4 m^3 per year up until 1950 and then over 2×10^5m^3 per year (Nriagu et al., 1983). In 1987, the TRCA began to monitor the dredged sediment for parameters such as trace metal concentrations. These concentrations also provide an overview of the historical trends of metal concentrations in sediment (TRCA, 2014). The dredged sediment concentration from 1987 – 2012 are shown in Figure 21, Figure 22, and Figure 23.
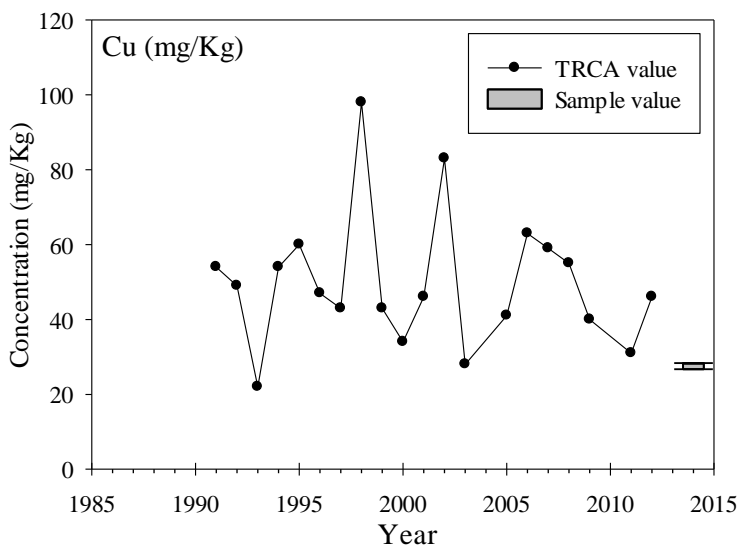
Figure 21 Copper concentrations (mg/kg) in the dredged Keating Channel sediment from 1991-2012 showing a decreasing trend (Data from TRCA, 2014). The sediment sampled in this study has a copper concentration of 28 mg/kg for 2014 and is in good agreement with the suggested trend.
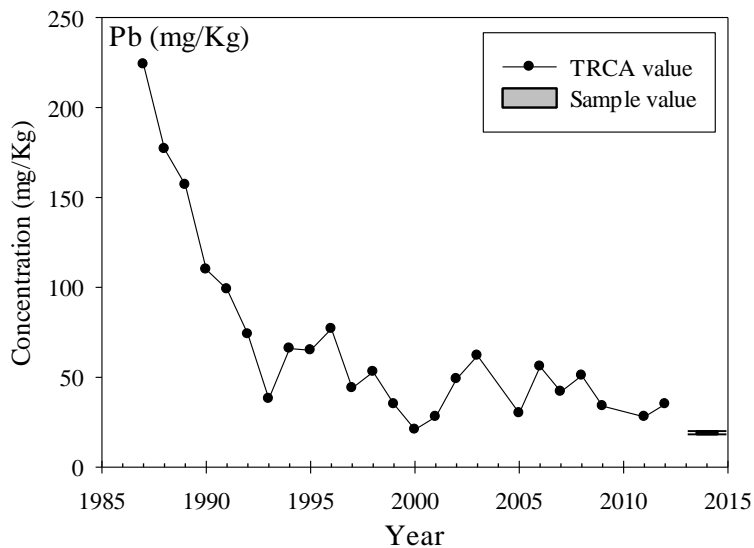
Figure 22 Lead concentrations (mg/kg) in the dredged Keating Channel sediment from 1987-2012. Data show a drastic decease in lead from 1987 to 1993 followed by a slower decreasing trend (Data from TRCA, 2014). The sediment sampled near Keating Channel in this study has a lead concentration of 19 mg/kg for 2014 and is in good agreement with the suggested trend.
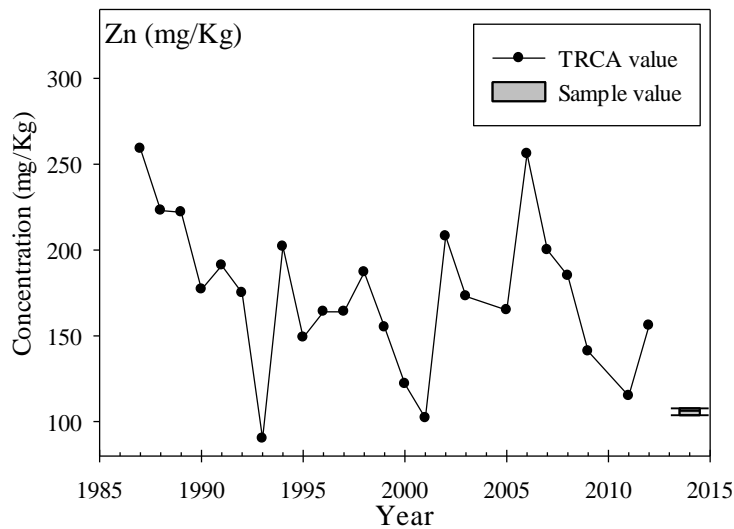
Figure 23 Zinc concentrations (mg/kg) in the dredged Keating Channel sediment from 1987-2012. Data points suggest a decrease in zinc concentrations from 1987 to 1993 followed by a slight increase in concentrations (Data from TRCA, 2014). The sediment sampled near Keating Channel

in this study has a zinc concentration of 106 mg/kg for 2014 and is in good agreement with the suggested trend.

Based on the data it appears as if the copper concentration have decreased in the last 24 years. Zinc shows a decrease in the first several years of monitoring before showing a possible increase. This may reflect improvements made in the wastewater treatment and runoff management of the area. The lead concentrations show the most drastic improvements which likely reflect the phase out of fuel additives in fuels starting in the 1980s. These findings reject the hypothesis that trace metals concentrations increase in sediments from 2000 to 2014 due to growing population density. The sediment samples taken near the mouth of the river in this study is included as 2014 sediment and show good conformity to the dredged concentrations. The lower core taken in this study shown in Figure 12 have unclear sedimentation rates that may have been subjected to mixing in the area. However, it does show an increase in metal concentrations compared to the upstream core, evidence of metal enrichment throughout the Don. Temporal trends are likely better drawn from the long term dredged sediment data from the TRCA in the Lower Don area.

5.2.2 Sequential extraction

Metals have different complexation mechanisms with different components of sediments and soils. Sorption is the transfer of ions such as Cu, Pb, and Zn from the aqueous phase to a solid phase such as a mineral surface. Sequential extractions characterize the heavy metals in the sediment and provide mobility information about the metal as well as provide information about their speciation. The main sediment phases examined using the Tessier (1979) method include exchangeable, carbonate associated, oxides, organics, and residual. Important environmental parameters that influence metal sorption to sediment surfaces from the dissolved phase are pH, pE, temperature, complexing agent concentration, metal concentration, metal speciation, and ionic strength.

Copper appears to be most strongly associated with the organics and the residual phase as seen in Figure 15. This agrees with the findings of Warren and Zimmerman (1994) that found coppers preference for the oxidizable phase. Bradl (2005) also indicate that copper in soils and sediment are primarily complexed with soluble organics in the form of humic acids. The copper partitioning shows spatial differences within the watershed. The top of the watershed near the headwater on both the east and west branch appear to have a large fraction of copper in organics and oxides. Moving southward, the midsection of the watershed shows a shift to most of the copper in the residual phase followed by oxides in the West Don.

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The East Don show a different shift toward a more equal distribution of copper in the organics, residual, and carbonate phases. In the lower half of the watershed the concentration were mostly in the organics phase. Copper loosely sorbed to the exchangeable phase are only seen in the northern part of the Eastern Don River.

Lead appears to be most strongly associated with the oxides and the residual phase as seen in Figure 16. Warren and Zimmerman (1994) also found that lead most strongly partitioned to the oxides. The upper segments of the river in both branches show the majority of the lead in the residual phase. In the mid-section of the watershed, the samples in the west branch are mostly in the oxides and carbonate phase and then shifts again to mostly oxides and residuals more downstream. The east branch data show the lead in mostly the residual and oxide phase. The concentration in Taylor Massey Creek was almost all in the residual phase. After the point in which the two branches merge, the lower Don sample had the concentration equally distributed to the oxides and residual phase. A small concentration of lead in the exchangeable phase was in samples throughout the river.

Zinc concentrations appears to be the most strongly associated with the oxide phase overall (Figure 17) within the watershed which is consistent with the findings from Warren and Zimmerman (1994). The partitioning of the zinc concentration were more consistent throughout the watershed compared to copper and lead. In the upper watershed of both branches of the river, zinc showed a fairly even distribution to the oxide and residual phase. Further downstream in both the east and west branches, there is a shift to most of the concentration associated with the oxide phase followed closely by residuals and carbonates in equal amounts. The two branches merge and the distribution pattern of the zinc concentration continues. Zinc in the exchangeable phase of the extraction are only seen in one sample at a very low proportion.

The spatial comparison conducted by Warren and Zimmerman (1994) showed little difference in their associations with all the metals between each site. This is likely a result of only having four sampling locations as well as using an average of multiple sampling times. In an oxic, high pH system such as the Don, temperature was found to be the most important factor influencing the partitioning of the metal to sediment. An increase in temperature was found to increase the partitioning to solid particulate matter (Warren & Zimmerman, 1994). During the winter months a higher concentration of sodium and chloride was found throughout the system due to the use of deicing agents and caused trace metals to remain in the dissolved form (Warren & Zimmerman, 1994).

There are very few or low concentrations of all three metals in the exchangeable phase. This agrees with Filgueiras et al. (2002) that found exchangeable generally represent less than 2% of the total metals in sediment. The exchangeable phase is the most loosely bound to the surface and the most easily desorbed. The few sites to which there were metals sorbed to the exchangeables were mainly near the headwater of the river. These correspond to areas that have lower ionic conductivity. In the more urban areas the freshwater have higher ionic strengths that may outcompete the metals on the solid surface. The sampling in this study was done in April and higher than average salt concentration is expected in the river from the deicing agents in the snowmelt. Most particulates are thought to be coated by oxides or organics that bind the metal in the dissolved phase. The binding is likely dependent on the concentration of the surface group since pH is consistent in the system.

Lead and zinc show a strong affinity to oxides, which are abundant in freshwater environments. Sorption to Fe and Mn oxides is competitive and can form multiple complexes. It is important to note that the oxide phase is sensitive to pE change and sediment that is transported downstream by the Don River may be released into the Toronto Harbour. Suspended particulate solids that reach the harbor may settle into the reducing anaerobic environment to eventually release their metal concentrations back into solution (Warren and Zimmerman, 1993). Surveys of the benthic community conducted more recently near the Keating Channel and in the Toronto harbor show indicators of eutrophic conditions (Duncan Boyd et al., 2001).

Copper appeared to rely mostly on organic matter while lead and zinc rely on oxides. Organic matter and oxides often coat suspended particulate matter which in turn influence the mobility of these metals. Errors in this experiment include the average recovery of the CRM that show an over recovery of approximately 23% for zinc concentrations. The sediment samples are initially dried, which may cause the overestimation of all the metals in the oxide fraction from the exchangeable and carbonate fraction (Rao, Sahuquillo, & Lopez Sanchez, 2007).

Chapter 6
Summary and Conclusion

Surface water and sediment in the Don River Watershed were examined to determine the patterns and mobility of urban metal pollutants in heavily urbanized watershed. Understanding the fate and transport of metals in urban areas is important for future management and decision making. The Don River watershed is the most urbanized watershed in Canada, but published studies examining trace metals are limited and dated. Long term monitoring data collected through multiple government agencies are often sparse and inconsistent. This study attempts to synthesize available data sets with new analyses, with a focus on copper, lead, and zinc. Surface water and sediment data are examined for spatial and temporal patterns. Sediment metal concentrations are also examined for their geochemical associations to provide information on their fate and availability.

The unfiltered surface water samples have undetectable copper and lead concentrations but zinc concentrations are above the provincial water quality guidelines in several locations. These areas are spatially spread out with the highest concentrations in the Upper West and German Mills subwatersheds. Data collected by the TRCA and PWQMN from 2008 – 2011 at six monitoring sites include many copper, lead, and zinc concentrations above guideline levels. The comparison of monitoring locations suggests elevated trace metal levels within the Lower Don River, Lower East River, and Taylor Massey Creek. Statistically, only the Lower Don River exhibited elevated concentrations of copper compared to all upper river segments. Long-term freshwater data for copper and zinc concentrations are only available from PWQMN in the Lower Don River. The site incorporates 12 years of data. No statistical difference between years could be detected despite the increasing urbanization and increasing annual rainfall. Lead concentrations are below detection and not discussed further.

Based on the consistently high pH of the Don River and its tributaries, trace metals are expected to be mostly bound to suspended particulate matter. Suspended solids increase significantly during wet weather events indicating the importance of runoff as a source of SPM and trace metals to the river. The metal concentrations in water samples collected in this study are mostly below the detection limits due to the lack of precipitation events in the days prior to sampling. The water monitoring data show higher trace metal concentrations in the lower river segments. This is due to accumulation effects, high percentage of impervious surfaces, high road density, and the presence of the wastewater treatment plant. Limited and uneven annual sample sizes hinders the statistical detection of temporal trends.

The concentrations of suspended solids that enter the river depend on rainfall which, in turn, changes seasonally. The 12 year PWQMN data separated by season show that the highest copper and zinc concentrations are observed in summer months and the lowest concentrations in winter. However, a study conducted by the TRCA found that the highest concentrations of copper and zinc generally occur during winter and spring. Spring experiences a high frequency of rain events that potentially supply more metal sorbed to suspended solids, while in winter high salt concentrations influence metal desorption. The PWQMN data were sampled independently of rain events 9 – 20 times annually and include limited winter samples. The long term surface water monitoring data don't show a change in copper and lead concentrations over time but the data are insufficient to draw major conclusions.

The total copper concentrations are above the Lowest Effect Level (LEL) in 17 sediment samples taken within the Don River while total lead and zinc concentrations are all below the LEL. Spatially, the elevated copper concentrations are mostly within the Lower Don River, Lower West Don River, and Taylor Massey Creek. Similarly, the highest concentrations of lead and zinc are found in the Lower Don and Taylor Massey Creek. This pattern is roughly in agreement with the few sediment samples taken by the OGS in the winter of 2008 that found the highest concentrations in the Lower Don River. Other comparisons could not be made due to the limited number of studies on Don River sediment geochemistry.

Areas with higher metal concentrations correspond to areas with high surface water trace metal concentrations. Suspended particulates contribute to sediment concentrations once they settle to the river bottom. Taylor Massey Creek exhibits the lowest discharge rate. Correspondingly this is where the enriched metal concentrations are found along the creek. The Lower Don River has high discharge rates except by the mouth near Keating Channel, this area also has enriched metals concentrations. The sediment samples collected in this study and the OGS samples show similar spatial patterns but both are limited to only one sampling event. More samples need to be taken to delineate the spatial metal distribution in bottom sediment of the Don River and its tributaries.

Long term trends for trace metals in sediment are examined through core samples. The 9 cm sediment core taken near the headwaters of the East Don River reveals a low and stable temporal trend for copper, lead, and zinc. Closer to the mouth of the Don River, the 18 cm core taken shows a more sporadic distribution with the exception of the upper 7 cm showing a possible decrease in copper, lead, and zinc

concentrations. The area near the mouth of the river likely experiences highly variable sedimentation rates and the sediments are likely mixed due to dredging activity. The annually dredged sediment in and near Keating Channel likely provides a more accurate record of the temporal trend in sediment quality. It shows a decreases in copper concentrations and a decrease in zinc concentrations from 1987 to 1993, before suggesting a potential increase after 1993. Lead appears to have drastically decreased from 1987 to 1993 and then stabilizes. There is a good correlation observed between metal concentrations and organic matter in the Lower Don core. Thus organic matter content in the sediment controls the total copper, lead and zinc concentrations. The same correlation is not seen in the Upper Don core likely due to the overall lower concentrations in the area.

The geochemical speciation of the trace metal sorbed to sediment provide information on their mobility and bioavailability. The exchangeable phase is the most loosely bound form and generally represents very small amounts of metal in the sediments. Trace metals in the exchangeable phase were generally found in the upper watershed. These areas are near the headwater and have lower ionic conductivities, and therefore less competition for sorption sites by major cations. Overall, copper preferentially associates with the organic fraction while lead and zinc prefer to sorb to oxides. This is in agreement with various fractionation studies conducted on trace metals. Both organic matter and oxides exist as coatings on suspended particulate matter. This makes it possible for metals to move downstream to be flushed out of the watershed, degrade or reduce, and re-release into solution. Lead speciation is found at low concentrations throughout the Don River. Speciation is often difficult to determine as lead concentrations are often below the ICP-OES detection limits.

Currently surface water monitoring is independent of weather events and occur every third week of the month. This likely misses important rain events that bring in large amounts of contaminants into the river. Event-based sampling is recommended for spatial comparisons to ensure concentrations high enough for comparison. The samples being taken don't represent annual concentrations accurately enough for comparisons between years and not enough samples are taken per month to currently be able to compare by season. Increased event-based surface water monitoring in one season every year is recommended for temporal comparisons. There are very few sediment data available for the Don River. Lab analysis of the dredged material at the Don River outflow should continue even with proposed improvements in the areas of the river mouth area as it is the most consistent temporal data. Addition sediment speciation studies should be conducted along with bioassays using river sediment. Temporal metal concentration data

suggest that metals may no longer be a concern. Continuing forward, studies analyzing emerging contaminants such as nanoparticles and pharmaceutical within the Don River should be investigated.
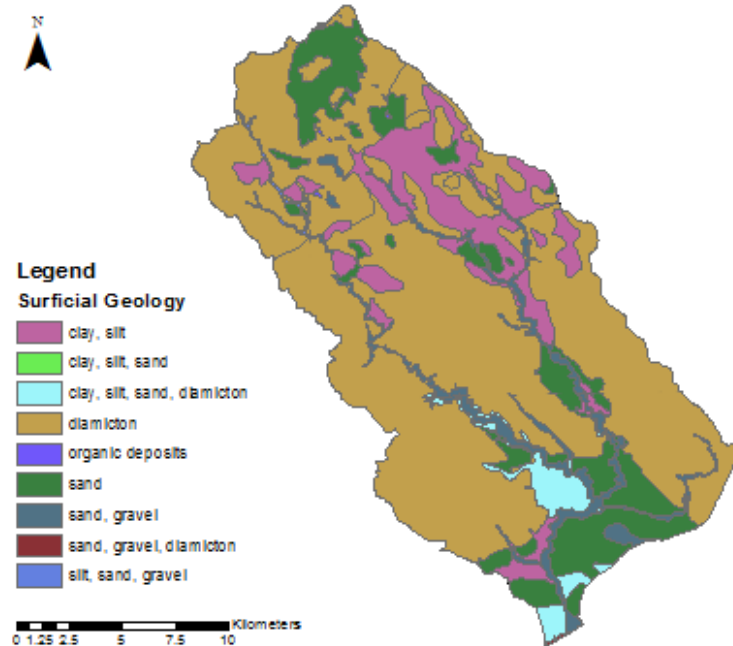
Appendix A
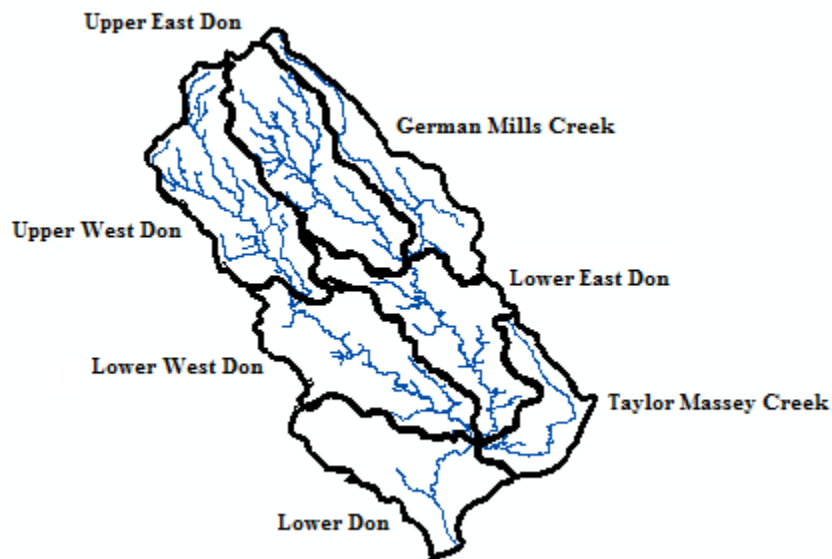
Figure A1 Don River subwatersheds delineation; Upper West Don, Upper East Don, German Mills Creek, Lower West Do, Lower Est Don, Taylor Massey Creek, and Lower Don. Mapped using ArcMap 10.1.

Figure A2 Environmental Canada weather monitoring stations in and near the Don River watershed. Mapped using ArcMap 10.1.

Figure A3 Surficial geology within the Don River watershed. Northern segments of the river show large areas of clay and silt while the southern portion show sand dominant sediments. Mapped using ArcMap 10.1. (Ministry of Northern Development, Mines and Forestry, 2003)

Table A1 Subwatershed water budget based on PRMS modelling studies (TRCA, 2012)

Subwatershed	Area (Km²)	Imperv. surface (%)	Precip. (mm)	Surface runoff (%)	Ground-water infiltration (%)	Evapotran-spiration (%)
Lower Don	38	33	865	31	15	55
Taylor Massey	34	37	872	33	14	53
Lower East Don	54	35	878	32	14	54
Lower West Don	64	31	871	32	16	52
Upper West Don	58	30	880	29	14	57
Upper East Don	63	19	902	25	19	57
German Mills	42	31	896	31	16	54
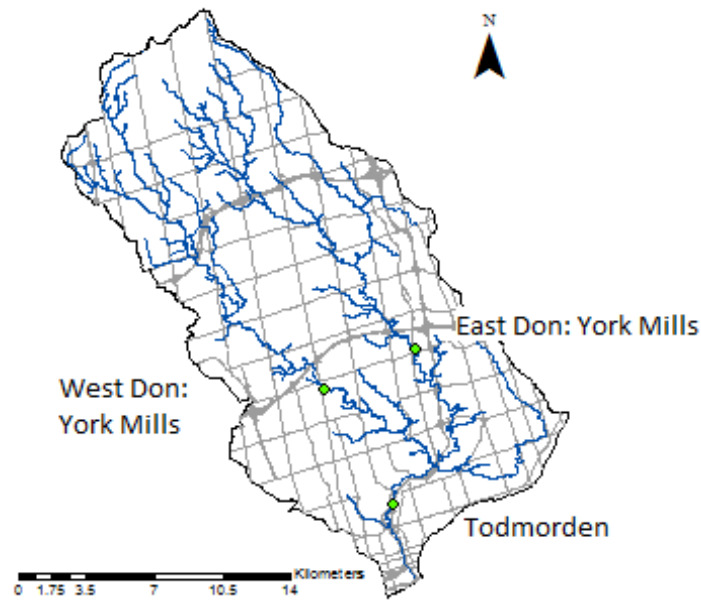
Figure A4 Water Survey Canada (WSC) stream gauge locations within the Don River. Mapped using ArcMap 10.1.
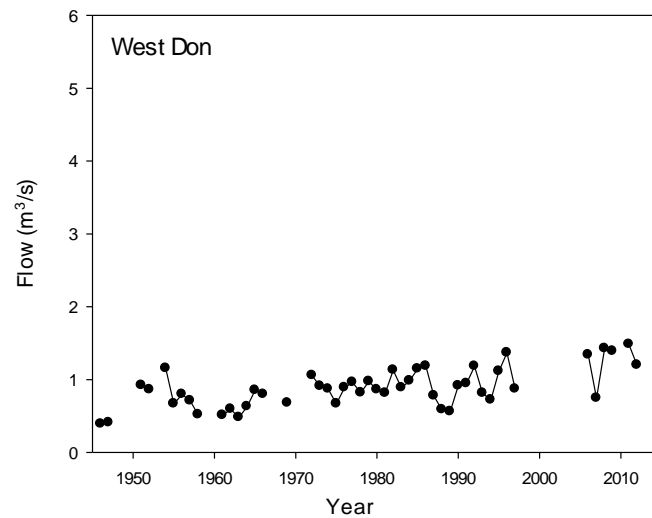
Figure A5 Average annual flow (m³/s) in the West Don (02HC005) location from 1946 to 2012. Missing data from 1948-1950, 1953, 1959, 1960, 1967, 1968, 1970, 1971, 1998 – 2005, and 2010. Available data show an increasing trend in discharge within the West Don River.
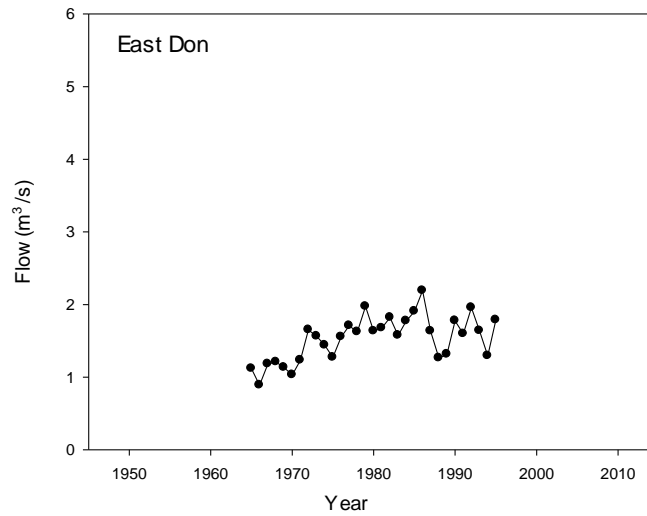
Figure A6 Average annual flow (m³/s) in the East Don (02HC029) location from 1965 to 1995. Data show an increasing trend in annual discharge rates in the East Don River.
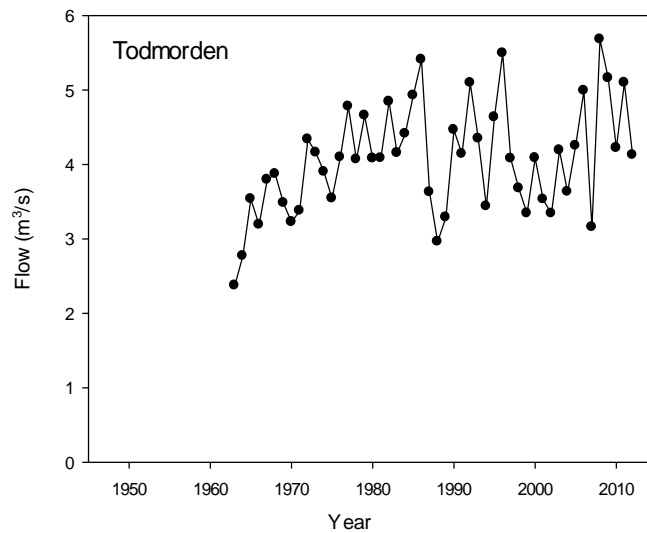
Figure A7 Average annual flow (m³/s) in the Todmorden (02HC024) location from 1963 to 2012. Data show an increasing trend in annual discharge rates in the Lower Don River.

Table A2 Don River watershed permit to pump 2003 data. (TRCA, 2009a)

Subwatershed	Surface (10^6 L)	Ground (10^6 L)	Both (10^6 L)	Total (10^6 L)
Lower Don	0	134	-	1445
Taylor Massey	-	-	-	-
Lower East Don	151	0	-	151
Lower West Don	31	142	-	173
Upper West Don	403	1042	30	1445
Upper East Don	94	1161	-	1291
German Mills	0	21	-	21
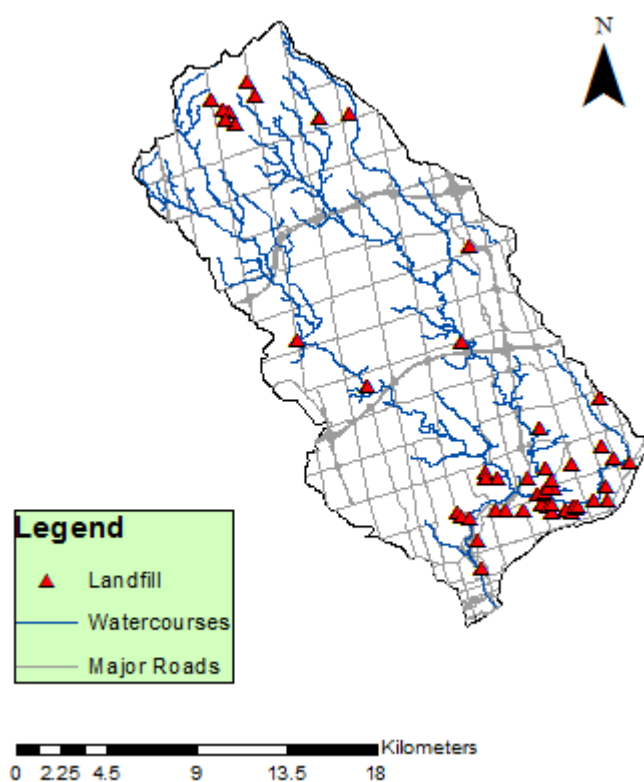
Figure A8 Past landfill and dump site locations within the Don River Watershed. A large cluster of closed landfills and dumpsites are shown located along Taylor Massey Creek. Mapped using ArcMap 10.1.
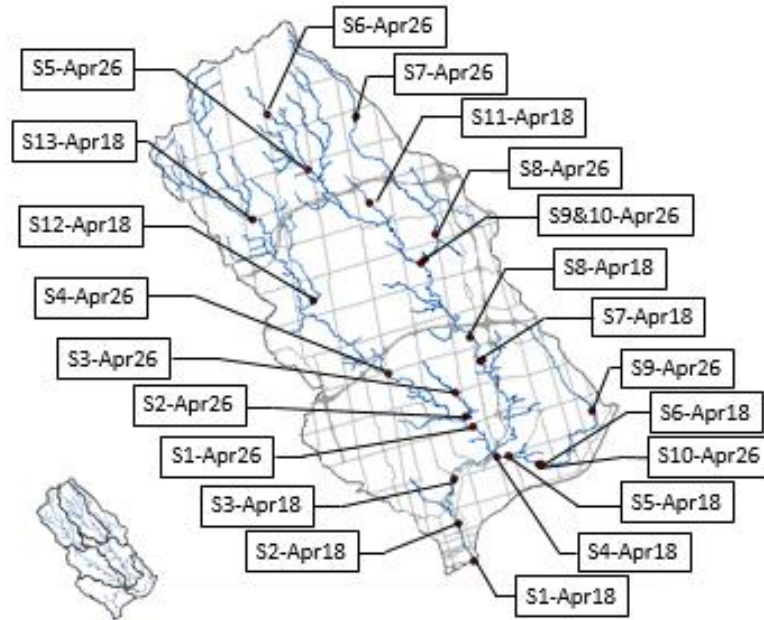
Figure A9 Twenty-two Sediment and water sampling locations in the Don River taken on April 18th and 26th 2014. Mapped using ArcMap 10.1.

Table A3 Surface water zinc concentrations (ug/L). Samples were microwave digested with aqua regia, diluted, and analyzed by ICP-OES.

	Zn conc (ug/L)	Zn SD
S1-Apr18	13	1.21
S2-Apr18	22	0.09
S3-Apr18	11	-
S4-Apr18	20	1.05
S5-Apr18	12	5.34
S6-Apr18	3	0.05
S7-Apr18	5	1.35
S8-Apr18	5	0.16
S9-Apr18	49	4.96
S10-Apr18	12	0.39
S11-Apr18	32	4.56
S12-Apr18	74	-
S13-Apr18	-	-
S1-Apr26	7	4.50
S2-Apr26	26	3.01
S3-Apr26	35	10.06
S4-Apr26	11	5.16
S5-Apr26	14	4.98
S6-Apr26	9	3.55
S7-Apr26	19	9.72
S8-Apr26	6	0.80
S9-Apr26	24	2.08
S10-Apr26	10	6.71

Table A4 Total copper, lead, and zinc concentrations (mg/kg) in sediment grab samples taken in the Don River.

	Cu (mg/kg)	SD	Pb (mg/kg)	SD	Zn (mg/kg)	SD
TEC	32	-	36	-	121	-
PEC	149	-	128	-	459	-
S1-Apr18	28	0.90	19	0.89	106	2.05
S2-Apr18	49	2.94	10	0.52	34	1.05
S3-Apr18	50	4.08	9	0.58	33	2.16
S4-Apr18	48	1.76	5	0.39	22	3.92
S5-Apr18	9	0.73	6	0.15	25	0.36
S6-Apr18	36	3.87	7	0.34	32	1.05
S7-Apr18	-	-	-	-	-	-
S8-Apr18	12	0.81	10	0.39	59	0.54
S9-Apr18	52	4.08	4	0.46	22	1.22
S10-Apr18	4	0.74	7	0.69	30	0.74
S11-Apr18	27	3.23	12	1.01	67	1.91
S12-Apr18	48	2.01	12	6.21	39	1.98
S13-Apr18	3	0.33	5	0.80	24	1.76
S1-Apr26	11	0.31	10	0.93	55	1.00
S2-Apr26	36	4.10	4	0.22	17	0.09
S3-Apr26	47	3.60	5	0.59	28	2.07
S4-Apr26	58	2.99	18	9.15	33	1.01
S5-Apr26	28	2.67	8	0.49	37	1.51
S6-Apr26	32	4.11	9	0.66	41	0.95
S7-Apr26	31	4.40	15	0.51	40	3.15
S8-Apr26	35	0.91	4	0.53	25	0.80
S9-Apr26	62	3.51	17	1.74	87	3.57
S10-Apr26	39	1.75	9	0.62	56	7.71
CRM	76	5.36	115	5.96	309	8.60

Table A5 Total copper concentrations (mg/kg) of sampled sediment compared to sediment values taken by the Ontario Geological Survey.

Cu	OGS Sample (2008)	Grab Sample (2014)
S3-Apr18 (Lower Don)	18	50
S7-Apr18 (Lower East)	10	12
S13-Apr18 (Upper West)	2	3
S5-Apr26 (Upper East)	4	8
S7-Apr26 (German Mills)	4	31

Table A6 Total lead concentrations (mg/kg) of sampled sediment compared to sediment values taken by the Ontario Geological Survey.

Pb	OGS Sample (2008)	Grab Sample (2014)
S3-Apr18 (Lower Don)	35.2	9
S7-Apr18 (Lower East)	15.9	10
S13-Apr18 (Upper West)	1.9	4
S5-Apr26 (Upper East)	7.5	8
S7-Apr26 (German Mills)	6.3	15

Table A7 Total zinc concentration (mg/kg) of sampled sediment compared to sediment values taken by the Ontario Geological Survey.

Zn	OGS Sample (2008)	Grab Sample (2014)
S3-Apr18 (Lower Don)	58	34
S7-Apr18 (Lower East)	73	60
S13-Apr18 (Upper West)	44	24
S5-Apr26 (Upper East)	53	37
S7-Apr26 (German Mills)	48	40

Table A11 Particle size analysis of the 22 sediment samples collected in April 2014.

	Clay (%)	Silt (%)	very fine sand (%)	Fine sand (%)	Medium sand (%)	Coarse sand (%)	Very course sand (%)	Sediment type
S1-Apr18	16	72	12	0	0	0	0	Silt loam
S2-Apr18	5	23	16	33	22	0	0	Sandy loam
S3-Apr18	6	32	22	38	2	0	0	Sandy loam
S4-Apr18	1	3	4	26	38	25	6	Sand
S5-Apr18	29	67	4	0	0	0	0	silty clay loam
S6-Apr18	5	16	8	18	3	0	50	loamy sand
S8-Apr18	12	65	23	0	0	0	0	Silt loam
S9-Apr18	3	10	7	30	50	0	0	Sand
S10-Apr18	7	33	22	37	1	0	0	Sandy loam
S11-Apr18	37	59	4	0	0	0	0	Silty clay loam
S12-Apr18	7	31	6	4	51	1	0	Sandy loam
S13-Apr18	6	25	13	29	27	0	0	Sandy loam
S1-Apr26	9	45	25	21	0	0	0	Loam
S2-Apr26	3	12	3	4	24	42	16	Loamy sand
S3-Apr26	6	16	8	25	33	13	0	Loamy sand
S4-Apr26	1	4	1	4	39	37	17	Sand
S5-Apr26	7	43	20	29	1	0	0	Sandy loam
S6-Apr26	6	71	21	2	0	0	0	Silt loam
S7-Apr26	12	77	12	0	0	0	0	Silt loam
S8-Apr26	5	22	19	38	15	0	0	Sandy loam
S9-Apr26	5	19	3	6	22	13	32	Loamy sand
S10-Apr26	7	31	21	40	2	0	0	Sandy loam
CRM	19	78	2	0	0	0	0	Silt loam
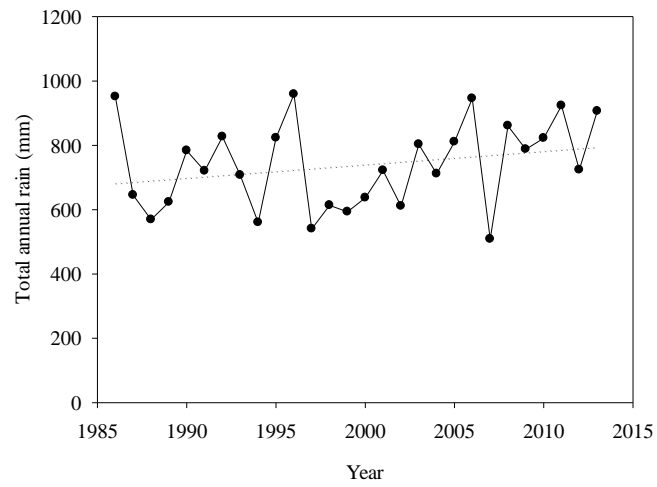
Figure A10. Trend of total annual rain from 1961 - 2013 based on the Environment Canada East York weather station in the Don River watershed.

Appendix B

Sequential Extraction

1. Weight out 1g dry weight sediment into acid washed and MilliQ rinsed 50 mL centrifuge tube

2. Add 8 mL 1 M NaOAc (sodium acetate solution) at pH 8.2 and continuously agitate for 1 hour on a tube rotator at 50 – 60 rpm.

3. Remove tubes from rotator and place in the centrifuge at 5000 rpm for 30 minutes. Remove supernatant with a 10 mL syringe and using a 25mm 0.45 um polypropylene syringe filter, filter supernatant into separate labelled tube. Add 8 mL of MilliQ water back into the tube to wash reagent residue off the sediment. Place tubes with MilliQ back into the centrifuge at 5000 rpm for 30 minutes and pipette MilliQ once complete.

4. Add 8 mL 1M NaOAc (sodium acetate solution) adjusted to pH 5.0 with acetic acid. Agitate on a tube rotator at 50 – 60 rpm for approximately 5 hours.

5. Repeat step 3

6. Add 20 mL of 0.04M $NH_2OH \cdot HCl$ (Hydroxylamine hydrochloride) in 25% v/v HOAc (Acetic acid) into tubes and place in oven at 96 +/- 3°C with occasional agitation.

7. Repeat step 3

8. Add 3 mL of 0.02 M HNO_3 (Nitric acid) and 5 mL of 30% H_2O_2 (Hydrogen peroxide) adjusted to pH 2 with HNO_3. Place tubes in oven at 85 +/- 2°C for 2 hours with occasional agitation. Remove sample from oven and place a second 3 mL aliquot of 30% H_2O_2 pH 2 and place back into oven at 85 +/- 2°C for 3 hours with occasional agitation. Remove the samples from the oven and let cool. Once cooled add 5 mL of 3.2 M NH_4OAc (Ammonium acetate) in 20% (v/v) HNO_3 and 12 mL of MilliQ. Agitate samples on the rotor continuously at 50 – 60 rpm for 3 mnutes.

9. Repeat step 3

10. Dry the sediment and place into Teflon microwave tube. Add 6 mL of HCl and 3 mL of HNO_3 (aqua regia) into tubes and microwave digest sediment sample using the sediment method.

11. Once microwave digestion is complete, remove and let cool. Pour solution from Teflon tube into new centrifuge tube using 0.45 um filter paper.

12. Dilute all samples 1:3 into ICP tubes for analysis

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