Trace Element Occurrence in Wastewater and Effects on Surface Water Quality in the Laurentian Great Lakes and the Grand River, Ontario

by

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Abstract

Wastewater treatment plays an integral role in maintaining surface water quality in industrialized societies around the world. Wastewater effluent and sewage sludge can both be important vectors of contaminants that are not fully eliminated during treatment, and thus understanding effluent and sludge composition is key to preventing deleterious environmental impacts to receiving environments. Trace elements are one important class of contaminants in wastewater, as their increased use in industrialized societies is reflected in their growing occurrence in anthropogenic waste streams globally**.** Yet, the potential large-scale sources of trace elements to wastewater and their behavior during wastewater treatment remain poorly understood and potential environmental impacts on receiving environments therefore unclear. Because only a handful of specific parameters in wastewater and sludge are regulated in Canada, not including many trace elements, monitoring of their occurrence and potential impacts is crucial. In this thesis, >40 wastewater treatment facilities in the North American Great Lakes basin were screened for major and trace elements and a black-box approach was deployed to calculate representative estimates for average per-capita trace element loads and basin-scale effluent discharge rates, as well as trace element removal efficiencies across different wastewater treatment technologies. In addition, I report concentrations of major and trace elements in >30 riverine and effluent samples collected in the Grand River catchment, Ontario, in an attempt to assess imprints of effluent discharge on riverine trace element loads. The findings of this thesis demonstrate the effectiveness of wastewater surveillance for a quantitative exploration of anthropogenic versus geogenic trace element emissions and highlight its value to further the understanding of the

current state of contaminants in wastewater and sewage sludge and their behavior during the wastewater treatment process.

Co-Authorship

Chapter 1, which is the introduction to this thesis, is original own work, with support, guidance, and edits provided by Dr. Bas Vriens.

Chapter 2 of this thesis includes the manuscript and supporting information of a first paper, published in the peer-reviewed journal Water Research. This chapter includes two co-authors, Bailey S. Jones and Dr. Bas Vriens. Bailey S. Jones contributed to the research of this chapter, specifically the geospatial sewershed modelling, and dr. Vriens contributed to the research, analyses and writing of this chapter.

Chapter 3 of this thesis contains the manuscript and supporting information prepared for publication in the peer-reviewed Journal of Environmental Quality. This chapter includes co-authorship between Dr. Bas Vriens and myself. Similar to chapter 1, Dr. Vriens provided assistance with research and data analysis as well as preparation of figures and manuscript text.

Chapter 4 contains general conclusions originating from this work and recommendations for future research and is own original work.

Statement of Originality

I hereby state that this thesis is the original work of the author. To my knowledge, this thesis contains no published or unpublished material written by another person, except where credit is explicitly stated.

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List of Abbreviations

Ag	Silver
Al	Aluminum
AOC	Area of Concern
Ar	Argon
As	Arsenic
Au	Gold
B	Boron
Ba	Barium
Be	Beryllium
Bi	Bismuth
BOD	Biological oxygen demand
Br	Bromine
C	Carbon
Ca	Calcium
$CaCO_3$	Calcium carbonate
CCME	Canadian Council of Ministers of the Environment
Cd	Cadmium
Ce	Cerium

CEC	Contaminants of emerging concern
CEPA	Canadian Environmental Protection *Act*
CFI	Canadian Foundation for Innovation
Chlor	Chlorination
Cl	Chlorine
cm	Centimetres
Co	Cobalt
Cr	Chromium
CSO	Combined sewer overflow
Cu	Copper
CWNS	Clean Watersheds Needs Survey
d	Day
D-Chlor	Dichlorination
Denitr	Denitrification
DIC	Dissolved inorganic carbon
DO	Dissolved oxygen
Dy	Dysprosium
e.g.	Example

EC	Electrical conductivity
ECCC	Environment and Climate Change Canada
Er	Erbium
Eu	Europium
F	Fluorine
Fe	Iron
Fe^{+2}	Ferrous iron
g	Gram
Ga	Gallium
Gd	Gadolinium
Ge	Germanium
GLNPO	Great Lakes National Program Office
GLWQA	Great Lakes Water Quality Agreement
H	Hydrogen
H_2O_2	Hydrogen peroxide
ha	Hectares
HCl	Hydrochloric acid
HDPE	High density polyethylene

He	Helium
Hf	Hafnium
HF	Hydrofluoric acid
Hg	Mercury
HNO_3	Nitric acid
Ho	Holmium
i.e.	That is
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
IJC	International Joint Commission
In	Indium
Ir	Iridium
K	Potassium
KED	Kinetic energy discrimination
kg	Kilogram
km	Kilometre
km^2	Kilometres squared
km^3	Kilometres cubed

L	Litre
La	Lanthanum
LDPE	Low density polyethylene
Li	Lithium
LOD	Limit of detection
Lu	Lutetium
m	Metres
m/z	Mass divided by charge number
m^2	metres squared
m^3	metres cubed
Mech-Biol	Mechanical Biological
Mg	Magnesium
mg	milligram
mL	millilitres
mm	millimetres
Mn	Manganese
Mo	Molybdenum
mS	Millisiemens
MΩ	Megaohm

N	Nitrogen
n	population/number of samples/number of values
N/A	Not applicable
Na	Sodium
Nb	Niobium
Nd	Neodymium
ng	nanogram
Ni	Nickel
Nitr	Nitrification
NLCD	National Land Cover Database
O_2	Oxygen
Oz	Ozonation
P	Phosphorus
PAAS	Post-Archean Australian Shale
Pb	Lead
Pd	Palladium
P-elim	Phosphorus elimination
PGE	Platinum Group Element

PO_4	Phosphate
ppb	Parts per billion
ppm	Parts per million
Pr	Praseodymium
Pt	Platinum
PTFE	Polytetrafluoroethylene
PWQMN	Provincial Water Quality Monitoring Network
PWQO	Ontario Provincial Water Quality Objectives
Rb	Rubidium
Re	Rhenium
REE	Rare Earth Element
RMSE	Root mean squared error
RSD	Relative standard deviation
Ru	Ruthenium
s	Seconds
S	Sulfur
Sb	Antimony
Sc	Scandium

Se	Selenium
Si	Silicon
Sm	Samarium
Sn	Tin
SO_4	Sulfate
Sr	Strontium
Ta	Tantalum
Tb	Terbium
TDS	Total dissolved Solids
Te	Tellurium
Ti	Titanium
Tl	Thallium
Tm	Thulium
TPY	Tonnes per year
TQ-ICP-MS	Triple quadrupole-inductively coupled plasma-mass spectrometer
U	Uranium
US	United States
USEPA	United States Environmental Protection Agency

USGS	United States Geological Survey
UV	Ultraviolet
V	Vanadium
W	Tungsten
WSER	Wastewater Systems Effluent *Regulations*
WWTP	Wastewater Treatment Plant
Y	Yttrium
Yb	Ytterbium
yr	Year
Zn	Zinc
Zr	Zirconium
µg	Microgram
µL	Microlitre
Σ	Sum
°C	Degrees Celsius

Chapter 1: Introduction

1.1 The Great Lakes

The five Laurentian Great Lakes (Superior, Michigan, Erie, Huron, and Ontario; **Figure 1.1**) sit on the boarder of Canada and the United States and have shoreline on one Canadian province (Ontario) and eight US states (New York, Pennsylvania, Ohio, Michigan, Indiana, Illinois, Wisconsin, and Minnesota). The lakes have a combined surface area of 245,643 km^2, a volume of 22,779 km^3, and span roughly 1200 km from east to west (**Table 1.1**), making them one of the largest resources of liquid fresh surface water on Earth, containing >20% of the worlds available amount (United States Environmental Protection Agency & Government of Canada, 1995). The Great Lakes drainage basin (watersheds + lakes) is 501,097 km^2 and houses approximately 38 million people, making up roughly 8% of the US population and 32% of the Canadian population (Fergen et al., 2022). The nearly 23,000 km^3 of water contained by the lakes has provided water for transportation, consumption, power generation, and recreation for centuries. The climate, soil types, topography, and geology in the basin vary widely, resulting in the opportunity for many different industries such as automobile manufacturing, steel production, forestry, mining, and agriculture to thrive in the basin, taking advantage of accessible shipping routes through its connecting channels and ultimately to the St. Lawrence River and Atlantic.

The southern region of the Great Lakes basin surrounding Lake Erie and Ontario is relatively temperate and contains soils with deep layers of fertile clay, silts and sands underlain by gently dipping Paleozoic sedimentary rocks (United States Environmental

Protection Agency & Government of Canada, 1995; Larson & Schaetzl, 2001). This region accounts for nearly 25% of Canadas agricultural production and 7% of American production, and houses some of North America's largest cities such as Toronto and Chicago (United States Environmental Protection Agency & Government of Canada, 1995). The northern portion of the Great Lakes basin is colder, less fertile, and the landscape is dominated by exposed granite of the Canadian Shield as well as thinner acidic soils overgrown by coniferous forest (United States Environmental Protection Agency & Government of Canada, 1995). The northern region is home to several important industries, including forestry and mining. Geologically, the northern region is dominated by the Precambrian granite, gneiss, metavolcanic, and metasedimentary rocks of the Canadian Shield (Larson & Schaetzl, 2001). Overall, the origin of the basin's shape and drainage patterns can be attributed to multiple late Cenozoic glaciations which channeled ice flow along pre-existing bedrock valley systems, and their subsequent retreat (Larson & Schaetzl, 2001).

The Great Lakes form a uniquely hydraulically connected system of lakes (**Figure 1.1**) that are often treated as one. However, each lake is also unique. Lake Superior has the highest elevation (183 m), is the deepest (max depth of 406 m) and has the largest volume (12,115 km^3), containing more water than all other lakes combined (**Table 1.1**). Because of its size and lack of surrounding agriculture or development, Lake Superior contains the lowest concentrations of salts and human contaminants compared to the other lakes (**Table 1.2**; see also below). The second largest lake is Michigan with a volume of 4,947 km^3, which is the only lake which lies entirely in the United States. Lake Michigan's watershed is host to major cities such as Chicago (partly in the Mississippi

basin), Milwaukee and Green Bay. Lake Huron is the third largest with a total volume of 3,567 km^3 and is home to the largest bay in the Great Lakes, the Georgian Bay. Lake Erie is the smallest of the lakes in total volume at 499 km^3 and is by far the shallowest with an average depth of only 20 m. This shallow nature along with its southern location and warmer climate result in Lake Erie being the most affected by eutrophication from agriculture and urbanization (United States Environmental Protection Agency & Government of Canada, 1995). The last lake in the sequence, Lake Ontario, has the smallest surface area at 18,960 km^2, and like Lake Erie it is greatly impacted by agriculture and urbanization. Lake Ontario's watershed houses major urban and industrial hubs such as Toronto and Hamilton. The physical characteristics of each of the Great Lakes are summarized in **Table 1.1**. The five Great Lakes and their watersheds all have distinctive characteristics that when looked at in totality, make them a complex and unique hydraulic system.

Table 1.1 *Physical characteristics of each of the five great lakes including elevation, drainage area, surface area, volume, average depth, maximum depth, outflow, and residence time. Adopted from (Chapra, Dove, & Warren, 2012).*

Basin	Elevation (m)	Drainage Area (km^2)	Surface Area (km^2)	Volume (km^3)	Maximum Depth (m)	Outflow (km^3/yr)	Residence Time (yr)
Superior	183	127,687	82,103	12,115	406	67	180
Michigan	176	115,804	59,600	4,947	282	50	110
Huron	176	131,313	59,750	3,567	229	167	21
Erie	173	62,263	25,220	499	64	188	3
Ontario	74	64,030	18,960	1,651	244	220	8
TOTAL	**-**	**501,097**	**245,633**	**22,779**	**-**	**693**	**322**

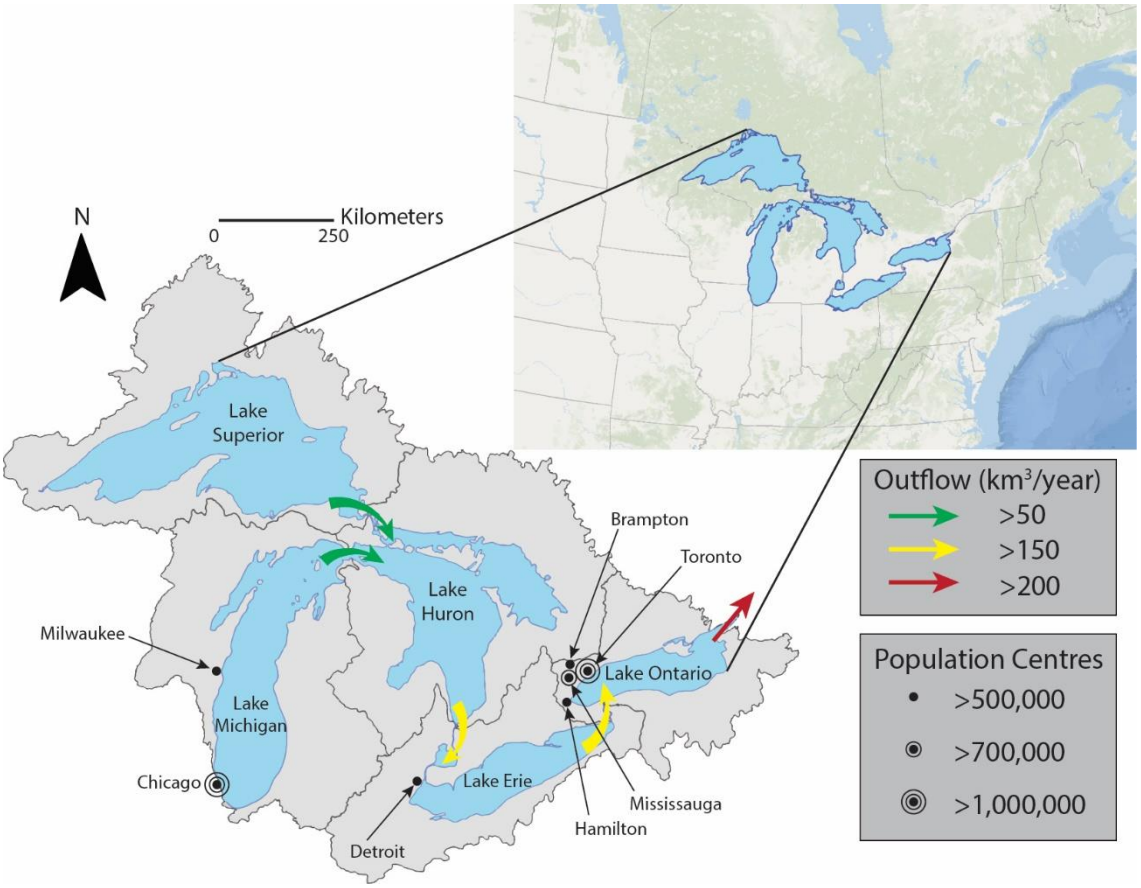

Figure 1.1 *Location of the Great Lakes within North America, as well as the major population centres within its basin and the outflow volumes of each lake. Legends on the bottom right show the relative size of the population centres as well as the volume of the outflows. A north arrow can be found on the top left, and a scale bar on the bottom middle of the figure.*

1.2 Great Lakes Water Quality

For decades, the Great Lakes have experienced many forms of contamination from numerous natural and anthropogenic sources such as salinification from road salt application (Chapra et al., 2009; Dugan et al., 2017), eutrophication and seasonal algal blooms (Ho & Michalak, 2017) and legacy pollution issues at designated “areas-of-

concern” (Hartig et al., 2020). Deterioration of water quality in the Great Lakes was first comprehensively addressed in the Great Lakes Water Quality Agreements (GLWQA) of 1972 and its amendments in 1978 and 2012, although concerns about serious eutrophication had been expressed as far back as the 1960’s (International Joint Commision United States and Canada, 1987; Pinto et al., 1986). The GLWQA were created by the International Joint Commission (IJC) of the United States and Canada with the general purpose of restoring and maintaining the chemical, biological and physical integrity of the waters of the Great Lakes (International Joint Commision United States and Canada, 1987). Particular focus of the GLWQA has been, and still is, the remediation of legacy contamination from the age of the industrial revolution, which has had significant impact on the industrial waterfronts of many cities along the shores of the Great Lakes (International Joint Commision United States and Canada, 1987).

Today, the water quality of the Great Lakes, its connecting channels and many of its tributaries is monitored at various scales by federal agencies such as Environment and Climate Change Canada (ECCC) and the U.S. Environmental Protection Agency’s Great Lakes National Program Office (GLNPO), among others. Environment and Climate Change Canada conducts biyearly ship-based sampling programs consisting of 334 sampling locations, including 74 in Lake Erie, 78 in Lake Huron, 96 in Lake Ontario and 86 in Lake Superior (Government of Canada, 2018). Its US counterpart conducts similar ship-based sampling programs (96 sampling sites over the 5 lakes) and does so twice a year in the spring and summer (United States Enviornmental Protection Agency, 2021). A summary of select recent water quality data from the ECCC ship-based sampling program, and a handful from the GLNPO, can be found in **Table 1.2**. Monitoring of Great

Lakes water quality is also done at a provincial/state level by various environmental offices: examples include the Government of Ontario, which invested $10.9 million in 2021 in a multi-year funding effort as part of the Canada-Ontario Agreement on Great Lakes Water Quality and Ecosystem Health, and the Michigan Department of Environment, Great Lakes and Energy (Government of Canada & Government of Ontario, 2021). At a regional/municipal scale, monitoring of smaller water bodies within the Great Lakes watersheds such as tributaries, rivers, and creeks as well as small subsections of the lakes themselves are completed by groups such as Conservation Authorities (e.g., the Grand River Conservation Authority), the Severn Sound Open Water Monitoring Program, or the Hamilton Public Health Services, among others. These monitoring programs are also assisted by the efforts of various research groups (e.g., the Cooperative Institute for Great Lakes Research or the Water Institute at the University of Waterloo) and scientists from numerous academic and non-academic institutions across the basin. The massive effort that is put forth by these various groups can be contextualized by some $4 billion that has been attracted to Great Lakes sustainability projects through the Great Lakes Impact Investment Platform (Great Lakes St. Lawrence Governors & Premiers, 2021).

There are many intra- and inter-lake factors that play a role in governing water quantity and quality in the Great Lakes as a whole, as well as in the variability seen from lake to lake. The main inputs to the water budget of the Great Lakes are atmospheric deposition, connecting channels, and runoff/tributaries, whereas water-balance studies on the Great Lakes have concluded that groundwater fluxes are difficult to measure but could constitute around 0.6-1.3% of yearly basin supply for the five lakes (Neff & Nicholas,

2005; Xu et al., 2021). The percentage of water inflow from atmospheric deposition, connecting channels, and runoff/tributaries respectively are 57%, 0%, and 43% for Lake Superior, 58%, 0% and 42% for Lake Michigan, 25%, 51% and 25% for Lake Huron, 11%, 78% and 11% for Lake Erie and 15%, 70% and 14% for Lake Ontario (Bentley et al., 2022). Overall, the Great Lakes are well-mixed even throughout winter months, turning over completely in the fall and spring (Weiler, 1981). Many physical attributes and aspects of surface water mixing play a role in the observed water quality of the lakes. Aspects such as wave induced mixing (Boegman, 2014), upwelling and thermocline orientation (Weiler, 1981), and the presence of large, shallow, productive bays (e.g. Green Bay, Saginaw Bay) (Weiler, 1981), among others, are thought to have effects on the large scale water quality of the lakes, but are not in the scope of this thesis. Natural river discharge points, also knows as coastal jets, are present in each of the lakes and are of particular importance to this research when compared to previously mentioned mixing aspects, as wastewater treatment plants (WWTP) often release effluent into rivers and streams, that subsequent feed into their receiving lakes (see below). Coastal jets can result in regions of increased ion and contaminant concentrations up to 25 km from the source and are a major influx factor for chemicals in the Great Lakes (Csanady, 1970).

As observed in **Table 1.2**, Lake Superior generally has the most pristine water in comparison to the other four lakes (lowest alkalinity, conductivity, turbidity, phosphorous, nitrogen, and magnesium concentrations), as it is the largest of the lakes in both volume and surface area (**Table 1.1**) and is the least impacted by anthropogenic activity with only ~600,000 watershed inhabitants (United States Environmental Protection Agency & Government of Canada, 1995; Chapra et al., 2012). Lake Michigan is co-first in the

downstream sequence (**Figure 1.1**), but carries a larger imprint of surrounding anthropogenic activities, as its basin is heavily industrialized housing ~13 million people (Chapra et al., 2012). Intermediate concentrations of water quality parameters such as alkalinity, conductivity, turbidity, phosphorous, nitrogen, magnesium and chloride (**Table 1.2**) observed in Lake Huron can be partially attributed to the similar inputs originating from Lakes Michigan and Superior, which lie upstream, as well as intermediate levels of on-shore anthropogenic activity when compared to the two aforementioned lakes with ~3 million inhabitants in its basin (Chapra et al., 2012; Schelske, 1985). Additionally, the heterogeneity of water quality in Lake Huron is complicated by two large bays: the Georgian Bay and Saginaw Bay. Lake Erie is considered to have poorest water quality of the five lakes (evident in the occurrence of algal blooms in the westernmost regions of the lake) due to elevated nutrient concentrations from agricultural runoff, and ~12 million inhabitants in its watershed (Dolan & McGunagle, 2005). Similar to Lake Erie, Lake Ontario experiences poorer water quality when compared to the upper lakes for a number of reasons including intense anthropogenic input from its watershed as well as input from the Lake Erie which is located directly upstream (Effler & Matthews, 2003). Overall, differences in lake quality tend to be the result of variations in anthropogenic activity within the watershed and physical attributes of the lakes such as depth and orientation which effect residence time and mixing.

Site specific legacy pollution in the Great Lakes can be best summed up by the Areas of Concern (AOCs) which were part of the 1987 Great Lakes Water Quality Agreement. This agreement outlines 26 AOCs in the United States, 12 in Canada and 5 binational locations, of which 7 have been remediated and 2 are in recovery (Hartig et al.,

2020). The remaining 34 sites are still considered a risk to the environmental, social, and economic well-being of the local communities and are a critical focus for water quality management and policy development for the Great Lakes region (Environment Canada, 2012). The AOCs are mostly located on the shores of population centres such as Toronto and Milwaukee, in major rivers such as the Detroit and Niagara Rivers, and in bays and harbours such as Saginaw Bay, Presque Isle Bay and Saginaw Harbour. In the 34 active AOCs, elevated levels of toxic anthropogenic chemicals such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are common and listed as an issue at 14 and 23 AOC's, respectively. The main sources of both PCBs and PAHs are listed as industrial discharges, historic manufacturing processes, and improper disposal of consumer products. Heavy metals such as copper, mercury, cadmium, chromium, lead, silver, and zinc are present at elevated levels at 19 locations. Their presence in these AOCs is due to post-industrial and municipal discharge, commercial and residential development, and region-specific activities such as mining (Environment Canada, 2012). Excessive nutrient levels (phosphorous and nitrogen) are listed as a problem at 7 AOCs, mainly because of agricultural runoff from heavily farmed areas. Other water quality issues in the AOCs include bacteria, particularly coliform bacteria, introduced by wastewater effluent, as well as suspended solids. Although the abovementioned contaminants are of great importance, they are not the only pollutants that need to be accounted for in the Great Lakes system. Current water quality issues include salinification from road salt application (Chapra et al., 2009; Dugan et al., 2017), eutrophication and seasonal algal blooms (Ho & Michalak, 2017), among others. Contaminants of emerging concern (CEC) such pesticides, pharmaceuticals, flame

retardants, plasticizers, and solvents are now being increasingly monitored (Elliott et al., 2017). However, as discussed below (section 1.5), anthropogenic trace metals in natural environments are rising at increasing rates and thus it is important for their presence in Great Lakes surface waters to be quantified (Aliff Elliott et al., 2020a, 2020b; Robinson, 2009). Although basin-scale trace metal concentrations have been studied in the Great Lakes in the 1980's (Allan et al., 1991; Rossmann & Barres, 1988) they have not been updated since, and many of the more 'recent' works (e.g., Poulton, 1992; Johnson, 1991; Twiss & Campbell, 1998) are focused on specific sites within the basin. The lack of large-scale monitoring of emerging contaminants in the Great Lakes makes lake-wide baseline calculations almost impossible and therefore an extremely important part in the assessment of Great Lakes water quality moving forward.

Table 1.2 *Select average major water quality parameters for the Great Lakes, including alkalinity, dissolved oxygen, pH, conductivity, turbidity, temperature, and concentrations of phosphorous, nitrogen, magnesium, and chloride. The Environment Canada data (EC) were retrieved from the Government of Canadas Great Lakes Water Quality Monitoring and Surveillance Data web page from their latest ship-based sampling program (August 2018); GLNPO data were retrieved from the US water quality portal and are based on their fall ship-based cruise in August 2018 (United States Geological Survey & United States Environmental Protection Agency, 2022; Government of Canada, 2018). Similar values to those listed from for lakes Superior, Huron, Erie, and Ontario from the EC cruise data were also recorded by the GLNPO but are not included in this table.*

Parameter	Unit	Superior EC	Huron EC	Erie EC	Ontario EC	Michigan GLNPO
Alkalinity	mg $CaCO_3$/L	43	68	82	86	
Dissolved O_2	mg/L	11	10	8.1	9.2	
pH	N/A	8.2	8.1	8.3	8.6	
Conductivity	uS/cm	100	204	272	327	
Turbidity	NTU	0.3	0.4	2.2	0.7	
Temperature	°C	14	18	24	19	22
Phosphorous	mg/L	0.003	0.004	0.01	0.01	0.0008
Nitrogen	mg/L	0.001	0.01	0.1	0.1	0.02
Magnesium	mg/L	2.8	6.6	8.0	8.3	
Chloride	mg/L	1.4	6.5	14	24	

1.3 The Wastewater Treatment Process

Wastewater treatment is a process used to remove contaminants from municipal and industrial sewage to convert it into an effluent that can be returned to the water cycle. Once wastewater is received through sewage pipes, pre-treatment is the first step in the process. Pre treatment uses bar screens to remove outliers such as flushable wipes and other large solids from the influent; these items are then sent to a landfill or solid waste handling facility. Grit chambers are the second step in pre-treatment and involve the removal of large particles that can not be chemically removed and may clog or damage pumps later in the process (WasteWater System, 2017). Primary treatment is the next step and involves pumping wastewater through primary clarifier or clarifiers which function on the principal of settling velocity to allow solids to settle out. The next step in the process is secondary treatment, the goal of which is to degrade biological content. In secondary treatment, aeration basins pump oxygen bubbles through the wastewater to feed bacteria and optimize the naturally occurring processes of microbial decomposition, a process known as aerobic digestion (SAMCO Tech, 2019). Anerobic digestion, although usually a longer process, can also be used during secondary treatment and relies on microbial

decomposition in the absence of oxygen. Effluent is then pumped through secondary clarifiers, which is another attempt at removing any solids and larger biological matter. This removal is sometimes accelerated through the use of flocculants. Increasingly often, additional disinfection after secondary treatment forms the final stage of the process, commonly done through chlorination, ozone (Paraskeva & Graham, 2002) or ultraviolet disinfection (United States Evnironmental Protection Agency, 1999). The final step is effluent release, where the treated water is released back into the environment (commonly a stream, river, or lake) or is sent to another treatment plant to be further treated and directly recycled for consumption.

1.4 The Impact of Wastewater on the Great Lakes and other Fresh Water Systems

It is widely known that the discharge of sewage (treated or untreated) to the environment can impact human health and the health of aqueous ecosystems, especially when mixing rates with receiving surface waters are low or when peak discharges are emitted with suboptimal or no treatment (e.g., stormwater runoff) (Carey & Migliaccio, 2009; Holeton et al., 2011). Although evidence of threats to human health and ecosystem degradation through wastewater release have been documented in the past, and even though we continue to improve wastewater treatment technologies, the growing global population continues to cause an increase in the disposal of domestic wastes to aquatic environments. It is therefore critical that the loads of potential contaminants from WWTP (wastewater treatment plant) to receiving environments are carefully monitored and managed, including within the Great Lakes. Contaminant loads to receiving surface water can be minimized by improving their elimination during wastewater treatment thus lowering concentrations in discharged effluent, but this is a difficult task considering

wastewater treatment operations must eliminate a whole suite of potential contaminants, including nutrients and organic matter, other organic chemicals, and inorganic compounds such as metals.

Residual organic matter associated with human waste is present in the influent of all municipal WWTPs. These substances result in high biological oxygen demand (BOD) when microbially degrading during treatment, as well as increased concentrations of total suspended solids (TDS), and phosphorus and nitrogen compounds such as phosphate, nitrate, and ammonia in sewage (Holeton et al., 2011). Although WWTP design and operation is heavily tailored towards the removal of these nutrients, WWTP were still the largest point-source of nitrogen and phosphorous to Canadian surface waters in 2008 (Environment Canada, 2009; Holeton et al., 2011). Treated effluent can also carry significant loads of chlorine, which is added to the untreated influent as a disinfectant, as well as other potentially hazardous compounds (e.g., pharmaceuticals) and elements (e.g., rare earth elements) which are not efficiently removed by the facilities treatment technologies, particularly if there are no regulations on such contaminants (Holeton et al., 2011). It has been noted that WWTP are among the most important sources of chemicals of emerging concern (CEC) entering the Great Lakes (Laitta et al., 2014).

The pollutants in wastewater discharge can negatively affect the quality of an aquatic environment and damage the biota that depend on it. Wastewater-related ecosystem impairment most commonly occurs through the processes of oxygen depletion, eutrophication, water temperature variability, turbidity changes, bacterial contamination and aquatic toxicity from other potential contaminants such as heavy metals, organic residues, or ammonia, among others (Holeton et al., 2011). Increases in

turbidity and temperature specifically, can alter the physical habitats of the receiving body often leading to changes in food web structure and function (Holeton et al., 2011). Bioaccumulation of wastewater derived contaminants such as heavy metals and nutrients as well as wastewater induced eutrophication have been reported to effect food webs through alteration of spatial patterns for fish biomass (Askey, 2007), amongst others. Recent studies further show that emerging wastewater-derived pollutants such as pharmaceuticals and personal care products can cause developmental, reproductive, and behavioral changes in fish and other aquatic organisms in environments downstream of treated sewage discharge (Al-Ansari et al., 2010; Brun et al., 2006). Humans can also be exposed to WWTP pollutants, e.g., through the ingestion of contaminated drinking water, interaction with contaminated water through recreational activities or the ingestion of food contaminated by sewage derived pollutants. Disease related to the ingestion of bacteria and other pathogens are the leading human health risks related to wastewater (Holeton et al., 2011). There are numerous studies that demonstrate the risks of wastewater discharge to both human and ecosystem health in the Great Lakes, such as the presence of possible WWTP derived human enteric viruses in drinking water sources (both ground and surface water) along the Grand River (Dorner & Slawson, 2007) and the divergence of fish communities along WWTP effluent gradients in the Hamilton Harbour (McCallum et al., 2019; Dorner & Slawson, 2007). Monitoring of both wastewater effluent and the receiving surface water quality, as discussed below in section 1.6, is an integral part to limiting the effects of WWTP discharge on the aquatic environment and human health.

Besides potential pollutants that are released through treated wastewater effluent, wastewater systems can also unintentionally release untreated sewage by way of

combined sewer overflows (CSO's) or treatment bypasses. Bypasses occur when WWTP inflow is rerouted during periods of high wastewater flow in collection systems with resulting incomplete separation of storm and wastewater when flow exceeds local capacity (Holeton et al., 2011). In Ontario alone, the total annual volume of bypass events ranged from 2.2 to 10.8×10^6 m^3 of untreated sewage and 3.5 to 9.6×10^6 m^3 of pre-secondary treatment sewage between 1991 and 2007 (Holeton et al., 2011). These bypasses are of particular concern to the health of receiving surface waters as these discharges are untreated and can contain a larger assortment and concentration of contaminants than treated wastewater. A model of CSO's created in 2007 (Benotti & Brownawell, 2007) indicates that CSO's can have concentrations 10 or more times those in treated wastewater. In addition, compounds that are not efficiently removed by WWTP processes (e.g., codeine, cimetidine) will have similar concentrations in CSO's and treated wastewater, whereas compounds that are efficiently removed by WWTP processes (e.g., acetaminophen, warfarin) will likely have significantly higher concentrations in CSO's than in treated wastewater (Benotti & Brownawell, 2007). Micropollutants including hormones (Phillips et al., 2012), pharmaceutical and illicit drugs (Munro et al., 2019), microbial pathogens (Al Aukidy & Verlicchi, 2017), personal care products (Heinz, 2009), pesticides (Gasperi et al., 2012a; Gasperi et al., 2012b; Launay et al., 2016), suspended solids, heavy metals, nutrients, and microplastics have all been deemed as contaminants sourced from CSO's (Al Aukidy & Verlicchi, 2017; Anne-Sophie et al., 2015; Kistemann et al., 2016; Masi et al., 2017; Munro et al., 2019; Suárez & Puertas, 2005; Tanaka & Takada, 2016; Tondera, 2013; Xu et al., 2018). There have been many studies that have demonstrated the effect of CSO's on their receiving

environment, such as CSO sourced estrogen as a cause of endocrine disruption in fish (Johnson et al., 2008), increase in organic content causing eutrophication (Viviano et al., 2017), reduced photosynthesis and phytoplankton activity due to CSO-induced turbidity (Viviano et al., 2017), degradation of organic matter by heterotrophic bacteria (Viviano et al., 2017), and inhibiting of reproduction due to CSO related metal contamination (Schertzinger et al., 2018).

The solid particles and biological components that are removed during the primary and secondary stages of wastewater treatment also must be considered when discussing the impact of WWTP derived contaminants on the environment. This insoluble solid residue remaining after sewage is treated is known as sludge, its chemical and physical characteristics depend on the quality of sewage and the treatment processes being used. Sewage sludge is composed mainly of organic compounds (50-70%), mineral components (30-50%), 3.4-4% nitrogen, 0.5-2.5% phosphorous, as well as various macro- and micronutrients, microorganisms, micropollutants and trace elements (Kacprzak et al., 2017; Singh & Agrawal, 2008). The disposal of sewage sludge is commonly done through land application (often as a fertilizer), incineration or landfilling and less commonly through composting, land building and production of construction materials (e.g., bricks) (Kacprzak et al., 2017). In 2009, Ontario alone generated approximately 300,000 dry tons of sewage sludge, with 40% being applied to land, 40% going to landfills and 20% being incinerated (Canadian Institute for Environmental Law and Poilicy, 2009). Although land application is one of the most common disposal mechanisms of sewage sludge due to its richness in organic and inorganic nutrients, the availability of potentially toxic metals and other contaminants are cause for concern

(Singh & Agrawal, 2008). Past studies have shown increased bioaccumulation of trace metals into crops grown on soils with higher doses of sludge-amendment compared to soils with lower or no applied sludge (Singh & Agrawal, 2008). However, the primary concern for sewage sludge is its use in agriculture and land application, where contamination of ground and surface water particularly by pathogens and viruses can occur (Powelson et al., 1991).

Although direct WWTP effluent discharge may only account for 0.3% (220 m^3/s) of the total amount of water (58,000 m^3/s) entering the Great Lakes, elemental concentrations in WWTP effluent are significantly higher than those in natural runoff, which can result in disproportionate contributions of element loads to lake-wide budgets (as will be shown in Chapter 2). For well-studied elements such as copper and nickel, WWTP effluent accounts for 2.5% and 2% of the basin wide budgets respectfully, which is significantly higher than the 0.3% for water (Pinter et al., 2021). A lack of monitoring data of CEC (including trace metals) in the surface waters of the Great Lakes (section 1.2) makes basin-wide calculations such as those for copper and nickel almost impossible for other emerging contaminants. Furthermore, the ability or effectiveness of WWTP to remove individual contaminants is also unknown for many CEC. Thus, the mechanisms underlying CEC elimination across the wide rage of treatment technologies need to be carefully studied in order to apply a proper treatment to CEC tainted wastewater where needed.

Basin-scale assessments of the contributions of WWTP loads to surface water quality deterioration have been completed for more common contaminants in the Great Lakes such as Robertson and Saad's 2011 work on phosphorous and nitrogen. Other

studies have successfully looked at the contribution of urban effluents to smaller-scale parts of the Great Lakes system, such as the work of Gobeil et al., 2005, on WWTP contributions to metal fluxes in the St. Lawrence River, or Poulton's work from 1992 where WWTP loads of heavy metals and other toxic contaminants were compared to those of natural loads in the Bay of Quinte. Although some work on the impact of common WWTP-derived contaminants has been performed, the assessment of WWTP derived CEC loads is largely unknown. Consequentially, the potential impact of CEC contamination at the basin-wide scale is severely understudied.

1.5 Trace Metals: Importance and Impact on Aquatic Environments

Trace elements such as rare earth elements (REE), platinum group elements (PGE), precious metals such as silver and gold, and other metals and metal(oid)s (e.g., antimony, tellurium, indium or germanium; **Figure 1.2**) have become critically important over the last few decades (Eggert, 2011). Many of these trace elements are heavily used in today's industries, including the renewable energy sector, defence and communication technologies, and the pharmaceutical and chemical industries. For example, silver may be used in self-disinfecting nanoparticles (Nie et al., 2021), cerium is used in polishing compounds (Hedrick & Sinha, 1994), platinum, palladium and rhenium are used in car exhaust catalysts (Whittington et al., 1995), lithium in lithium-ion batteries (Yoshino, 2012), gadolinium as a contrast agent in medical imaging (Reynolds et al., 2000) and both gallium and indium are used in solar cells (Jackson et al., 2015). As a result of increased use, the extraction and production of these trace elements has grown extensively (Du & Graedel, 2011) and their emission to the environment has increased at each phase of their life cycle (Li et al., 2013; Robinson, 2009; Zimmermann & Sures, 2004). The increased environmental trace metal emissions through human waste streams for some elements (e.g., osmium and mercury) are now known to be large enough to alter their biogeochemical distribution patterns and cause quantifiable environmental impacts, and this may be true for other trace elements although this is not yet known for certain (Lottermoser, 1994; Nriagu & Pacyna, 1998).

The ecotoxicological knowledge base for trace elements is mostly very scarce despite growing use and potential mobilization into the environment, in addition their baseline fluxes are poorly understood, including in the Great Lakes (Nriagu & Pacyna,

1998). Trace metal concentrations in the Great Lakes have been published, for example (Rossmann & Barres, 1988) but in 1993, Nriagu et al., expressed doubt on most of the published data on trace metal concentrations in the Great Lakes. Since then, loads for elements such as copper, nickel, zinc and lead in the Great Lakes have been more reliably established (Bentley et al., 2022), but trace metal baseline fluxes are still non-existent. Some trace metals such as cadmium, mercury, lead and copper are understood to be pollutants to surface water environments due to their environmental persistence, toxicity, and capacity to be integrated into food chains (Arvela et al., 1976; Bakyayita et al., 2019; Edokpayi et al., 2016; Qiu et al., 2011). The relationship between some trace metal levels in surface waters and the resulting bioaccumulation in fish species is well documented, such as the high levels of nickel and copper associated with kidney pathologies and strontium with those of skeletal tissues (Moiseenko & Kudryavtseva, 2001). These types of physiological effects can then further affect the food webs, in the case of the salmonid fish the physiological processes affected by trace metal contamination can lessen their ability to form dominance hierarchies (Sloman, 2007). Trace metal integration into food chains and drinking water sources can also lead to toxicity effects in humans when ingested above tolerable levels (Bakyayita et al., 2019). For instance, exposure to large amounts of REE through ingestion of contaminated fish or drinking water can lead to health complications for humans including the function of digestive enzymes, causing malabsorption and indigestion (Bakyayita et al., 2019). The contaminant status of metallic elements and metallic oxides (many are unknown) within the Great Lakes are well documented (Aliff et al., 2020b) and can be seen in **Table 1.3**. To prevent or at least assess such impacts, the effects of anthropogenic trace element

emissions, their occurrence, and pathways into human waste streams must be quantitatively understood. More importantly, the quantification of human imprints of trace metals on surface water environments can only be done once baselines for these trace metals in such environments are established.

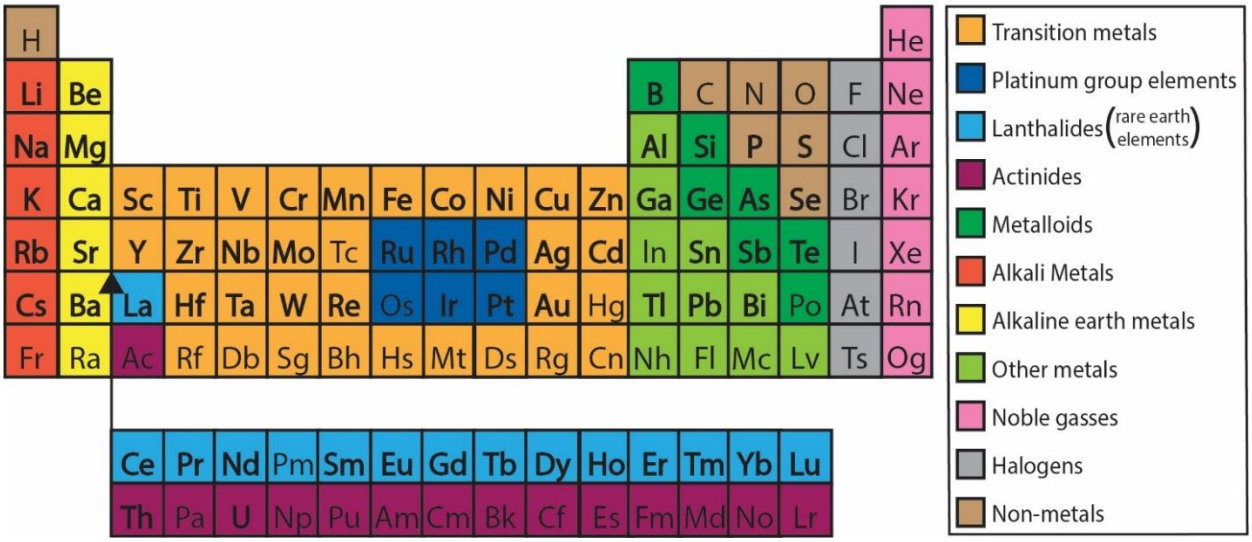

Figure 1.2 *Periodic table highlighting the trace elements in which data is reported on in this thesis (bold).*

Table 1.3 *The contaminant status of select metallic and other elements in the Great Lakes as of 2020. Adopted from (Aliff et al., 2020b).*

	Element	Contaminant status in the Great Lakes
Alkali Metals	Lithium	Unknown but possible
	Rubidium	None known
	Cesium	Yes, in the form of ^{137}Cs
Alkaline earth metals	Magnesium	Some historical contamination associated with taconite tailings in the western part of Lake Superior
	Strontium	Yes, related to mining, fossil fuels, and other industries
	Barium	Yes, listed as contaminant in the Saginaw Bay and the Rouge River Great Lakes AOCs
Transition metals	Titanium	Some atmospheric contamination from emissions and erosion
	Vanadium	Yes, e.g., in Lake Michigan due to past contamination from the BP Whiting Refinery
	Chromium	Yes, listed as a sediment contaminant or water contaminant in 17 AOCs
	Cobalt	Yes, from mining, fossil fuel combustion, and other industrial sources
	Nickel	Yes, listed as a sediment contaminant or water contaminant in 16 AOCs
	Copper	Yes, listed as a sediment contaminant or water contaminant in 31 AOCs
	Zinc	Yes, listed as a sediment or water contaminant in 30 AOCs
	Cadmium	Yes, listed as a sediment contaminant or water contaminant in 11
	Mercury	Yes, related to coal fired power plants, mining, and other industries
	Molybdenum	Likely
	Yttrium, Zirconium, Niobium, Hafnium, Tantalum, Scandium	None known
Lanthanides	Samarium, Gadolinium	None known but potentially an emerging contaminant of concern
	Lanthanum, Cerium, other REE	None known but potential
Basic metals	Gallium	None known but possible
	Tin	Yes, attributed to industry and fossil fuel emissions
	Lead	Yes, related to fossil fuel emissions, mining
Semi-metals	Arsenic	Yes, listed as a sediment contaminant or water contaminant in 10 AOCs
	Antimony	Yes, related to mining and other industries
Actinide series	Thorium, Uranium	Yes, part of the Port Hope AOC

1.6 Wastewater and Sewage Sludge Regulation in the Great Lakes Basin

Wastewater regulation and management in Canada is accomplished by regional, provincial, and federal governments. Federal guidelines for waste management and the impact of wastewater release on both humans and the environment are presented in the Canadian Environmental Protection *Act* (CEPA) and the Fisheries *Act* (Governemnt of Canada, 1985; Government of Canada, 1999). Subsequently, the CCME released an updated Canada-wide Strategy for the Management of Municipal Wastewater Effluent in 2009 (Canadain Council of Ministers of the Environment, 2009). This strategy promotes a harmonized approach to better manage the discharge of wastewater effluent from the 3500+ WWTP's in Canada (Canadain Council of Ministers of the Environment, 2009). The federal government devoted a new and separate regulation under the Fisheries *Act* titled Wastewater Systems Effluent *Regulations* (WSER) (SOR/2012-139) to facilitate regulations developed as a response to the CCME national strategy (Government of Canada, 2012). The WSER was published in 2012 and then amended in 2015 (Government of Canada, 2012). The regulations in the WSER present national standards of effluent quality for suspended solids, total residual chlorine, carbonaceous biochemical oxygen demanding matter, and ammonia. Regulations in the WSER provide a significant upgrade to prior federal guidelines for wastewater management as they also include standards for monitoring equipment, test methods, laboratory certifications, record keeping, and compliance obligations, therefore providing a basis for provincial and local wastewater effluent provisions such as those in the Ontario Water Resource *Act* (Government of Ontario, 2021). Primary responsibility for the regulation of wastewater treatment and governance of the standards in the WSER and CEPA lie on the shoulders

of provincial and territorial governments (Holeton et al., 2011). Wastewater treatment facilities in Canada are typically owned by municipalities or regions and require permits or licences from provincial or territorial governments to operate. These permits or licences are where issuing parties can implement regulations that go beyond federal or provincial requirements based on factors unique to that WWTP, such as the number of people served or water quality of the receiving body (Holeton et al., 2011).

Like the management of wastewater effluent in Canada, sewage sludge guidelines are derived and imposed through a coordinated effort by federal and provincial governments. At the federal level, the Government of Canada lists maximum application rates of selected elements (kg element/ha/year) in land applied sewage sludge under the Fertilizers *Regulation*, including arsenic, cadmium, chromium, cobalt, copper, mercury, molybdenum, nickel, lead, selenium, thallium, vanadium, and zinc (Government of Canada, 2020). These limits are supported by CCME guidance documents for the management of biosolids including treatment, disposal, environmental considerations, etc., (Canadian Council of Ministers of the Environment, 2012a, 2012b). At the provincial level, the government of Ontario sets maximum application rates of particular elements (kg/element/year and mg/kg soil) in land applied sewage sludge under the Nutrient Management *Act*, including arsenic, cadmium, cobalt, chromium, copper, lead, mercury, molybdenum, nickel, selenium and zinc (Government of Ontario, 2002). The Government of Ontario also provides guidelines for sludge storage and disposal in their document Design Guidelines for Sewage works (Ministry of the Environment, 2008). In the United States, pollutant limits for multiple uses or disposals of sewage sludge are published, including for arsenic, cadmium, copper, lead, mercury, molybdenum, nickel, selenium,

and zinc when used in land application and for arsenic, chromium, and nickel when used in surface disposal and incineration (United States Environmental Protection Agency, 2018). No different than in Canada, limits for pollutants in sewage sludge at the state level in the US correspond with those published at the federal level. In contrast to the elements listed above, there are no current limits for most other trace metals (**Figure 1.2**) in wastewater effluent or sludge. To a large extent, this is because the lacking understanding into their baselines and potential environmental impacts as well as a lack of evidence to suggest that these trace metals currently cause harm to surrounding environments.

1.7 Knowledge Gaps and Thesis Research Questions

Wastewater is a critical human waste stream as it constitutes an important pathway for contaminants to enter surrounding ecosystems (effluent discharge and sludge processing) and increasing levels of emerging contaminants in both wastewater effluent and sewage sludge are expected in industrialized countries worldwide. The discharge of trace elements through (un)treated wastewater effluent may be hypothesized to imprint receiving aqueous environments and have potential deleterious effects. However, for trace elements, there is lacking mechanistic insight into their elimination in the wastewater treatment process, and a poor understanding of the role of WWTP-derived inputs into freshwater systems, mostly because baseline concentration ranges and loading rates are non-existent. In this thesis, I will aim to address following research questions:

1. What are current, representative concentration ranges of trace metals in WWTPs within the Great Lakes basin and how large are average per-person trace metal fluxes to wastewater?

2. What are the removal efficiencies of trace elements during different WWTP processes and resulting fractionation between the sludge and effluent?

3. Can qualitative geospatial analysis of sewersheds be used for trace element source attribution?

4. What can individual tributary-scale trace element dynamics tell us about the potential imprint of WWTP effluent discharge on natural freshwaters?

The Great Lakes basin is ideally suited to study these questions as it holds >20% of the worlds fresh water, houses ~40 million people and >1000 WWTP (United States Environmental Protection Agency, 2012; Government of Ontario & Ontario Ministry of the Environment, 2019).

1.8 Thesis Organization

Below is a summary of the structure of the thesis and a brief summary of each chapter:

- Chapter 1 is a broad introduction to relevant background information and knowledge gaps within this specific research topic.
- Chapter 2 , “Loads and elimination of trace elements in wastewater in the Great Lakes basin”, is the first publication of this thesis. This chapter was published in the peer-reviewed journal Water Research with the help of co-authors Bas Vriens and Bailey Jones. This chapter contains a screening of >60 major and trace elements in 40 WWTP in the Great Lakes basin, calculations of per-person influent loads and basin-scale effluent discharge loads, evaluations of trace metal removal efficiencies in different WWTP treatment designations, and a quantitative geospatial analysis of sewersheds for trace element source attribution.

- Chapter 3, “Imprints of Wastewater Discharge on Trace Element Dynamics in the Grand River, Ontario”, is intended for publication in Environmental Monitoring and Assessment. This chapter includes an analysis of trace element dynamics in the Grand River, as well as assessment of major water quality trends, WWTP trace element loads, mass-balance calculations of effluent versus tributary inputs, and subsequent attempt to quantify human imprints on trace metals loads.
- Chapter 4 includes final conclusions and recommendations for further research.

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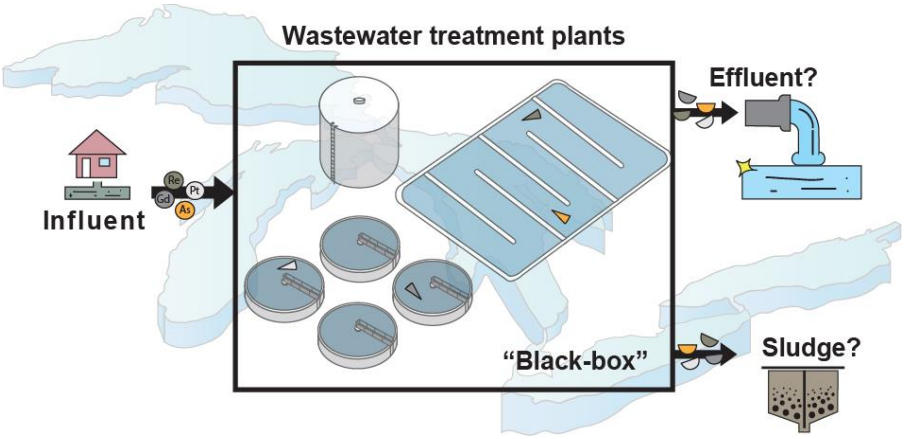
Chapter 2: Loads and Elimination of Trace Elements in Wastewater in the Great Lakes basin

2.1 Abstract

The growing use of trace elements in industrialized societies is driving an increase in the occurrence of trace elements in anthropogenic waste streams globally. Yet, the large-scale sources of many trace elements to wastewater and their elimination during treatment remain poorly understood and potential environmental impacts on freshwater systems therefore unclear. We screened 42 wastewater treatment facilities in the North American Great Lakes basin and deployed a black-box approach to calculate representative estimates for average per-capita trace element loads and basin-scale effluent discharge rates, as well as trace element removal efficiencies across different treatment technologies. Our results show different removal of specific groups of trace elements during wastewater treatment: average removal efficiencies were 25% for alkali metals, 50% for alkaline earth metals, 74% for transition metals, and 85% for rare earth elements. Higher elimination of the majority of trace elements was generally achieved by more advanced, tertiary treatment types. Elemental loads generally followed natural abundance patterns, but anomalous loading rates were observed for various trace elements across the sampled facilities. By examining geospatial attributes of the sampled sewersheds, trends in select trace element loads were qualitatively tied to possible point sources and diffuse sources. Overall, these results illustrate the potential of wastewater surveillance to inform environmental management of emerging trace element contaminants.

Graphical Abstract



Keywords

Wastewater, Trace Elements, Great Lakes, Emerging Contaminants, Geospatial Analysis

Highlights

- Screening of >60 major and trace elements in >40 wastewater treatment facilities
- Calculation of per-person influent loads and (basin-scale) effluent discharge loads
- Higher trace element removal efficiencies generally found with tertiary treatment
- Qualitative geospatial analysis of sewersheds for trace element source attribution

2.2 Introduction

In recent decades, many trace elements have become critically important for the pharmaceutical and chemical industries, the (renewable) energy sector, as well as for defense and communications technologies (Eggert, 2011). Examples of such trace elements include rare earth elements (REE), platinum group elements (PGE), precious metals such as Au and Ag, as well as other transition metals and metalloids (e.g., Te, Tl, Ga, In or Ge). Consequently, the mining, processing and industrial and societal uses of these trace elements have grown exponentially around the world (Du & Graedel, 2011; Nriagu & Pacyna, 1988), leading to increased environmental emissions along their life cycle, i.e., from mining of ore itself (Li et al., 2013) to consumer use and product degradation (Robinson, 2009; Zimmermann et al., 2013). Industrial and societal anthropogenic waste streams and corresponding environmental emissions of some trace elements are now large enough to alter their biogeochemical distribution patterns and cause detrimental effects to local environments (Lottermoser, 1994; Holeton et al., 2011; Rauch et al., 2010). However, except for selected heavy metals (e.g., Hg and Pb) and at specific contaminated sites (e.g., downstream of industrial discharge; Richman & Dreier, 2001), there is comparatively little information on the large-scale anthropogenic sourcing and environmental fate of most other trace elements. The paucity of long-term monitoring data for trace elements in waste streams and receiving environmental reservoirs (e.g., the atmosphere, soil, and surface- and groundwater), particularly on regional, national, or global scales, complicates comprehensive ecotoxicological impact assessment (Ontario 2020; USGS National Water Information System; Gonzalez et al., 2015). To mitigate or prevent potential deleterious effects of anthropogenic trace element emissions on the

environment, their occurrence and sourcing into human waste streams must thus be more quantitatively understood.

Wastewater mirrors our society in the sense that many anthropogenic pollutants, including microplastics, engineered nanoparticles and pharmaceuticals, find their way into municipal and/or industrial wastewater (Petrie et al., 2015; LaGuardia et al., 2010; Kim et al., 2010; Kiser et al., 2009). As a result, wastewater surveillance has become an established tool to assess human imprints on contaminant dynamics and environmental emissions. Recently, wastewater surveillance is even providing a cost-effective means to monitor COVID-19 prevalence in populations in useful spatiotemporal resolution (Larsen & Wigginton, 2020). Wastewater also constitutes an ideal screening target to examine the sources and potential environmental footprints of human trace element use (Vriens et al., 2017; Merschel et al., 2015; Lim et al., 2017). Yet, systematic data on trace element concentrations in wastewater and other urban runoff is scarce as these elements are typically not part of governmental surveillance programs (Vriens et al., 2017; Westerhoff et al., 2015; Nickel et al., 2021; Östman et al., 2017; Ontario 2019; USEPA CWNS, 2012), at least in part due to the cost and challenges involved with their quantification at ultra-trace levels. Wastewater may be considered a trace element source to the environment through multiple pathways, e.g., through direct release of effluent to surface waters (Gobeil et al., 2005; Dickenson et al., 2011) or through agricultural application of processed sewage sludge (Singh & Agrawal, 2008). Unfortunately, the loading rates of many emerging trace elements from and into wastewater treatment plants (WWTP) are not well understood.

Different WWTP types (primary, secondary, or tertiary) consist of a series of sequential unit operations aimed at removing solids, biogeochemical oxygen demand, nutrients, and other remaining suspended, colloidal, and dissolved constituents of concern (CCME, 2009). Municipal treatment systems are becoming increasingly effective towards abovementioned performance criteria, but they do typically not target specific (groups of) trace elements, even though previous studies have implied that wastewater loads of trace elements such as Cu, Zn, Hg and As can be substantial and their removal by conventional treatment technologies may not very effective (Agoro et al., 2020; Karvelas et al., 2003; Balogh & Nollet, 2008). Because of the generally limited data available for less-abundant trace elements (e.g., REE and PGE; Vriens et al., 2017; Verplanck et al., 2010; Westerhoff et al., 2015), their behaviour and elimination during wastewater treatment remains unclear and the imprint of wastewater loads on natural trace element cycles poorly quantified.

The Laurentian Great Lakes hold >20% of the world's freshwater, but also house >40 million people and >1,000 WWTP (Ontario 2019; USEPA CWNS, 2012). While there are significant differences in water quality across the Great Lakes basin, many subregions are under stress from historic contamination as well as continued urbanization and industrialization (Baldwin et al., 2016; Holeton et al., 2011; Bentley et al., 2022). Wastewater effluent and stormwater runoff have been identified as a major environmental stress factors, especially near urban areas (Marsalek & Schroeter, 1988; Arvai et al., 2014). Previous work on the concentration ranges of pollutants in wastewater effluents and sewage sludges in the Great Lakes basin has focused mostly on nutrients, heavy metals, conservative elements (e.g., chloride) or organic pollutants (Poulton, 1992; Arvai

et al., 2014; Baldwin et al., 2016; Zhang et al., 2021; Lu et al., 2017). Comparable information on the occurrence or loads of emerging trace elements in this region is comparatively scarce (Gagnon et al., 2021), and studies often only consider one or a few selected WWTPs or are geographically constrained to contaminated areas (e.g., (Poulton, 1992)). In addition, the international and state boundaries that divide up the Great Lakes basin and the different reporting requirements in these jurisdictions make it difficult to find consistent data on wastewater or biosolids quality for this region in the public domain. In both Canada and the US, treated sewage sludge may be applied on agricultural land, provided certain quality limits are adhered to, yet few federal or provincial/state regulations exist for trace elements (Ontario 2019). Thus, quantitative data on emerging trace element concentrations and loads sourced from WWTP in the Great Lakes region is critically needed.

To this end, we analyzed trace element concentrations in wastewater effluents and digested sludges from 42 US and Canadian WWTP across the entire Great Lakes basin. The main objectives were i) to quantitatively assess representative concentration ranges, loading rates and removal efficiencies of trace elements during treatment in a representative selection of WWTP, and ii) to qualitatively explore potential sourcing of anthropogenic and geogenic trace element emissions through geospatial analysis of the connected sewersheds.

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2.3 Materials and Methods

2.3.1 Sample Collection

Samples of treated wastewater (effluent) and digested sludge were collected from 42 WWTP throughout the Great Lakes basin in August and September of 2019 and 2020. Sludge samples were on average composites of 1-month of the final (digested) sludge, i.e., the aggregate of primary, secondary and/or tertiary treatment, if present. Effluent samples were 24-hour aggregates (a combination of multiple samples taken from the same day) of the final effluent sent for discharge. Samples were taken once, at a time chosen by the WWTP operators, to allow for an unbiased sampling regime: the strategy was to assess spatial rather than temporal trends. The sampled facilities were selected such to provide reasonable representation of the >1,000 WWTPs in the Great Lakes basin, based on geographic distribution (WWTP from each of the five individual Great Lake watersheds were included), number of connected population equivalents, size and treatment type, and catchment area (sewershed) characteristics (**Table S.2.1**). A comparison between characteristics of the sampled WWTP versus those of other WWTP in the basin is provided in **Table S.2.2**.

All sampled facilities are considered municipal WWTP and typically treat a combination of household wastewater, industrial and commercial effluent, and road runoff. Together, the sampled WWTPs service >3.0 million people, roughly 8% of the total population in the Great Lakes basin (Ontario, 2019; USEPA CWNS, 2012). Select parameters of the sampled WWTP, including average daily flow, average daily sludge production, connected population equivalents and treatment type, can be found in **Table S.2.1**, but the sampled facilities requested to remain anonymous otherwise.

The WWTP were provided with prepackaged sampling kits that were shipped back by courier immediately upon sample collection. Digested sludge samples were collected in precleaned, acid-washed 250 mL HDPE wide-mouth sample bottles (Nalgene) and wastewater effluent samples were collected in precleaned, acid-washed 500 mL PTFE sample bottles (Kartell). Upon receipt, effluent samples were immediately filtered through 0.2 µm PTFE membrane filters and analyzed for pH and conductivity (Mettler Toledo SevenExcellence multimeter). A 10 mL aliquot of the filtered wastewater was digested in-bottle with 500 µL ultrapure 67-70% nitric acid (HNO_3; Anachemia) before elemental analysis (see Section 2.2.2). Because effluents were filtered prior to acidification, reported concentrations for these samples reflect an operationally defined dissolved element concentration. All sample bottles, vials and processing materials were rinsed with ultrapure MilliQ deionized water (18.2 MΩ) and 1% ultrapure HNO_3 before use and all samples were stored at 4°C in the dark between receipt, processing, and analysis.

2.3.2 Analytical Methodology

2.3.2.1 Acid Digestion of Sludge Samples

Due to the variable water content (between 1% and 34%) of the sludge samples, sludges were freeze-dried and homogenized prior to acid-digestion. Approximately 50 mL of sludge was frozen at -15°C for 72 hours, and subsequently freeze-dried for 48 hours to a constant dry weight using a -50°C Freezone Labconco Benchtop Freeze Drier. Freeze-dried samples were individually homogenized using an agate mortar and pestle. Total elemental fractions were recovered using two acid-digestion techniques for which at least one method guaranteed optimal recovery rates and element stability for long periods of time (Vriens et al., 2017): (i) acid-digestion using nitric acid (HNO_3),

hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2), and (ii) acid-digestion with nitric acid (HNO_3), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), and hydrofluoric acid (HF). All acids and peroxides used were of ultra-pure grade; 47-51% hydrofluoric acid (OmniTrace), 67-70% ultrapure nitric acid (Anachemia), 30-32% ultrapure hydrogen peroxide (VWR Avantor), and 36.5-38.0% high-purity hydrochloric acid (Fisher Chemical).

For acid-digestion, 50 mg freeze-dried sludge was added to a 50 mL HVT50 Teflon digestion vessel followed by the addition of 9 mL HNO_3, 3 mL HCl, and 2 mL H_2O_2 for method 1, or the addition of 9 mL HNO_3, 3 mL HCl, 2 mL H_2O_2 and 3 mL HF for method 2. The acids and peroxide were added slowly to prevent loss of material due to the release of CO_2 from organic matter oxidation in the samples. The mixtures were subsequently digested for 40 minutes at 210°C using an Anton Paar Multiwave5000 with in-situ temperature sensor. After digestion, samples were cooled for 60 minutes and carefully transferred into precleaned Falcon centrifuge tubes where they were diluted to 47.5mL using ultrapure milliQ deionized water.

For quality assurance, every batch of digestions included two blanks of each of the digestion acid-mixtures, up to four sample duplicates, and two certified reference materials (VHG-SL1, metals in sewage sludge, and VHG-SSD1A, metals in sewage-amended soil) in duplicate. The average elemental recovery, i.e. across all certified elements, ranged from 83-98% for VHG-SL1 and from 110-129% for VHG-SSD1A (**Table S.2.3**). Elements with anomalous recoveries were not further investigated. One digestion method was used for the quantification of an individual element in sludge, which was

selected based on the best recovery from above certified reference materials and attainable detection limits in the resulting matrix (**Table S.2.4**).

2.3.2.2 Elemental Analysis of Sludge and Water Samples

Total concentrations of 63 major and trace elements in the digested sludge and filtered and acidified wastewater effluent samples were measured on an iCAP triple quadrupole-inductively coupled plasma-mass spectrometer (TQ-ICP-MS; Thermo Scientific). The instrument was operated in three modes based on lowest detection limit: single quadrupole with no gas, single quadrupole in KED mode (He collision gas) and triple-quadrupole (O_2 reaction gas), utilizing mass shifting for Sc, V, Cr, As, Sr, Y, Zr, Nb, Mo, Ba, Ce, Pr, Nd, Sm, Gd, Tb, Ho, Er, Tm, Lu, Hf, Ta. Blanks and in-house and commercial certified aqueous reference materials (AQUA1, SLRS6 and NIST1643f) were measured every n=10 samples, measured values were in agreement with expected values of both aqueous reference materials. A single isotope was used to quantify each element's total concentration (typically the most abundant isotope) and when possible, a secondary isotope was used to confirm the absence of isobaric interference. Total P was additionally measured as phosphate in digested sludges and effluents on a Thermo Gallery Discrete Analyzer photometer. Details of the employed ICP-MS methodology, including monitored isotopes and utilized analysis modes, can be found in **Table S.2.4**. An overview of the methodological detection limits for the 63 elements analyzed in the sludge and effluent samples is provided in **Table S.2.5**.

2.3.3 Geospatial Analyses

2.3.3.1. Sewershed Estimation

Trends and anomalies in the measured sludge and effluent concentrations and in calculated elemental loads were investigated by contrasting these to select characteristics of the wastewater catchment areas (sewersheds) of the sampled facilities. For 18 out of 42 sampled WWTP, a map of their connected sewersheds was publicly available and directly adopted. For the remaining 24 facilities, sewershed coverage was approximated as follows.

First, delineations of known sewersheds were retrieved directly from municipal websites or WWTP technical staff. These sewershed shapes are seemingly irregular and odd-shaped, but for increasing numbers of considered facilities can be assumed to approach a likely maximal radial extent (**Figure S.2.1**). Therefore, initial estimates for the maximal sewershed boundaries were imposed at particular radial distances from each WWTP based on a relationship between the maximal sewershed extents and connected population equivalents for a subset of 32 WWTP (18 of which included in the sample set; 14 additional) in the Great Lakes basin (**Figure S.2.2**).

Subsequently, the calculated maximal radial extents of estimated sewersheds were projected over the corresponding WWTP at their geometric center in ArcGIS Pro, after which developed land and road surface were clipped within the imposed circular sewersheds. For this, land cover data was retrieved from the Ontario Geohub and the National Land Cover Database (NLCD), and road network data was retrieved from the ESRI database and UCLA Geoportal (data sources detailed in **Table S.2.6**). To ensure consistency between data for the US and Canada, resolution for land cover data was

unified at 3 m and intensity categories for developed land were aggregated into a single classifier across the basin. Basin-wide road network data was adopted at a spatial resolution of 1 m, and polylines were buffered at 25 m on each side to ensure inclusion of stormwater infrastructure and residential, commercial, and industrial properties along roads into the predicted sewershed. To remove overlap of predicted sewersheds in agglomerated areas, census subdivisions (**Table S.2.6**) were used to separate service areas at the municipality level. A comparison of the modeled versus known sewersheds, in terms of size (area), population equivalents, and land-use, can be found in **Figure S.2.3**. The final estimated sewersheds varied between 3 and 555 km^2 in size, which is well within the respective range for known sewershed areas, and also service population equivalents in the predicted sewersheds (ranging between 1,100 and 1,100,000) match well with those in the adopted 'known' sewersheds as well as with population sizes in the catchment areas calculated from federal and municipal geospatial data on population (**Figure S.2.3**). Land cover of both known and estimated sewersheds was dominated by developed land, which covered roughly 75% of the sewershed surface areas; the remaining 25% mostly consisted of a combination of barren land, grassland, agriculture or forest (**Figure S.2.3**). The estimated and known sewershed delineations were subsequently used to assess various geospatial attributes of the connected WWTP service areas, including locations of hospitals, road density and predicted groundwater As levels (**Table S.2.6**), as potential sources of trace elements to wastewater, as discussed in the Supporting Information (**Methods M1**).

2.3.2. Source Attribution

Potential sources of trace elements to wastewater were qualitatively investigated by examining correlations between measured sludge or effluent concentrations or calculated elemental loads and geospatial sewershed attributes using (log-)linear regression in JMP 16 (SAS Software). Elements for which >50% of sampled locations exhibited either sludge or effluent concentrations below detection limits (**Table S.2.5**) were not further considered, as loads could not be reliably calculated. Elements for which <50% of measurements were below their detection limit were further analyzed by treating values below these detection limits as objectively ranging between 0 and the respective limit, in order to assess minimal and maximal possible concentrations at these locations. All geochemical concentrations or loads and geospatial sewershed attributes were converted to continuous numeric values and log-normalized to account for skew, when applicable. A detailed description of the performed data processing for three investigated correlations between trace element loads and sewershed attributes is provided in the Supporting Information (**Methods M1**).

2.4 Results and Discussion

2.4.1 Elemental Concentrations in Effluent and Sludge Samples

The concentration ranges of elements measured in the digested sludge and effluent samples are summarized in **Figure 2.1**; detailed statistics are provided in **Table S.2.7** (effluents) and **Table S.2.8** (sludges). Measured pH and conductivity ranges in the effluents are provided in **Figure S.2.4**.

In effluent samples, the most abundant elements included major elements such as Ca, Na, K, S, as well as Sr, B, Li and Mg, with concentrations ranging between <100 µg/L and >0.1 g/L. Among the least abundant elements in the effluents were PGE and REE,

including Er, Pr, Lu, Pt, Tm and Tb, at concentrations <10 ng/L on average. From most to least abundant, the concentrations in effluents differed by over 9 orders-of-magnitude. In sludge samples, the most abundant elements similarly consisted of Ca, Na, K, S, Mg, as well as P, Fe and Al, at concentrations between <100 mg/kg to >100 g/kg. Major elements with even higher expected abundances in sludge samples (e.g., C, N) were not quantified. The least abundant elements in sludge samples were generally the REE, as well as trace elements such as Re and Pt, with concentrations down to <0.01 mg/kg. Overall, the concentrations in the sludge samples varied by over 6 orders-of-magnitude, so substantially less than the variability observed in effluent concentrations. The distribution of measured effluent concentrations of select elements, including Mg, S, Ca, Sn, La, Yb and Re, was highly skewed, i.e., at up to 100x the median concentration between sampled locations (**Figure 2.1**). The distributions for sludge concentrations were generally less skewed: only Re had a measured value >100x the median (Section 3.5). The lower variability and skew in sludge concentrations compared to the effluent samples is likely explained by the longer retention time represented by these samples (1-month versus 1-day aggregates for the sludge versus effluent samples, respectively), but further research (e.g., using hydrodynamically resolved time-series sampling at various treatment stages in WWTP) is required to confirm this.

Overall, we observed highly variable distributions of elemental concentrations between sampled facilities, even though average measured values were typically in line with their natural abundance patterns (see comparison in **Figure S.2.5**). However, various elements exhibited concentrations <LOD in either the sludge or effluent samples at >40% of sampled locations, including Na, Al, K, Ti, Be, and Ta. Further work is required to

accurately quantify these elements at trace levels, as well as other trace elements not measured in this work (e.g., Ru, Ir, Os, Rh).

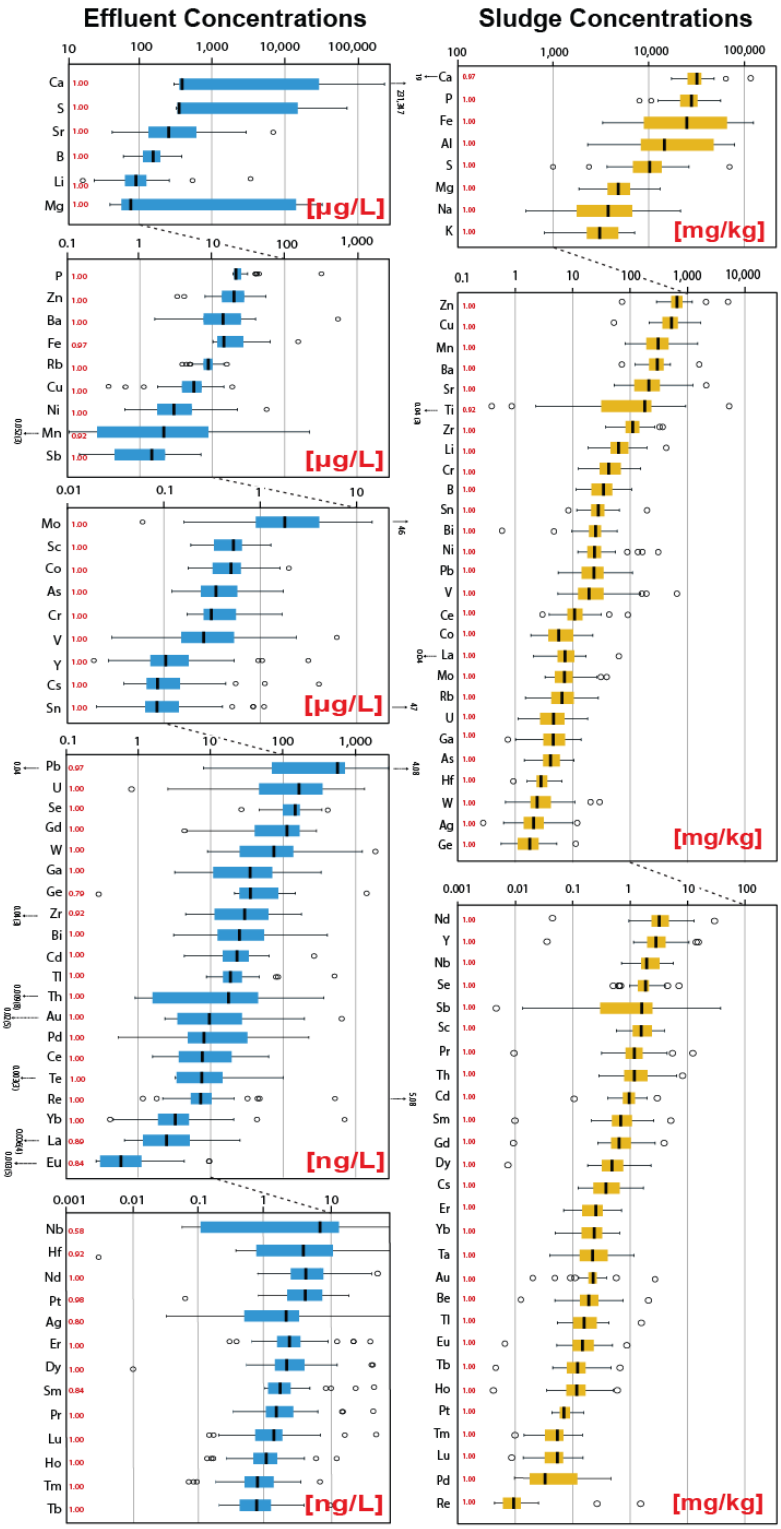

Figure 2.1 *Major and trace element concentration ranges measured in effluent (left) and digested sludge (right) samples from 42 WWTP in the Great Lakes basin (logarithmic x-axes). The thick black bars within each box mark the median concentration, the colored boxes represent the 0.75 and 0.25 percentiles, respectively. Whiskers attached to the boxes indicate the highest and lowest values within 1.5 times the interquartile range. Outliers are represented by circles or arrows if they exceed the corresponding log-scale. For statistical analysis, all values <LOD were given a value of 1/100 LOD, the fraction of measurements >LOD is indicated by the red numbers. A detailed breakdown of measured concentrations is provided in* ***Tables S.2.7*** *and* ***S.2.8****. It can be noted that measured concentrations of Yb seem high possibly due to isobaric interference, but further investigation is required.*

2.4.2 Comparison with Previous Studies and Legal Guidelines

Despite substantial variability in sludge and effluent concentrations, concentration ranges in this study generally agree well (i.e., within an order-of-magnitude) with those reported previously in studies conducted in the United States (Westerhoff et al., 2015; Verplanck et al., 2010; Kiser et al., 2009), Switzerland (Vriens et al., 2017; Kaegi et al., 2021), the United Kingdom (Jackson et al., 2010; Sterritt & Lester, 1980), France (Buzier et al., 2006), Japan (Kawasaki et al., 1998), Germany (Nickel et al., 2021) or Italy (Carletti et al., 2008). Further comparison of previously reported values with the concentration ranges observed in this study is provided in **Tables S.2.9** and **S.2.10**. Notably, the average effluent concentrations of Li and Y, as well as the average sludge concentrations of Li, Zr, Tm and Lu, appear somewhat higher in this work than in previous studies,

although the general scarcity of data prevents further interpretation of these discrepancies.

Measured sludge and effluent concentrations are compared with select applicable legal limits sludge (for 9 elements) and effluents (for 20 elements) in **Table S.2.11** (Ontario, 2019; USEPA CWNS, 2012). None of the sampled locations in the US or Ontario appeared to exceed applicable guidelines for sludge concentrations, although direct comparison was complicated by the fact that available concentration limits vary with the destination of the processed biosolids (e.g., incinerated, landfilled or used as fertilizer) and other sludge properties (e.g., nutrient content). For effluents, guidelines outlined in the Ontario Provincial Water Quality Objectives (PWQO) apply to surface water concentrations after dilution and mixing of effluent with the receiving surface water body. The average dilution for the sampled Canadian facilities was a factor 21 (data not shown). Without dilution, there would have been 8 elements for which at least one sampled WWTP exceeds guideline concentrations at the point-of-discharge; however, all dilution-corrected concentrations were below half the respective PWQO surface water limits (**Table S.2.11**). Sampled US facilities also did not surpass effluent quality guidelines. The effluent concentrations of Cu and Zn were closest to their applicable limits (albeit being below threshold values), which highlights the importance of their continued monitoring, especially considering that effluent and sludge guidelines apply to temporal averages and calculated concentration ranges in this work only provide a snapshot view of trace element levels in the sampled WWTP. While the observed adherence to available guidelines indicates that further reduction of at least the regulated trace elements in

WWTP is not critical, the lack of guidelines for most other trace elements warrants that the possible impacts of the observed concentration ranges are further investigated.

2.4.3 Calculation of Per-Person Influent Loads and Basin-wide Effluent Discharge

For a mass-balance assessment of elemental loads into, and out of, the sampled WWTPs, each facility was considered a black-box: elements enter the facility via the (raw) wastewater influent and leave through either the sludge or effluent fraction. Volatilization can be reasonably assumed negligible for most trace elements: previous mass-balance assessments suggest some (<5%) mass loss for volatile elements such as Hg, but negligible losses of trace metals such as Cu, Cr, Ni, Pb, Mn, Cd and Zn during the wastewater treatment process (Balogh & Nollet, 2008; Karvelas et. al, 2003). Therefore, the sum of the sludge and effluent loads at each WWTP represents the total influent load (in=out). The average per-person influent load at a facility was subsequently calculated by dividing the total elemental load with the connected population equivalent, and these were averaged for all sampled facilities across the Great Lakes basin, as follows:

$$L_X = \sum_{i=1}^{n} \left(\frac{[(F_{sludge} \times [X]_{sludge}) + (F_{effleunt} \times [X]_{effleunt})]_i}{[\text{connected population equivalent}]_i} \right) \quad \text{eq.1}$$

where L_x is the average per-person load of element *x*, $[X]_{sludge}$ and $[X]_{effluent}$ are the concentrations of element *x* in the sludge or effluent sample of each facility, respectively, and F_{sludge} and $F_{effluent}$ are the average sludge production and effluent discharge rates of each facility, respectively (**Table S.2.1**). The basin-wide average per-capita loads were only calculated for n=35 out of 42 sampled WWTP (7 facilities exhibited effluent or sludge concentrations <LOD), and for 59 out of 63 analyzed elements (>50% of measured Al, Ti, Be and Ta concentrations were <LOD). The resulting average influent loads varied from >1 g/person/day for major elements and nutrients such as Na, Ca, K, Si or P to <10

µg/person/day for trace elements such as Ho, Re, Tm or Lu (**Figure 2.2**; **Table S.2.12**). The reported average per-person influent loads reflect averages from a service population of 3.09 million people (roughly 7.7% of the population in the Great Lakes basin) across a wide variety of treatment types, facility sizes and sewershed characteristics, providing an argument that these estimated loads are representative for the region. The fact that the calculated per-person loads are comparable, i.e., within the same order-of-magnitude, to per-capita calculated in previous work (Vriens et al., 2017; **Table S.2.13**) further suggests that trace element loads may be comparable across widely different geographic regions.

Building on the same black-box approach discussed above, we further assessed basin-wide elemental loads discharged to surface waters by extrapolating the average effluent loads of the sampled WWTP onto the total of ~335 Canadian and ~1,112 US facilities that discharge effluent into the Great Lakes watershed (Ontario, 2019; USEPA CWNS, 2012). For this, we considered all WWTP for which effluent concentrations could be measured (n=40) and the same 59 elements considered in the influent load calculations discussed above. The extrapolations indicate that the average basin-wide WWTP-derived effluent discharge loads vary between >10,000 tonnes/yr (TPY) for major elements to <100 kg/yr for trace elements (**Figure 2.2**). For the Great Lakes basin, a few estimates exist for the large-scale loading rates of major elements (Cl, Na) and heavy metals (Cu, Zn, Ni, Pb) via atmospheric deposition or riverine input (total runoff) (Nriagu et al., 1995; Chapra et al., 2009; Bentley et al., 2022). A *back-of-the-envelope* comparison with these studies suggests that, on a basin-wide scale, the estimated WWTP-derived inputs of heavy metals (e.g., 43 TPY Cu, 39 TPY Ni, or 6 TPY Pb) are well-below natural riverine loading rates (e.g., >2,000 TPY Cu, >1,800 TPY Ni, or >300 TPY Pb (Bentley et

al., 2022)), even in the more densely populated subbasins (e.g., Lake Erie, Lake Ontario). However, this does not preclude impact of WWTP effluents on water quality on tributary-specific or localized scales (Bentley et al., 2022). In addition, the natural (background) fluxes in the Great Lakes basin or its specific tributary systems are unknown for most other trace elements investigated in this work.

Finally, the estimated basin-wide elemental effluent discharge loads display patterns between trace elements that are different than those observed between the average per-person influent loads (compare plots in **Figure 2.2**). This difference is reflective of the varying removal efficiencies of the investigated trace elements in the studied WWTPs, as is discussed next.

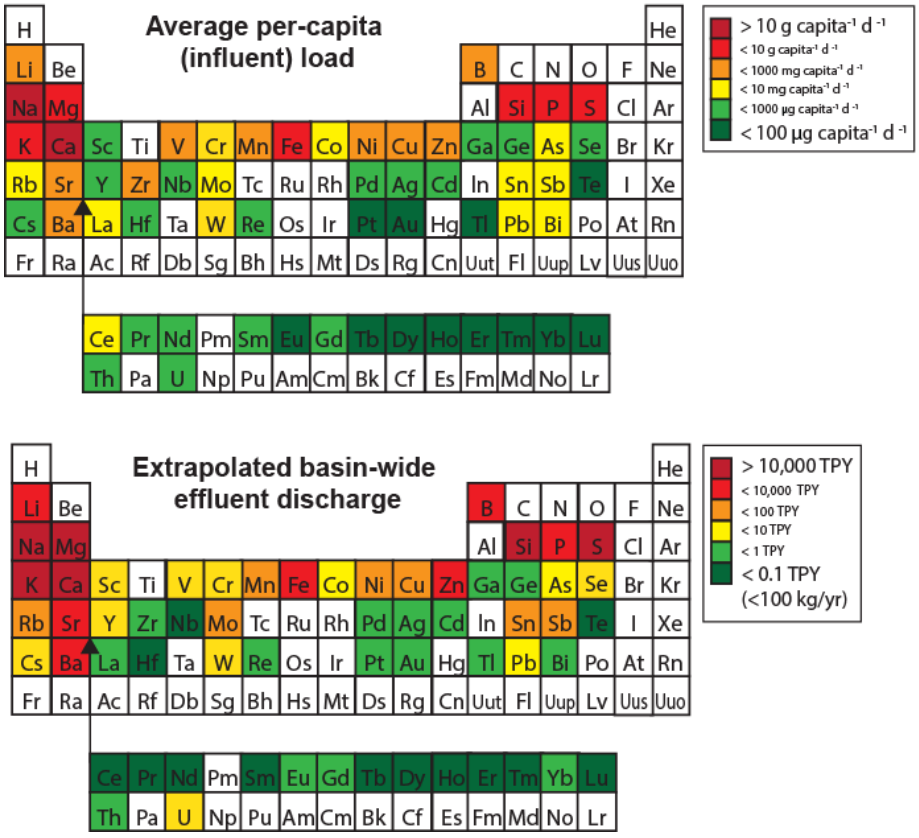

Figure 2.2 *Average per-capita influent loads (top) and extrapolated basin-wide effluent discharge loads (bottom) of 59 major and trace elements calculated using concentrations measured in the effluent and sludges from WWTP in the Great Lakes basin. The (logarithmic) color coding of the elements in the periodic tables is explained in the respective legends. It is possible that certain elements such as Fe and Al may have particularly higher influent loads than effluent loads as they are often added to wastewater during the treatment process.*

2.4.4 Removal Efficiencies of Trace Elements Across Treatment Types

Deploying the same black-box approach discussed above, the elimination rate or removal efficiency of a given element in a given facility was assessed from the preferential enrichment of the influx of an element into the sludge fraction (and therefore not effluent). The elimination rate or removal efficiency for an element e_x in each of the WWTP was calculated as:

$$e_X = \left(\frac{[F_{sludge} \times [X]_{sludge}]}{[(F_{sludge} \times [X]_{sludge}) + (F_{effleunt} \times [X]_{effleunt})]}\right) \times 100 \qquad \text{eq. 2}$$

where $[X]_{sludge}$ and $[X]_{effluent}$ are the concentrations of element *x* in the sludge or effluent sample of each facility, respectively, and F_{sludge} and $F_{effluent}$ are the average sludge production and effluent discharge rates of each facility, respectively (**Table S.2.1**). The sampled WWTP for which elimination rates could be calculated were subdivided into three treatment designations, according to the classification used by the Canadian Council of Ministers of the Environment (CCME, 2009): 12 were considered tertiary, 17 as secondary, and 6 as less than secondary (including primary, preliminary, and lagoon systems; **Table S.2.1**). Elemental elimination rates or removal efficiencies were subsequently compared across different treatment types, as well as between different

(trace) element groups (**Figure 2.3**, **Figure S.2.7**, **Table S.2.14**, **Table S.2.15**). The uncertainty in the calculated elimination rates or removal efficiencies (error propagated from temporal variability in fluxes and concentrations) is therefore somewhat offset by aggregating these elimination rates across WWTP and element groups.

A major performance criterion for wastewater treatment is P removal. Across the sampled facilities, the average P removal efficiency between influent and effluent varied between 76% and >99.9% (**Table S.2.14**), and the extent of P elimination consistently increased with treatment designation, i.e., highest P removal efficiencies were obtained with advanced tertiary treatment facilities (**Figure 2.3**). The behaviors of P and Fe during wastewater treatment are highly coupled and P precipitation by addition of Fe is a commonly deployed P-removal technique (Wilfert et al., 2016), including in the facilities investigated in this work (**Table S.2.1**). Therefore expected, a comparison of the total effluent loads of P and Fe across the sampled facilities reveals a strong correlation that spans across treatment types (**Figure 2.3**). The removal efficiency of Fe, and that of most other investigated elements (**Table S.2.14**), followed the trend of P: when comparing average removal efficiencies across all studied elements, tertiary WWTP achieved an average element removal efficiency of 74%, secondary WWTP had an average removal efficiency of 71%, and WWTP with a designation of less than secondary showed an average removal efficiency of 65% (**Table S.2.15**). A comparison of removal efficiencies of specific groups of elements reveals that the generally less-reactive and more soluble elements (e.g., alkali and alkaline earth metals, including Na, K, Ca and Mg) are not as efficiently removed as more reactive and insoluble elements (e.g., transition metals and REE) (**Figure 2.3, Figure S.2.7**). The average removal efficiency across 35 WWTP was

25% for alkali metals, with Li and Rb being particularly low at 15% and 16%, respectively, 50% for alkaline earth metals, 74% for transition metals, and 85% for REE. This ranking of element groups is observed at all treatment designation levels but increasing levels of treatment (<secondary < secondary < tertiary) do not coincide with improved elimination of all elements. For instance, elements such as Pb and W are consistently eliminated with >97% in all treatment designations. However, most transition metals and REE are on average not only more efficiently removed than alkali and alkaline earth metals but also exhibit improved elimination when the treatment designation increases from <secondary to secondary to tertiary (**Figure 2.3**). Interestingly, removal efficiencies for REE at all three treatment designations are poorer for heavier REE such as Lu, Yb and Tm when compared to lighter REE such as Ce, Pr, and Nd (**Figure S.2.7**), although Gd presents a clear outlier as discussed in Section 3.5.2.

The removal of trace elements from wastewater may be controlled by various mechanisms, ranging from purely chemical precipitation to biological adsorption (Costley & Wallis, 2001; Chen et al., 2009), yet their elimination in the sampled tertiary facilities appears comparatively high irrespective of the deployed tertiary treatment technology (e.g., UV, ozonation, membrane filtration; all of which are typically not tailored to eliminate particular trace elements of concern). It can be hypothesized that the increase in trace element removal during tertiary treatment is due to increased chemical precipitation or biological adsorption due to specific tertiary treatment methods (e.g. removal of P with alum) or simply by increased time in solution. Although the adopted black-box approach and lack of information on the aqueous speciation of the investigated trace elements preclude any speculation about the mechanisms underlying their elimination, the higher

average elimination of many trace elements observed in tertiary treatment facilities reflects an overall increased performance of tertiary wastewater treatment over secondary and primary treatment steps alone.

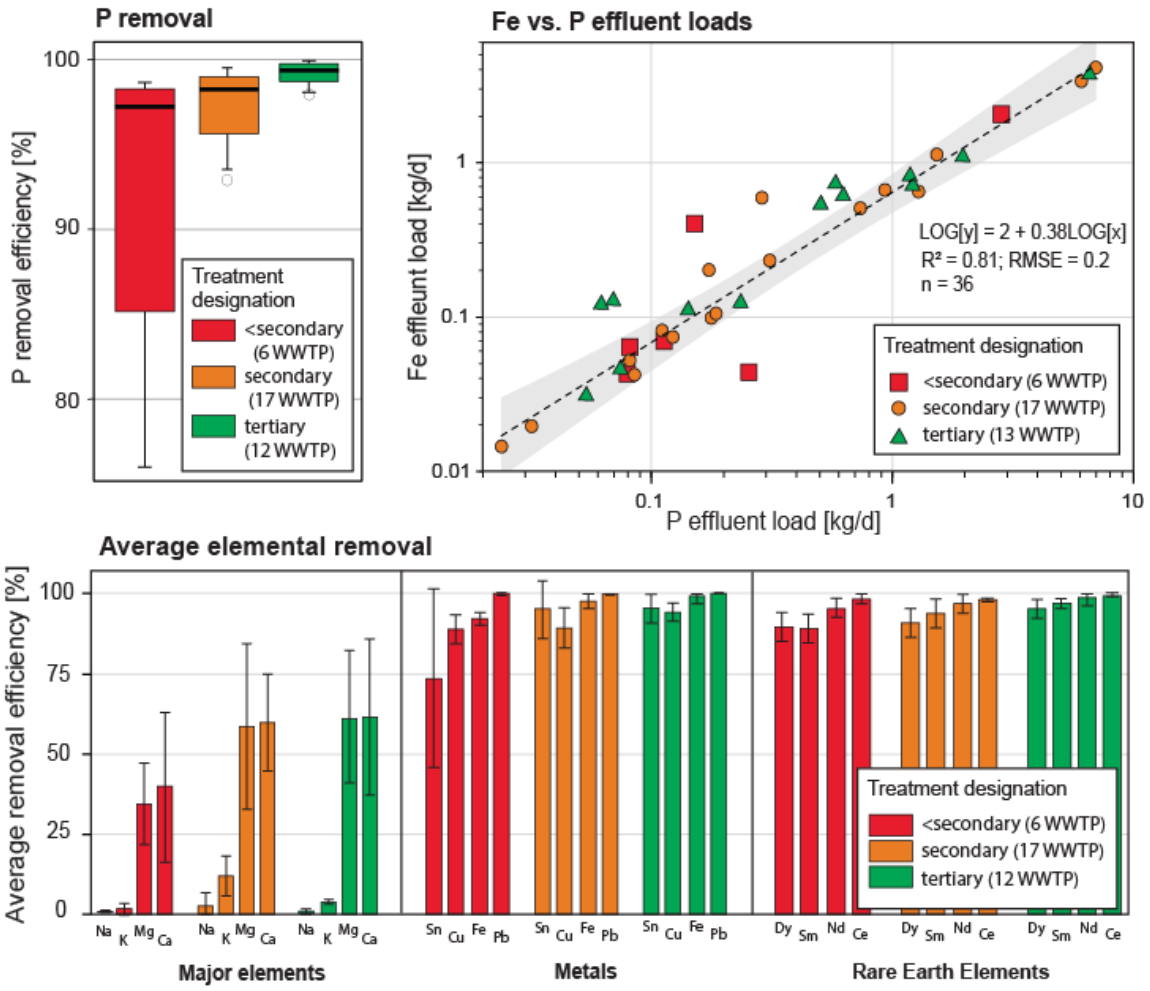

Figure 2.3 *Trends in the removal of different (groups of) elements across different treatment types. Top left: average P removal efficiencies contrasted between different treatment designations. The thick black bars within each box mark the median removal efficiency across the number of WWTP contained in each category; the colored boxes represent the 0.75 and 0.25 percentiles, respectively. Whiskers attached to the boxes*

indicate the highest and lowest values within 1.5 times the interquartile range across the number of WWTP contained in each category (see legend). Outliers are represented by circles. Top right: comparison between Fe and P effluent loads in 36 WWTP (double-logarithmic plot). The equation, R-squared value & root mean squared error (RMSE) of the indicated dotted trend line are provided in the top right; the confidence band for the associated 95% confidence interval is indicated by the grey shading. Bottom: comparison of the average elimination rates of select conservative elements (Na, K, Ca, Mg), heavy metals (Fe, Cu, Pb, Sn) and REE (Dy, Sm, Nd, Ce) across different treatment designations. The error bars on the bar charts indicate the standard deviation in each element and treatment type across the number of WWTP contained in each category (see legend). The color coding is consistent between the panels.

2.4.5 Trends and Anomalies in Concentrations and Loading Rates

After evaluation of the distributions and skew of the measured concentration ranges (**Figure 2.1**), anomalies in measured concentrations and calculated loading rates were arbitrarily defined as having a concentration or load that is at least 5x higher or lower than the median for a particular element; extreme anomalies are considered those with concentrations or loads that are 10x higher or lower than the median value for a particular element. Overall, such operationally defined outliers were scarce among the dataset: effluent and sludge concentrations in the studied facilities were reasonably normally distributed for most elements (**Table S.2.7, Table S.2.8**).

Anomalies were more abundant in the effluents than in the sludges, but outliers in effluent concentrations generally do not correlate to outliers seen in sludge samples. Numerous facilities (n=17) exhibited effluent samples simultaneously enriched in Mg, S

and Ca, at >10x above-average concentrations (**Figure S.2.8**), suggesting a bimodal distribution in their influent load or elimination efficiency. Most other facilities with anomalous effluent or sludge concentrations only exhibited anomalies for one particular element, suggesting that the majority of individual outliers originated from unique sources specific to the WWTP sewershed, as will be further discussed below. Effluent samples from two WWTP showed anomalously high REE levels at >10x the median concentration of 10 REE and effluent samples from two other WWTP were depleted in REE, having 5 different REE concentrations at more than 5x below the median concentration. The consistent enrichment or depletion of REE concentrations at specific facilities is expected from the reasonably similar geochemical properties of these REE, provided they are of geogenic origin (Kaegi et al., 2021).

While there were >100 positive outliers in the sludge and effluent concentration data in this dataset overall, there were only 7 positive outliers in the calculated loads, most of which presented an outlier in the effluent concentration data at the corresponding facilities. This reduction in the number of outliers and variance in the dataset illustrates how consideration of loading rates over concentrations may render the interpretation of patterns across facilities less sensitive to WWTP-specific factors such as differences in treatment capacity and therefore potential dilution of effluent or sludge concentrations. We further examined trends in selected trace elements and their potential anthropogenic versus geogenic sourcing (point- versus diffuse) through qualitative geospatial analyses. The following sections aim to provide examples of the types of exploratory analyses of trace element behavior in wastewater systems that may be expanded to other trace element contaminants in future research.

2.4.5.1 Point-Sourced Anomalies

The element Rhenium (Re) was the only element with an outlier present at >100x the mean in both the sludge and effluent sample for a single WWTP. Although Re is mostly used as a catalyst in the chemical industry, as an alloy for jet engines or as an electrical contact (Carlen & Bryskin, 1994; Lunk et al., 2021), none of these applications were apparent in the connected sewershed. Instead, the sewershed houses a recycling plant for Re and other transition metal alloys with >5 metric ton/yr capacity, which likely acts as a point source for Re to the municipal wastewater system. Another anomaly at 10x median loads was observed for Ni effluent and sludge loads at a facility near Sudbury, Ontario. Colloquially referred to as “Nickel City”, Sudbury hosts extensive Ni-Cu deposits that have been mined since the late 1800’s. The high Ni concentrations observed in this location could stem from anthropogenic enrichment in the surface environment (e.g., seepage or runoff from mining operations) as well as from naturally high Ni levels in ground- and drinking water from the Ni-rich formations in the region (Crawford, 1995), but further investigation is required to quantitatively apportion the contributions of these natural versus anthropogenic factors.

2.4.5.2 Diffuse Anthropogenic Sources

Gadolinium is a REE that is used as a contrast agent in medical imaging (e.g., MRI scanners): unlike geogenic (natural) Gd, this anthropogenic Gd is in the form of stable organo-Gd complexes that are poorly soluble and highly recalcitrant during wastewater treatment (Verplanck et al., 2010; Hissler et al., 2014; Bau et al., 2006). In this work, Gd exhibited an average elimination of only 55% across all investigated WWTP investigated (**Table S.2.14**), but Gd concentrations were otherwise reasonably normally distributed

with an overall skew <0.2 in the effluent and sludge samples (**Table S.2.7**). To quantify the contribution of anthropogenic and potentially hospital-sourced Gd to the observed Gd loads in the sampled WWTPs, Gd concentrations were normalized to REE natural abundance patterns, and the anthropogenic anomaly quantified by analyzing REE ratios (Supporting Information **Methods M1**). The resulting best-fit correlation with the number of hospital beds in each of the corresponding sewersheds shows a relatively strong positive log-linear regression (**Figure 2.4**), corroborating a likely sourcing of anthropogenic hospital-derived Gd throughout the basin (Lerat-Hardy et al., 2019).

The platinum group elements Pt, Rh, and Pd are used in catalytic converters in automobiles and may be emitted during use, mobilized as road dust, and eventually find their way into municipal wastewater (Lesniewska et al., 2004; Rauch et al., 2005). To qualitatively assess this potential pathway of Pt to wastewater sampled in the present study, the relationship between total WWTP influent Pt loads and average road density in each of the connected sewersheds was explored (Supporting Information **Methods M1**). As can be seen in **Figure 2.4**, the obtained best-fit log-linear regression is positive but weaker than the example of Gd. Potential factors complicating a more direct correlation between Pt loads and road density include the fact that Pt may be equally emitted from other applications and industrial processes, and that road length or density statistics alone do not account for road usage or intensity, particularly across rural versus urban areas. Further work is therefore required to quantitatively substantiate this potential pathway of Pt sourced to wastewater across geospatially heterogeneous study areas.

2.4.5.3 Diffuse Natural Sources

In contrast to the examples discussed above, As has limited applications in society or industry that would serve as a major source of As to municipal wastewater systems, mainly because of its well-established toxicity. While As-rich industrial wastewater generated by mining and metal smelting activities is typically treated on-site, As may be introduced to municipal wastewater from background levels of As in drinking water. The Great Lakes region is one with generally low groundwater As levels (Welch et al., 2001; McGuigan et al., 2010), but subtle variations in As levels in local drinking water supplies may be hypothesized to be reflected in WWTP loads. We therefore contrasted the total As influent loads of WWTP serving sewersheds that are predominantly reliant on ground water to the probability of groundwater As levels exceeding 10 µg/L, determined by a global groundwater prediction model (Podgorski & Berg, 2020) (Supporting Information **Methods M1**). Despite a lack of direct mechanistic support for the type of regression explored in this descriptive statistical assessment, the resulting positive relationship (**Figure 2.4**) suggests that at least some of the As sourced to municipal wastewater may be of geogenic origin, particularly in the considered (rural) areas that do not draw drinking water from one of the Great Lakes directly. Because diffusion of localized high As concentrations on the sewershed scale may obscure the influence of industrial wastewater discharges or non-point source human waste streams, additional data would be required to conclude that As dynamics at a particular WWTP outside the median are predominantly caused by geogenic sources. Parallel screening of As loads in drinking water versus influent wastewater may help quantify the potential contributions of these pathways to As loads observed in WWTP.

2.4.5.4 Uncertainty in source attribution

Overall, the presented examples illustrate that both anthropogenic versus geogenic sources may possibly and differently contribute to trace element loads into WWTPs in the Great Lakes basin. While correlation does not equal causality, future work on trace element sourcing to wastewater is required to resolve these various potential contributing factors. Firstly, additional data collection might help alleviate some of the uncertainty associated with the presented estimates of concentration ranges and loading rates, as well as with the subsequent geospatial analyses. This includes time-resolved sampling at different treatment stages and assessment of hydraulic retention rates or contact times in the sampled facilities, as well as potential information from isotope or aqueous speciation analyses. Secondly, improved and systematic delineation of sewershed coverage and characterization of its attributes across the entire wastewater infrastructure network is needed to refine source attribution across large spatial scales, and ultimately help better predict trace element loading rates and mitigate wastewater-derived environmental emissions.

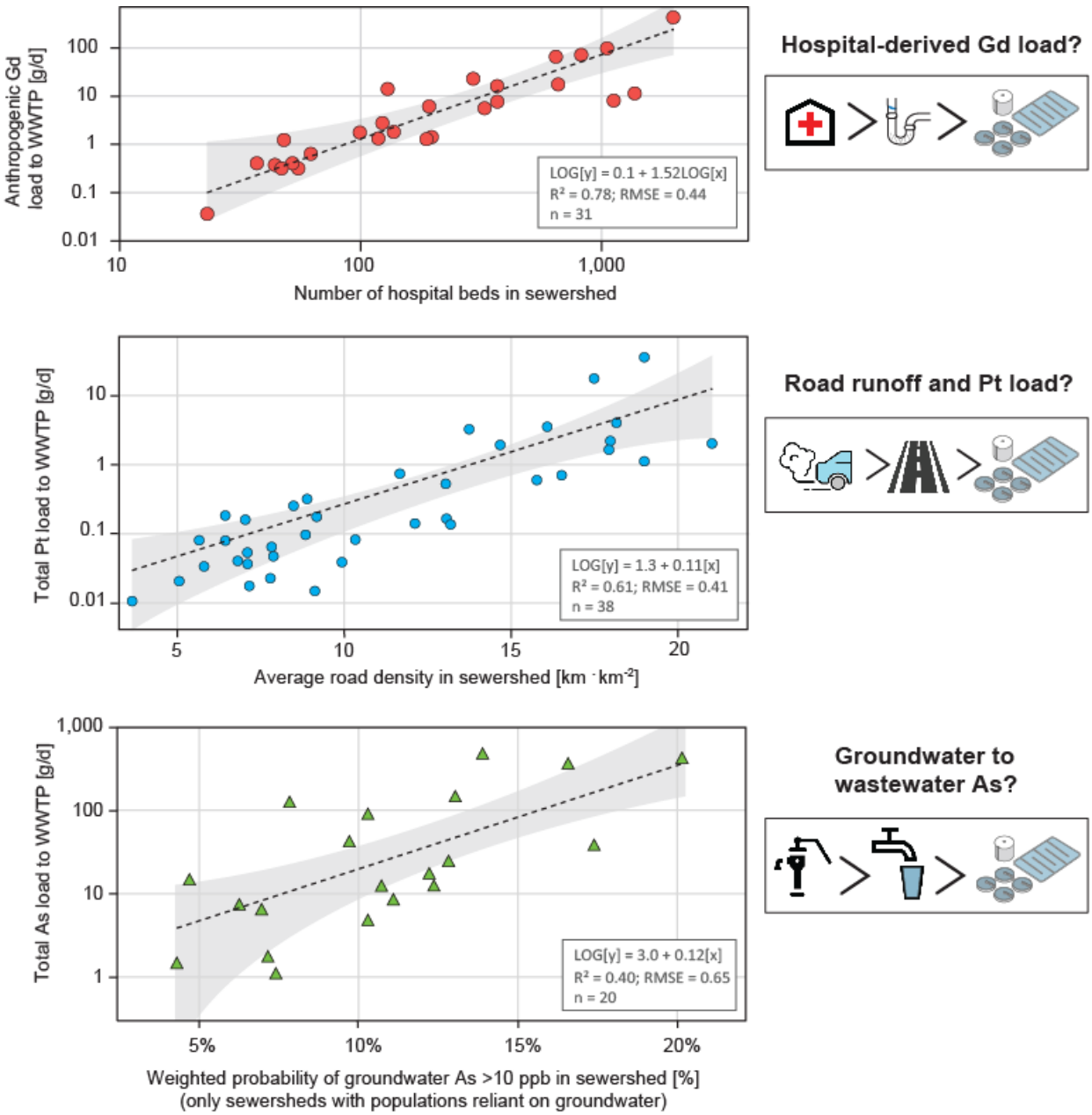

Figure 2.4 *Analysis of potential sources of trace elements to wastewater. Top: regression between WWTP influent loads of anthropogenic Gd and the number of hospital beds in the corresponding connected sewersheds; middle: regression between WWTP influent loads of Pt and the average road length density in the corresponding connected sewersheds; and bottom: regression between total As influent loads to WWTP and a weighted measure of the probability of groundwater As levels exceeding 10 ppb. Note the*

(double) logarithmic axes. The equations, R-squared values and root mean squared error (RMSE) of the indicated dotted trend lines are provided in the bottom right of each panel; the confidence band for the associated 95% confidence interval is indicated by the grey shading. The potential trace element sourcing pathways are schematically illustrated to the right of each panel.

2.5 Conclusions

This study provides new insights into the concentration ranges, loadings rates and removal efficiencies of trace elements in a representative selection of wastewater treatment facilities in the North American Great Lakes basin. From our sampling, trace element analyses, black-box mass-balance calculations, and geospatial analyses, we conclude that:

1) The concentration ranges of trace elements in effluents and biosolids, as well as the therefrom calculated average per-person trace element loads, mostly follow natural abundance patterns and are similar across the various Great Lakes subbasins and similar to concentrations and loads reported in previous studies in other geographic regions;
2) In contrast to conservative major elements and many transition metals, PGE and REE are effectively eliminated (>>90%) during wastewater treatment, whereby facilities with tertiary treatment technologies outperform those with primary/secondary treatment across all groups of (trace) elements;
3) Analysis of the geospatial attributes of the sampled sewersheds, including demographics, land use, road surface or particular industrial activities, may allow one

to contextualize specific trends in trace element loads and explore plausible natural or anthropogenic source pathways.

Our results illustrate that wastewater surveillance may be effectively used to quantify wastewater fluxes and emissions and contribute to an improved understanding of the sourcing of emerging trace element contaminants and their behavior during wastewater treatment. Additional data on emerging trace elements and their loads passing through wastewater treatment facilities in the Great Lakes region is critically needed to understand their potential environmental impacts more quantitatively and to optimize large-scale environmental policy and wastewater management accordingly.

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Conflicts of interest

The authors declare no conflicts of interest.

Supplementary Information

Supplementary Information (Supporting Methods, Figure S.2.1-S.2.8 and Tables S.2.1-S.2.15) contains additional methodology (details on analytical settings and quality control results), and additional results (statistics on observed concentrations, calculated element-specific loads and elimination rates).

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2.7 Supporting Information

2.7.1 Supporting Methods

Methods M1 Source attribution through geospatial and regression analysis

We qualitatively investigated the potential sourcing of a selection of trace elements to wastewater by contrasting their calculated influent loads to specific geospatial sewershed attributes across the sampled facilities. The selected trace elements included Gd, Pt and As, primarily because their effluent and sludge concentrations (and therefore influent loads) could be reliably measured >LOD (**Table S.2.6**, **Table S.2.7**), and a potential wastewater source pathway had been identified in previous works. The data processing and regression analyses performed for these three examples are detailed below.

M.1.1 Gd loads and hospital beds

To isolate the anthropogenic component within the total Gd wastewater influent load, measured Gd concentrations were normalized to REE natural abundance patterns, and the anthropogenic anomaly quantified by examining REE ratios (Kaegi et al., 2021). First, effluent and sludge REE concentrations were normalized to the Post Archean Australian Shale (PAAS; Taylor and McIennan, 2009) reference standard to reduce the Oddo−Harkins effect in natural abundance patterns among REE. The shale-normalized REE patterns corroborated the significantly higher enrichment of REE in the sludge over the effluent samples (**Figure S.2.3**). Effluent samples generally showed positive Gd anomalies and an enrichment of heavy REE over light REE, whereas sludge samples display individual spikes for select REE (**Figure S.2.3**). Subsequently, four REE pattern-filling equations (interpolation) were used to isolate the anthropogenic Gd component from the measured effluent and sludge Gd concentrations:

1. $\frac{Gd}{Gd^*} = \frac{Gd_{SN}}{(0.33Sm_{SN}+0.67Tb_{SN})}$ (Hatje et al., 2016)

2. $log(Gd^*_{SN}) = 0.5\ (Log\ Sm_{SN}\ +\ Log\ Dy_{SN})$ (Ogata, 2006)

3. $\log\ Gd^*_{SN} = \frac{(4logEu_{SN}-logNd_{SN})}{3}$ (Kulaksiz & Bau, 2013)

4. $\frac{Gd_{SN}}{Gd^{*}_{SN}} = \frac{Gd_{SN}}{(0.33Sm_{SN}+0.67Tb_{SN})}$ (Hissler et al., 2014)

where the subscript SN indicates the shale-normalized concentrations and the asterisk Gd* indicates the natural (geogenic) Gd component (total = anthropogenic + geogenic). All four methods yielded very similar anthropogenic Gd fractions (<10% discrepancy; data not shown), of which the average was taken. The anthropogenic sludge and effluent concentrations were subsequently used to calculate anthropogenic *loads*, which were summed to calculate the total anthropogenic Gd influx. These anthropogenic Gd influx loads to the sampled WWTP were correlated to the number of hospital beds within each corresponding sewershed. Therefore, for each of sampled WWTP, the total number of hospital beds within its connected sewersheds was determined from the Homeland Infrastructure Foundation-Level Data (US) and the Ontario Ministry of Health and Long-Term Care (Canada) databases on hospital locations (**Table S.2.5**), which were clipped to the known and estimated sewershed areas (main text, Section 2.3.1). Some sampled facilities had no hospital beds in their sewersheds or REE concentrations <LOD (not for Gd, but for e.g., Eu or Sm that were used to back-calculate anthropogenic Gd anomalies; see above), so that the total number of datapoints was reduced to n = 31 for this analysis (**Figure 2.4**). The ultimate correlation between (per-person and total) Gd influent loads and sewershed hospital beds was investigated in JMP (SAS Software), using descriptive log-linear regression while the outcome variable (loads) nor the descriptor (hospital beds) were normally distributed (skew > 0.2) and the number of samples in this dataset was relatively small.

M.1.2 Pt loads and road density

Total Pt influx loads (sum of sludge and effluent loads) in the sampled WWTP were contrasted to average road density statistics for the respective connected sewersheds. For this, we first calculated the total length of roads within the known and predicted sewersheds (main text, Section 2.3.1) using geospatial datasets on North American roads (**Table S.2.5**). From this, the average road-length density was calculated by dividing total road length by the total surface area of each of the investigated sewersheds. The resulting average road-length densities (between 3 and 22 km km^{-2}) were comparable to those reported by Oswald et al., (2019) for other Ontario sewersheds (between 1 and 20 km

km^{-2}). No WWTP had Pt effluent or sludge concentrations <LOD, so that n = 38 datapoints were considered in this analysis (**Figure 2.4**). Total Pt influx loads were log-normalized before applying log-linear regression to the average road densities.

M.1.3 As loads and predicted As occurrence in groundwater

Total As influx loads (sum of sludge and effluent fractions) in a selection of the sampled WWTP were contrasted to weighted sewershed-wide probabilities of As concentrations in groundwater exceeding the WHO guideline of 10 µg/L. For this, a global prediction map of As groundwater concentrations was adopted from the Groundwater Assessment Platform (GAP; **Table S.2.5**) (Podgorski & Berg, 2020). A raster layer with probabilities of groundwater As concentrations >10 ppb at every square kilometer of the Great Lakes basin was converted to polygons using the Raster Calculator tool in ArcGIS Pro (decimal probability to integer percentage), after which the polygons were clipped to the known and predicted sewershed areas (main text, Section 2.3.1). The area-weighted probabilities of groundwater As levels >10ppb in each sewershed were subsequently calculated across the total sewershed surfaces, with polygons partially covering area outside the sewershed being excluded from the weighted average.

A significant number of the sampled sewersheds house populations that are predominantly reliant on drinking water sources other than groundwater, most notably urban areas that draw water directly from the Great Lakes (e.g., MOECP, 2018). Therefore, sewersheds in which water sources other than groundwater were a major source of drinking water (n = 22) were excluded from this analysis. No sampled facilities had sludge or effluent As concentrations <LOD, so that the total number of datapoints was n = 20 for this analysis (**Figure 2.4**). Total As influx loads were log-normalized before applying log-linear regression to the weighted probabilities of As concentrations exceeding 10 µg/L.

2.7.2 Supporting Figures

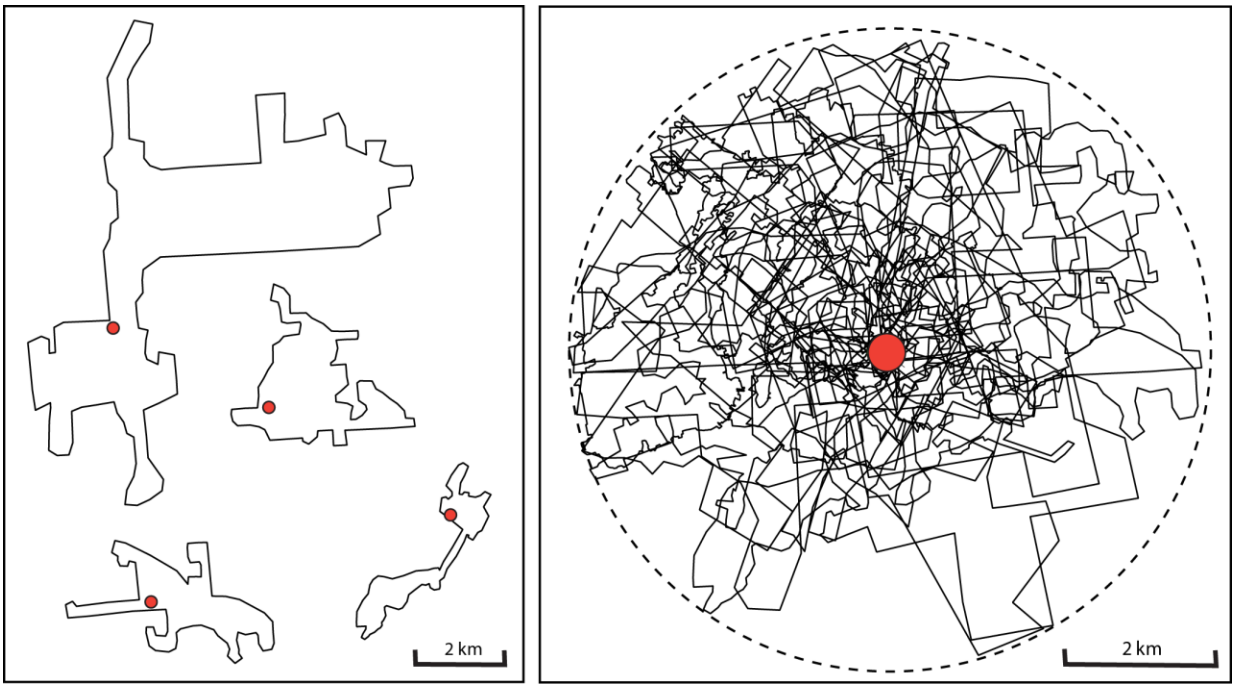

Figure S.2.1 Examples of irregular and odd-shaped sewershed coverages for select facilities in the Great Lakes basin (left), as well as a WWTP-centered overlay of n=32 sewersheds to illustrate the approximation of a reasonably circular maximum radial distance of sewershed coverage (right).

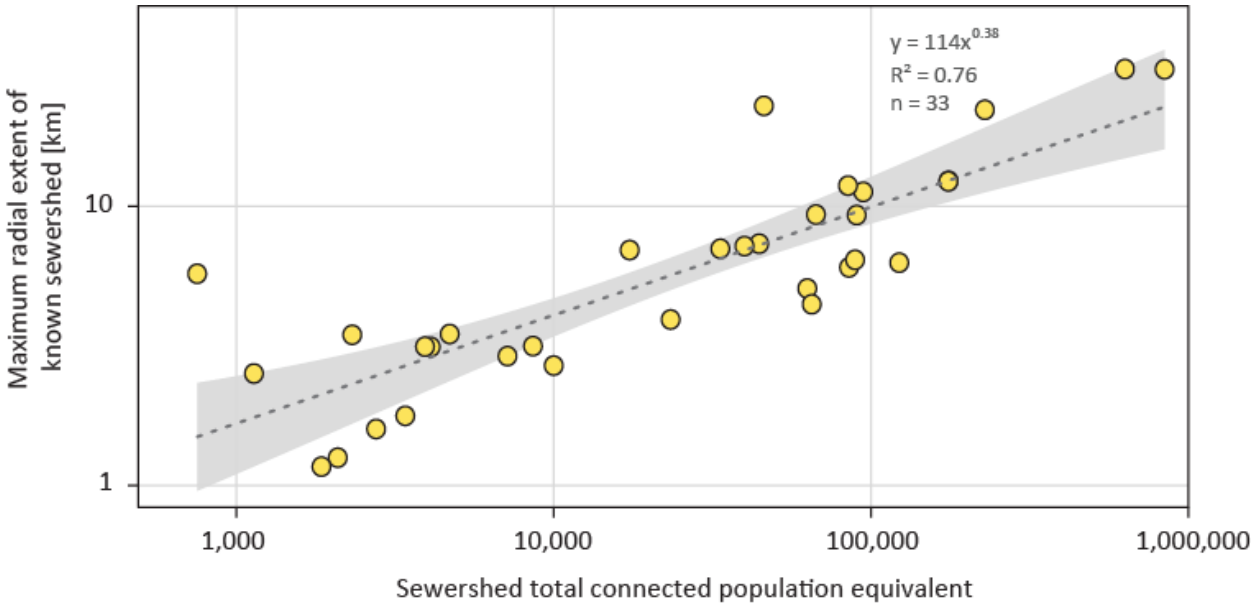

Figure S.2.2 Correlation between the connected population equivalents and maximum radial extents of a selection of known sewersheds in the Great Lakes basin (double-logarithmic plot). The equation, R-squared value for the indicated dotted trend line are provided in the top right; the confidence band for the associated 95% confidence interval is indicated by the grey shading.

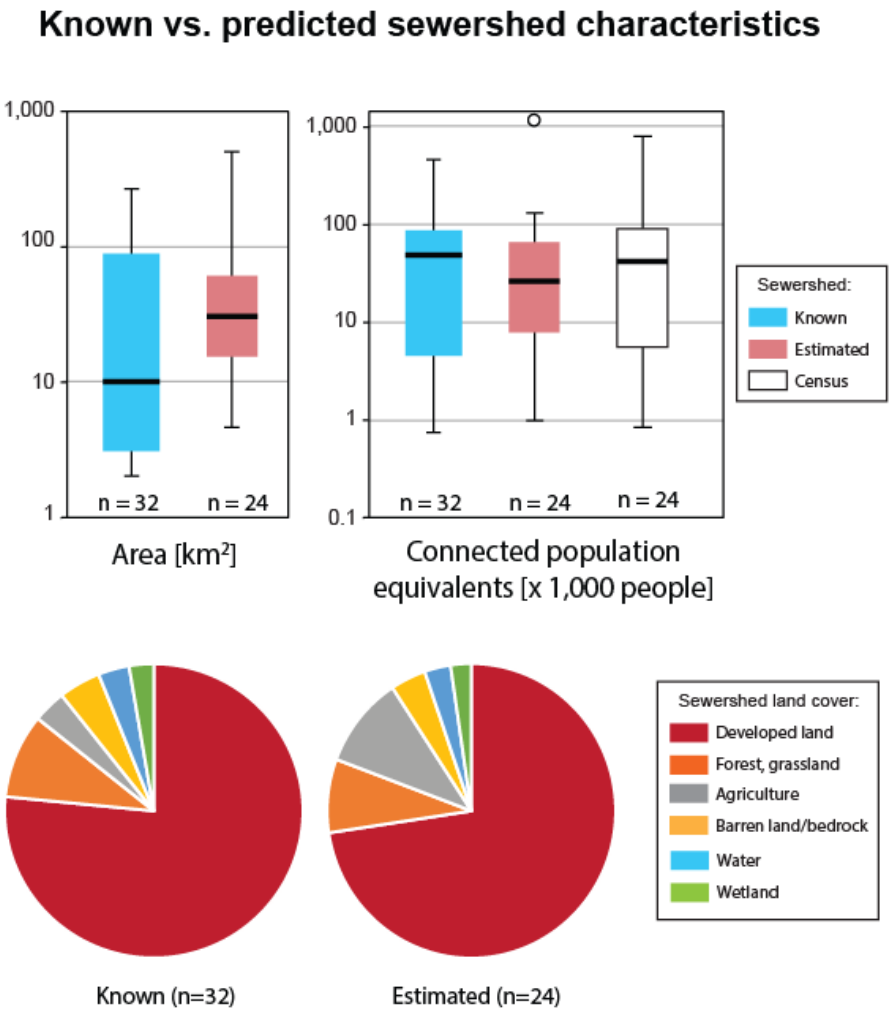

Figure S.2.3 Similarities between characteristics of known and predicted sewersheds. The top left boxplot contrasts the range of predicted surface area of modeled sewersheds to the reported surface areas of publicly available sewersheds. The top right boxplot contrasts the connected population equivalents in the predicted sewersheds to those reported for the known sewersheds as well as to those calculated from geospatial census data on population (**Table S.2.6**). The thick black bars within each box mark the median, the top and bottom of the colored boxes represent the 0.75 and 0.25 percentiles, respectively. Whickers attached to the boxes indicate the highest and lowest values within 1.5 times the interquartile range. Outliers are indicated by circles. The pie-charts (bottom) compare the average land cover category classifications between the known and predicted sewersheds.

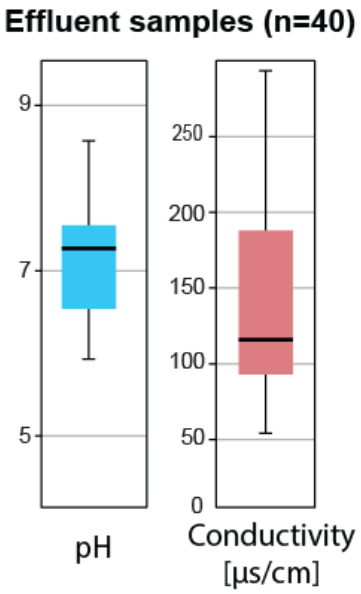

Figure S.2.4 Effluent pH and conductivity ranges measured in 40 WWTP in the Great Lakes basin. The thick black bars within each box mark the median, the top and bottom of the colored boxes represent the 0.75 and 0.25 percentiles, respectively. Whiskers attached to the boxes indicate the highest and lowest values within 1.5 times the interquartile range.

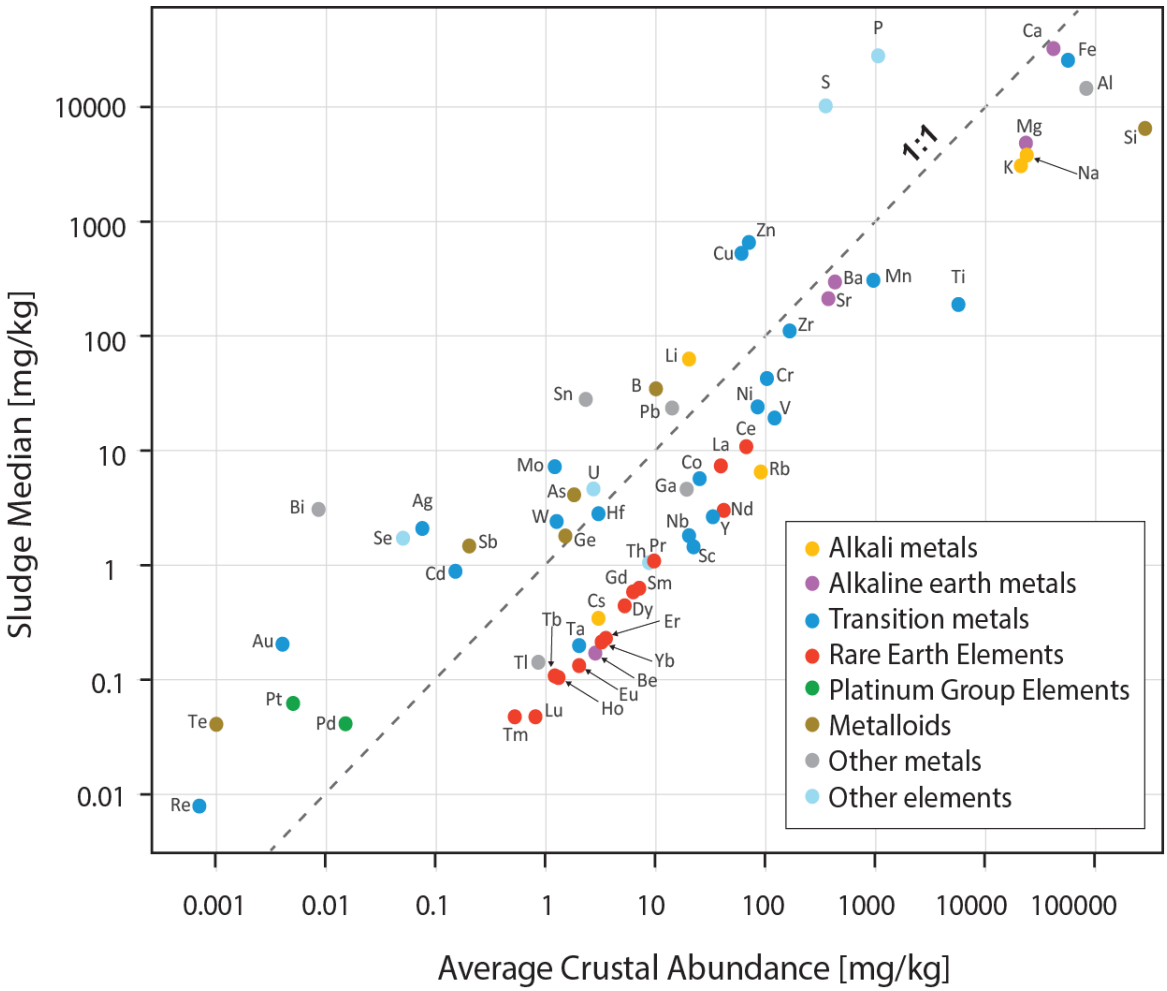

Figure S.2.5 Double-logarithmic scatterplot showing the relationship between median elemental concentrations of (trace) elements measured across the samples WWTP in this study (**Table S.2.8**) and their average crustal abundances (CRC Handbook of Chemistry and Physics, 2016). The various elements are color-coded and grouped as per the legend (lower right); the dashed line illustrates a 1:1 concentration proportionality.

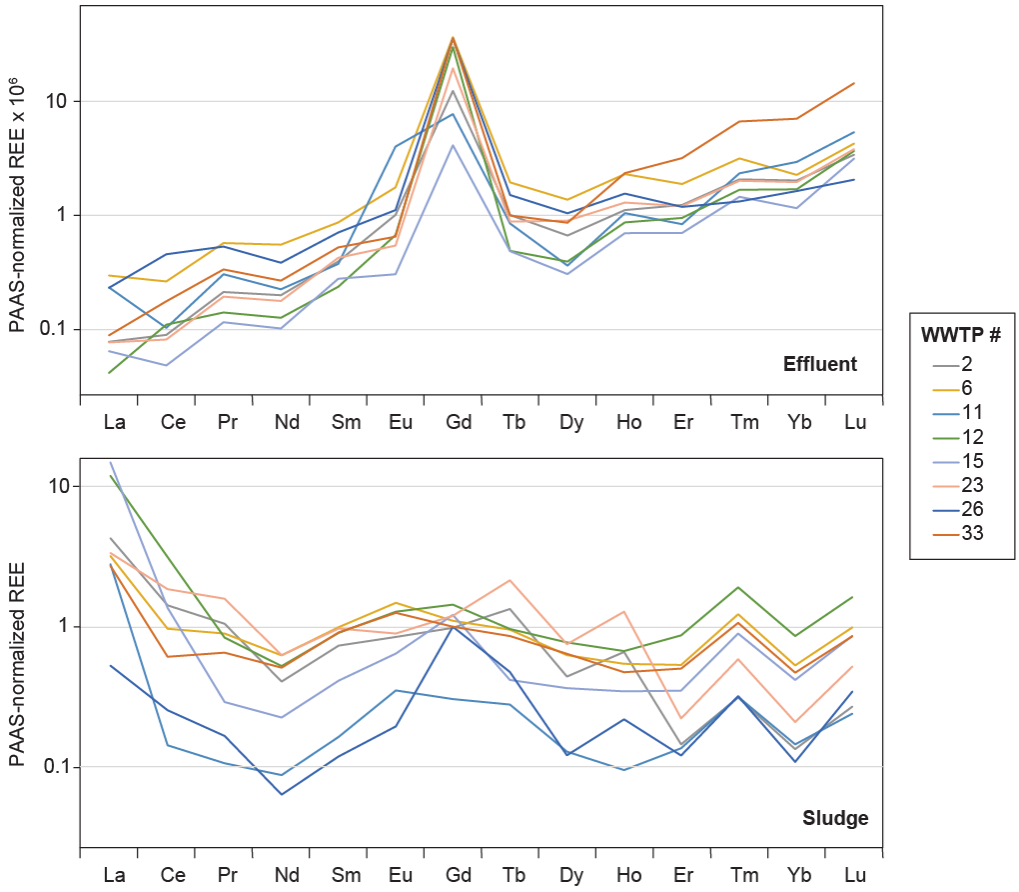

Figure S.2.6 Post-Archean Australian Shale-normalized REE patterns in wastewater effluent (top) and sewage sludge (bottom) from a selection (n = 8) of sampled WWTP in the Great Lakes basin. Legend applies to both frames.

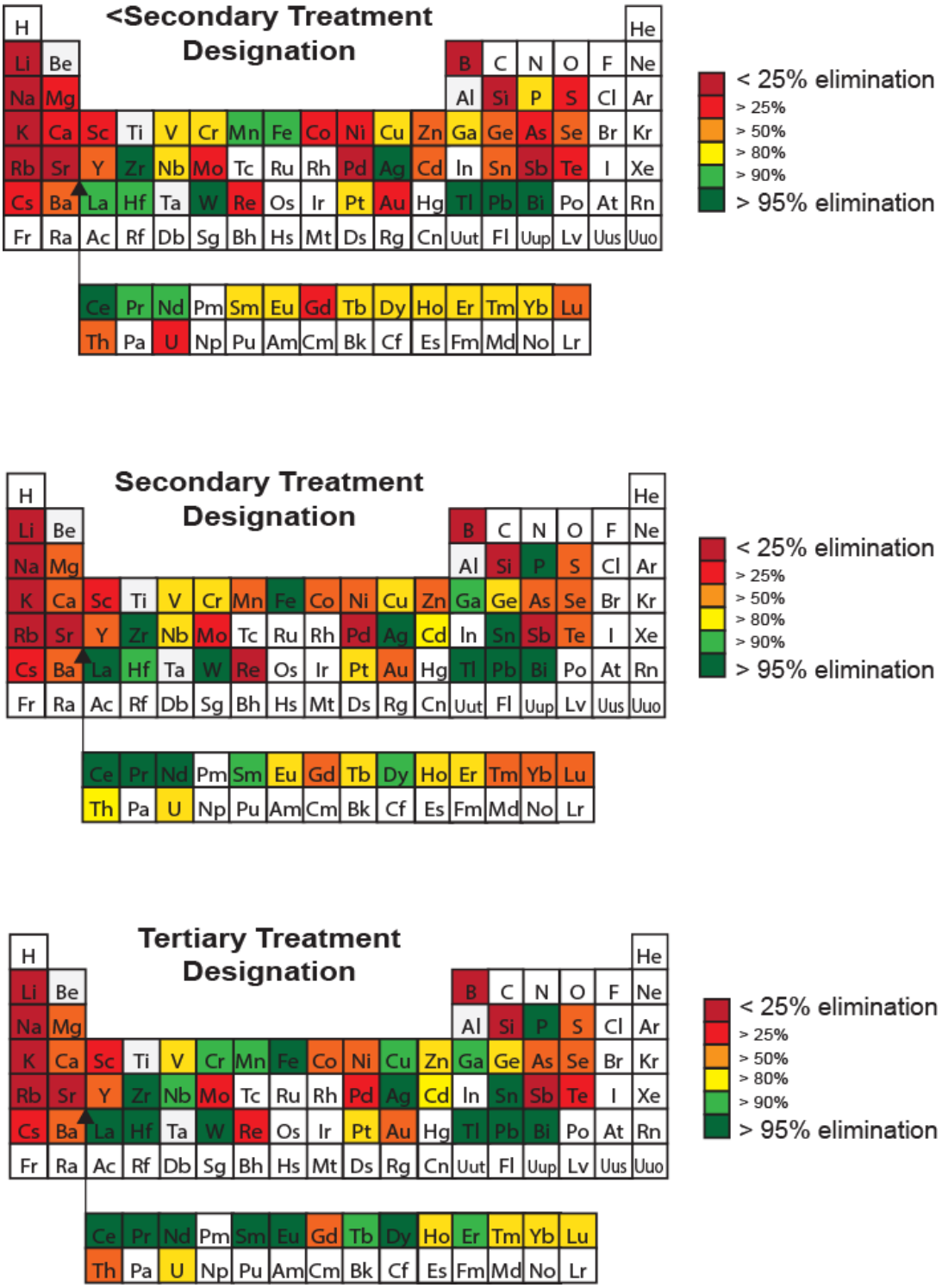

Figure S.2.7 Average WWTP removal efficiencies of 59 measured elements across following treatment designations: <secondary (n=6; top); secondary (n=17; middle); tertiary (n=12; bottom).

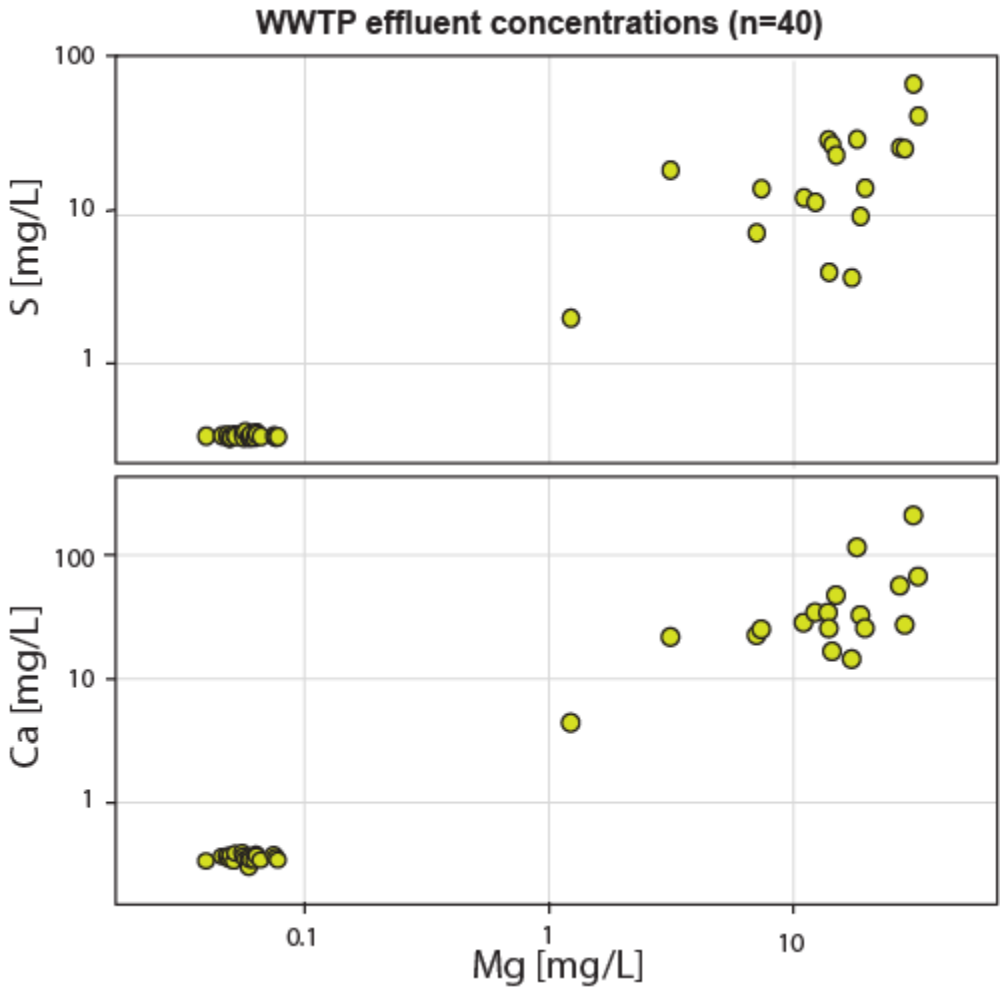

Figure S.2.8 Clustering (bimodal distribution) of S, Mg and Ca concentrations measured in the effluents of 40 sampled WWTP.

2.7.3 Supporting Tables

Table S.2.1 Selected parameters of the sampled wastewater treatment plants.

WWTP Number	WWTP Watershed	Altitude (m)	Population Equivalents	Average Daily Flow (m^3/day)	Average Sludge Production (kg/day)	Treatment Level	Treatment Type
1	Upper St. Lawrence	90	10,109	4,560	1754	Lagoon	Nitr, P-elim (alum), Chlor, D-chlor
2	Lake Huron	74	8,795	5,740	1,050	Secondary	Mech-Biol, P-elim (ferric chloride), Chlor (sodium bisulfate), D-Chlor
3	Lake Superior	199	108,000	61,814	33,000	Secondary	Mech-Biol, P-elim (aluminum sulfate), Nitr, UV
4	Lake Huron	275	4,100	1,545	310	Secondary	Mech-Biol, P-elim, Nitr
5	Lake Ontario	77	50,720	34,795	3,962	Secondary	Mech-Biol, Chlor
6	Lake Erie	200	94,400	31,002	9,500	Secondary	Mech-Biol, E-phos, Chlor, D-Chlor
7	Lake Ontario	100	7,000	3,432	442	Lagoon	Mech-Biol, P-elim (ferric chloride), Nitr
8	Lake Ontario	329	9,674	2,850	752	Tertiary	Mech-Biol, Chlor, D-Chlor, P-elim, Nitr, Tertiary filtration
9	Lake Ontario	80	61,495	22,879		Tertiary	Mech-Biol, UV, P-elim (alum), Nitr, Tertiary filtration
10	Lake Ontario	82	30,000	34,551	2,666	Secondary	Mech-Biol, Chlor, D-Chlor, E-phos, Nitr
11	Lake Michigan	207	12,000	9311	1,391	Secondary	Mech-Biol, P-elim, Oz, Chlor,D-Chlor
12	Lake Ontario	84	8,000	6048	1,063	Secondary	Mech-Biol, Nitr
13	Lake Huron	323	991	900	37	disinfection	Mech-Biol
14	Lake Erie	258	1,300,000	349,204	118,156	Secondary	Mech-Biol, Chlor, Nitr, P-elim (iron salts), D-Chlor, Dentri
15	Lake Michigan	256	5,759	4,890	782	Secondary	Mech-Biol, Chlor, D-Chlor, P-elim, Nitr
16	Lake Erie	206	11,000	8,400	295	Secondary	Mech-Biol, P-elim
17	Lake Erie	183	12,312	2,765	3,900	Tertiary	Mech-Biol, Nitr, UV, P-elim, Tertiary filtration
18	Lake Erie	223	8,449	3,819	710	Preliminary	Mech
19	Lake Michigan	341	2,939	2651	364	Tertiary	Mech-Biol, UV, tertiary filtration, P-elim, Nitr,
20	Lake Erie	320	8,600	4,731	67	Secondary	Mech-Biol, Nitr, Chlor, D-Chlor,
21	Lake Michigan	239	3,612	420	12	Secondary	Mech-Biol, Tertiary filtration, UV
22	Lake Michigan	280	150,000	96,528	222,000	Tertiary	Mech-Biol, P-elim, Nitr, Chlor, D-chlor
23	Lake Ontario	91	3,935	4,000	1,287	Primary	Mech-Biol, Nitr, Chlor, D-Chlor, Nitr, P-elim

Table S.2.1, cont.

WWTP Number	WWTP Watershed	Altitude (m)	Population Equivalents	Average Daily Flow (m^3/day)	Average Sludge Production (kg/day)	Treatment Level	Treatment Type
24	Lake Ontario	77	148,464	68,794	11,547	Tertiary	Mech-Biol, UV, P-elim, Nitr,
25	Lake Erie	300	89,000	170,360	23,083	Secondary	Mech-Biol, UV, P-elim, Nitr
26	Lake Erie	178	228,300	60,779	44,175	Tertiary	Mech-Biol, UV
27	Lake Ontario	107	15,892	9,321	2,900	Secondary	Mech-Biol. P-elim, Nitr, Chlor, D-Chlor
28	Lake Ontario	146	33,489	11,224	2,525	Tertiary	Mech-Biol, P-elim, Nitr, UV
29	Lake Erie	300	12,400	4,111	3,888	Secondary	Mech-Biol, P-elim
30	Lake Erie	223	61,187	35,711	8,050	Secondary	Mech-Biol
31	Lake Ontario	173	48,321	39,468	5,146	Secondary	Mech-Biol, P-elim
32	Upper St. Lawrence	80	4,300	3,730	417	Tertiary	Mech-Biol, P-elim, UV
33	Lake Huron	186	65,000	58,833	7,467	Secondary	Mech-Biol, Chlor, D-Chlor, E-phos, Nitr
34	Lake Ontario	74	67,000	28,763	5,995	Tertiary	Mech-Biol, P-elim, UV
35	Lake Ontario	75	175,000	97,546	9,209	tertiary	Mech-Biol, UV
36	Lake Erie	345	31,465	20,349	1,579	Tertiary	Mech-Biol, UV, P-elim
37	Lake Huron	348	92,043	47,026	14,018	Secondary	Mech-Biol, Chlor, D-Chlor, P-elim, Nitr.
38	Lake Ontario	412	30,113	12,558	2,300	Secondary	Mech-Biol, D-Nitr., chlor, D-chlor,
39	Lake Erie	191	62,875	134,004	21,600	preliminary	Mech-Biol. P-elim, Nitr, Chlor, D-Chlor
40	Lake Erie	329	32,387	44,235	1,851	Secondary	Mech-Biol, UV P-elim, Nitr,
41	Lake Ontario	79	5,000	1,182	313	Secondary	Mech-Biol, P-elim,
42	Lake Ontario	80	460,000	326,613	211,085	Tertiary	Mech-Biol, P-elim (ferric sulphate), Chlor, D-chlor

*Abbreviations: Mech-Biol: Mechanical Biological, P-elim: Phosphorus elimination, UV: Ultraviolet disinfection, Nitr: nitrification, Denitr: denitrification, Chlor: chlorination, D-Chlor: Dichlorination, Oz: ozonation.

Table S.2.2 Comparison of sampled WWTP characteristics versus those of others WWTP in the basin.

	Sampled WWTPs (42 Canadian and US)		**Other WWTPs in Great Lakes Basin (335 Canadian; 1,112 US)**	
Treatment level	**Distribution**	**% (excluding unknowns)**	**Distribution**	**% (excluding unknowns)**
tertiary	13	31	666	52
secondary	23	55	588	46
<secondary	6	14	16	1
unknown	0	-	177	-
Watershed	**Distribution**	**% (excluding unknowns)**	**Distribution**	**% (excluding unknowns)**
Lake Erie	12	30	527	36
Lake Huron	6	15	202	14
Lake Michigan	5	14	395	27
Lake Ontario	16	39	260	18
Lake Superior	1	3	63	4
Upper St. Lawrence	2	-	0	-
Mean Daily Flow (m^3/day)	**Value**		**Value**	
Mean	44,558		14,586	
Median	11,891		757	
Min	420		1	
Max	349,204		3,002,692	
Population Served	**Value**		**Value**	
Mean	85,098		16,187	
Median	30,057		1,741	
Min	991		9	
Max	1,300,000		2,357,666	

Table S.2.3 Certified concentrations and average recovery rates of certified elements after acid-digestion of two reference materials using two acid-digestion methods.

	VHG-SL1 metals in sewage sludge			**VHG-SSD1A metals in sewage-amended soil**			
Element	Certified Concentration (mg/kg)	Recovery Digestion Method 1 (%)	Recovery Digestion Method 2 (%)	Certified Concentration (mg/kg)	Recovery Digestion Method 1 (%)	Recovery Digestion Method 2 (%)	Method Used
Na	199		128	122		97	2
Mg	624		77	311		103	2
Al	906		88	705		318	2
P				154	103		1
S				102		86	2
K	259		74	303		125	2
Ca	2,001		93	1,097		112	2
Ti	11		140	2		544	2
Li				90		127	2
Be	13		85	2		87	2
B	32		38	5		114	2
V	9	98		6	134		1
Cr	19	94		5	165		1
Mn	14	103		9	78		1
Fe	1,063	90		700	101		1
Co	4	133		4	147		1
Ni	7	66		3		124	2
Cu	39		98	17		92	2
Zn	57		90	27		83	2
As	13		85	2		95	2
Se	22		31	3		43	2
Sr	24	95		12	101		1
Mo	8		88	2		90	2
Ag	5		45	2		91	2
Cd	6	78	91	3	80	92	2
Sn	7	127		5	106		1
Sb	8		90	3		105	2
Ba	67		81	39		77	2
Tl	9		71	2		107	2
Pb	6	89		4	111		1

Table S.2.4 Details of employed ICP-MS methodology.

Element	Matrix (digestion method)	Quantification isotope (m/z)	ICP-MS Mode	Element	Matrix (digestion method)	Quantification isotope (m/z)	ICP-MS Mode
Li	2	7	(CH-SQ-N/A)	Ag	2	107	(CH-SQ-KED)
Be	2	9	(CH-SQ-KED)	Cd	2	111	(CH-SQ-KED)
B	2	11	(CH-SQ-KED)	Sn	1	118	(CH-SQ-KED)
Na	2	23	(CH-SQ-N/A)	Sb	2	121	(CH-SQ-KED)
Mg	2	24/26	(CH-SQ-KED)	Te	1	125	(CH-SQ-KED)
Al	2	27	(CM-SQ-N/A)	Cs	2	133	(CH-SQ-KED)
Si	1	29/30	(CH-SQ-KED)	Ba	2	138	(CH-TQ-O2)
P	1	31	(CH-TQ-O2)	La	2	139	(CH-SQ-KED)
S	2	32/34	(CH-TQ-O2)	Ce	2	140	(CH-TQ-O2)
K	2	39	(CH-SQ-N/A)	Nd	2	144	(CH-TQ-O2)
Ca	2	42/44	(CH-SQ-KED)	Sm	2	149	(CH-TQ-O2)
Sc	1	45	(CH-TQ-O2)	Eu	2	151/153	(CH-SQ-KED)
Ti	2	48/49	(CH-TQ-O2)	Gd	2	157	(CH-TQ-O2)
V	1	51	(CH-TQ-O2)	Tb	2	159	(CH-TQ-O2)
Cr	1	52	(CH-TQ-O2)	Dy	2	163	(CH-TQ-O2)
Mn	1	55	(CH-SQ-KED)	Ho	2	165	(CH-TQ-O2)
Fe	1	57	(CH-SQ-KED)	Er	1	166	(CH-TQ-O2)
Co	1	59	(CH-SQ-N/A)	Tm	1	169	(CH-TQ-O2)
Ni	2	60	(CH-SQ-KED)	Yb	1	172	(CH-SQ-KED)
Cu	2	65	(CH-SQ-KED)	Lu	1	175	(CH-TQ-O2)
Zn	2	66	(CH-SQ-KED)	Hf	1	178	(CH-TQ-O2)
Ga	2	71	(CH-SQ-KED)	Ta	1	181	(CH-TQ-O2)
Ge	2	73	(CH-SQ-KED)	W	1	182	(CH-SQ-KED)
As	2	75	(CH-TQ-O2)	Re	1	185	(CH-SQ-KED)
Se	2	78	(CH-SQ-KED)	Pt	1	195	(CH-SQ-KED)
Rb	2	85	(CH-SQ-KED)	Au	1	197	(CH-SQ-KED)
Sr	1	88	(CH-TQ-O2)	Tl	2	205	(CH-SQ-KED)
Y	2	89	(CH-TQ-O2)	Pb	1	208	(CH-SQ-KED)
Zr	1	90	(CH-TQ-O2)	Bi	2	209	(CH-SQ-KED)
Nb	1	93	(CH-TQ-O2)	Th	2	232	(CH-SQ-KED)
Mo	2	98	(CH-TQ-O2)	U	1	238	(CH-SQ-KED)
Pd	2	105	(CH-SQ-KED)				

Table S.2.5 Overview of methodological elemental detection limits.

Element	Detection Limit Effluent Samples (ppb)	Detection Limit Sludge Samples (ppb)	Element	Detection Limit for Effluent Samples (ppb)	Detection Limit for Sludge Samples (ppb)
Na	13	24	Ag	0.003	0.012
Mg	35	125	Cd	0.0042	0.0017
Al	180	55	Sn	0.015	0.024
Si	4002	N/A	Sb	0.0075	0.0034
P	11	56	Te	N/A	0.026
S	29	293	Cs	0.0037	0.0190
K	134	1156	Ba	0.0073	0.0079
Ca	17	11090	La	0.0008	0.0045
Fe	10	4.6	Ce	0.0006	0.0008
Ti	4.9	4.3	Nd	0.0005	0.0007
Li	0.38	1.11	Sm	0.0010	0.0005
Be	0.055	N/A	Eu	0.0003	0.0002
B	0.62	0.46	Gd	0.0000	0.0009
Sc	0.0007	0.015	Tb	0.0000	0.0002
V	0.0030	0.0028	Dy	0.0002	0.0001
Cr	0.036	0.0089	Ho	0.0001	0.0001
Mn	0.051	0.0059	Er	0.0002	0.0002
Co	0.015	0.0084	Tm	0.0001	0.0001
Ni	0.014	0.0049	Yb	0.0002	0.0002
Cu	0.054	0.028	Lu	0.0001	N/A
Zn	0.12	0.41	Hf	0.0003	0.0068
Ga	N/A	0.0021	Ta	0.0097	0.025
Ge	0.019	0.026	W	0.0035	0.0045
As	0.0040	0.010	Re	0.0004	0.0009
Se	0.025	0.13	Pt	0.0076	0.0004
Rb	0.0052	0.020	Au	0.0022	0.0072
Sr	0.0047	0.011	Tl	0.0005	0.0020
Y	0.0008	0.0005	Pb	0.0037	0.0089
Zr	0.0040	0.011	Bi	0.0007	0.0003
Nb	0.0058	0.010	Th	0.0009	0.0181
Mo	0.017	0.017	U	0.0002	0.0001
Pd	0.0021	0.0081			

Table S.2.6 Geospatial data sources.

#	Type of Data	Feature / Attribute	Region	Source	Year
1	Spreadsheet	WWTP location	Ontario	Ontario Ministry of Natural Resources and Forestry (OMNRF)	2018
2	Spreadsheet	WWTP location	USA	US EPA	2012
3	Shapefile (Polygon)	Land cover	Ontario	Ontario land Cover COMPILATION V.2.0. Ontario GeoHub. (2016)	2016
4	Shapefile (Raster)	Land cover	United States	NLCD 2019 Land Cover (CONUS). Data | Multi-Resolution Land Characteristics (MRLC) Consortium.	2019
5	Shapefile (Polygon), Spreadsheet	Census boundaries, population	USA and Canada	Statistics Canada Census Data; United States Census Bureau	2016, 2019
6	Shapefile (Polygon)	Hospital location	USA	Homeland Infrastructure Foundation-Level Data (HIFLD)	2020
7	Shapefile (Polygon)	Hospital location	Canada	Ontario Ministry of Health and Long-Term Care (OMHLTC)	2011
8	Shapefile (Polyline)	Roads	North America	North American Detailed Streets (Arcgis.com) and North America Roads and Highways - UCLA Geoportal	2015, 2019
9	Shapefile (Raster)	Arsenic in Groundwater	North America	GAPMAP	

1: https://data.ontario.ca/dataset/municipal-treated-wastewater-effluent

2: https://www.epa.gov/cwns

3: https://geohub.lio.gov.on.ca/documents/lio::ontario-land-cover-compilation-v-2-0/about

4:https://www.mrlc.gov/data?f%5B0%5D=category%3ALand+Cover&f%5B1%5D=region%3Aconus&f%5B2%5D=year%3A2019

5: https://www12.statcan.gc.ca/census-recensement/2011/geo/bound-limit/bound-limit-2016-eng.cfm
https://www12.statcan.gc.ca/census-recensement/2016/dp-pd/hlt-fst/pd-pl/comprehensive.cfm
https://www2.census.gov/geo/tiger/TIGER2019/

6: https://hifld-geoplatform.opendata.arcgis.com/datasets/6ac5e325468c4cb9b905f1728d6fbf0f_0/explore

7: http://geo2.scholarsportal.info/#r/details/_uri@=3570906326

8: https://www.arcgis.com/home/item.html?id=f38b87cc295541fb88513d1ed7cec9fd#
https://apps.gis.ucla.edu/geodata/dataset/north-america-roads-and-highways/resource/db6ce0cc-ee1f-4393-9568-5871bb58fa12.

9: https://www.gapmaps.org/Home/Public

Table S.2.7 Summary of measured concentrations in effluent samples.

Concentration ranges in WWTP effluent (n=40)							
Element	Unit	Min	Median**	Max	LOD	#<LOD	Median***
Na	mg/L	6.28	100.9	337.4	0.00	22	0.00
Mg	mg/L	0.04	0.08	32.4	0.04	0	0.08
Si	mg/L	7.89	8.51	8.8	4.01	0	8.51
P	mg/L	0.02	0.02	0.28	0.01	0	0.02
S	mg/L	0.33	0.35	71.1	0.03	0	0.35
K	mg/L	1.04	14.6	25.3	0.13	22	0.00
Ca	mg/L	0.30	0.39	231	0.02	0	0.39
Fe	mg/L	0.01	0.01	0.15	0.01	1	0.01
Ti	µg/L	5.04	5.67	6.33	4.93	28	0.00
Li	µg/L	16.10	93	3344	0.38	0	93
Be	µg/L	0.15	0.15	0.15	0.06	39	0.00
B	µg/L	60.50	156	385	0.62	0	156
Sc	µg/L	0.19	0.55	1.29	0.1	0	0.55
V	µg/L	0.03	0.27	6.21	0.01	0	0.27
Cr	µg/L	0.17	0.31	2.14	0.04	0	0.31
Mn	µg/L	0.11	2.6	219	0.05	2	2.09
Co	µg/L	0.18	0.50	1.93	0.02	0	0.50
Ni	µg/L	0.62	3.04	56.4	0.01	0	3.04
Cu	µg/L	0.37	5.5	18	0.05	0	5.5
Zn	µg/L	3.29	19	55	0.13	0	19
Ga	ng/L	3.15	35	740	3.0	0	35
Ge	µg/L	0.02	0.05	1.40	0.02	8	0.04
As	µg/L	0.12	0.36	1.74	0.05	0	0.36
Se	µg/L	0.03	0.15	0.41	0.03	0	0.15
Rb	µg/L	3.86	8.8	15.9	0.01	0	8.8
Sr	µg/L	42.21	260	6923	0.5	0	260
Y	µg/L	0.02	0.11	2.8	0.01	0	0.11
Zr	ng/L	4.49	33	177	3.98	3	29
Nb	µg/L	0.01	0.01	0.19	0.01	16	0.01
Mo	µg/L	0.05	1.8	46.4	0.02	0	1.8
Pd	ng/L	0.7	9.5	210	0.5	0	9.5
Ag	ng/L	0.4	2.4	3.5	0.3	8	1.8
Cd	ng/L	4.27	22.9	263.8	4.23	0	22.9
Sn	µg/L	0.02	0.09	57.9	0.02	0	0.09
Sb	µg/L	0.15	1.45	6.96	0.01	0	1.45
Te	ng/L	2.6	7.5	100	1.0	0	7.5
Cs	µg/L	0.04	0.08	3.5	0.01	0	0.08
Ba	µg/L	1.60	14	545	0.01	0	14

Table S.2.7, Contd.

Concentration ranges in WWTP effluent (N=40)							
Element	Unit	Min	Median**	Max	LOD	#<LOD	Median***
Ce	ng/L	1.58	7.9	63	0.62	0	7.9
Pr	ng/L	0.33	1.5	58	0.28	0	1.5
Nd	ng/L	0.78	4.2	41	0.46	0	4.2
Sm	ng/L	0.99	2.0	40	0.97	7	1.76
Eu	ng/L	0.26	0.6	9.6	0.26	6	0.56
Gd	ng/L	4.43	111	286	0.25	0	111
Tb	ng/L	0.21	0.76	57.6	0.13	0	0.76
Dy	ng/L	0.53	2.26	42.7	0.11	0	2.26
Ho	ng/L	0.14	1.08	56.5	0.08	0	1.08
Er	ng/L	0.29	2.38	39.5	0.16	0	2.38
Tm	ng/L	0.07	0.80	57.1	0.06	0	0.80
Yb	ng/L	0.41	3.29	881	0.18	0	3.29
Lu	ng/L	0.15	1.4	59.2	0.05	0	1.4
Hf	ng/L	0.37	5.7	80.9	0.32	3	4.10
Ta	µg/L	0.01	0.02	0.04	0.01	32	0.005
W	µg/L	0.01	0.08	1.85	0.005	0	0.08
Re	ng/L	1.16	7.8	5082	0.41	0	7.8
Pt	ng/L	0.7	3.8	19	0.1	0	3.8
Au	ng/L	2.30	15.6	634	2.24	5	10.7
Tl	µg/L	0.01	0.02	0.6	0.01	0	0.02
Pb	µg/L	0.01	0.6	4.1	0.01	1	0.56
Bi	ng/L	3.05	25	400	0.71	0	25
Th	ng/L	0.90	27	359	0.88	8	19.8
U	ng/L	0.82	169	1329	0.19	0	169

Median** ignores the values <LOD, Median*** treats values <LOD as 0

Table S.2.8 Summary of measured concentrations in sludge samples.

Concentration ranges in WWTP Sludge (N=38)							
Element	Unit	Min	Median**	Max	LOD	#<LOD	Median***
Na	g/kg	0.52	3.79	21.5	0.02	0	3.79
Mg	g/kg	1.8	4.8	13.1	0.13	0	4.8
Al	g/kg	2.3	14.5	79.1	0.06	0	14.5
Si	g/kg	5.4	6.4	6.9	0.001	0	6.4
P	g/kg	7.9	27.9	56.4	0.06	0	27.9
S	g/kg	1.0	10.2	70.8	0.29	0	10.2
K	g/kg	0.8	3.7	7.1	1.16	0	3.7
Ca	g/kg	17.3	32.2	112	18.79	1	32.0
Fe	g/kg	3.3	25.5	125	0.1	0	25.5
Ti	mg/kg	0.39	188	5302	4.35	3	179
Li	mg/kg	18.7	63.1	425	1.12	0	63.1
Be	mg/kg	0.01	0.17	1.94	0.01	1	0.17
B	mg/kg	11.5	34.6	106	0.47	0	34.6
Sc	mg/kg	0.53	1.45	3.72	0.02	0	1.45
V	mg/kg	5.5	19.3	653	0.02	0	19.3
Cr	mg/kg	12.5	42.5	152	0.01	0	42.5
Mn	mg/kg	82	307	1508	0.01	0	307
Co	mg/kg	1.8	5.7	22.5	0.01	0	5.7
Ni	mg/kg	12.2	24.0	280	0.01	0	24.0
Cu	mg/kg	52	526	1679	0.03	0	526
Zn	mg/kg	70	655	4897	0.42	0	655
Ga	mg/kg	0.4	4.6	13.9	0.03	0	4.6
Ge	mg/kg	0.57	1.8	11.3	0.03	0	1.8
As	mg/kg	1.4	4.1	10.6	0.01	0	4.1
Se	mg/kg	0.4	1.7	6.7	0.13	0	1.7
Rb	mg/kg	1.5	6.5	28.0	0.02	0	6.5
Sr	mg/kg	52	211	2116	0.01	0	211
Y	µg/kg	25	2646	14739	0.48	0	2646
Zr	mg/kg	37.5	110	369	0.01	0	110
Nb	mg/kg	0.65	1.8	5.3	0.01	0	1.8
Mo	mg/kg	3.3	7.2	39	0.02	0	7.2
Pd	µg/kg	0.01	0.04	0.55	0.01	0	0.03
Ag	mg/kg	0.28	2.10	9.45	0.01	0	2.10
Cd	µg/kg	101	887	2778	1.67	0	887
Sn	mg/kg	8.4	27	189	0.02	0	27
Sb	µg/kg	3.9	1476	36358	3.40	0	1476
Te	mg/kg	0.03	0.04	0.22	0.03	19	0.03
Cs	mg/kg	0.11	0.34	1.57	0.02	0	0.34

Table S.2.8 Contd.

Concentration ranges in WWTP Sludge (N=38)							
Element	Unit	Min	Median**	Max	LOD	#<LOD	Median***
Ba	mg/kg	71	296	1597	0.01	0	296
Ce	µg/kg	126	10858	88866	0.81	0	10858
Pr	µg/kg	7.9	1094	11789	0.17	0	1094
Nd	mg/kg	0.03	3.02	28.4	0.005	0	3.02
Sm	mg/kg	0.01	0.63	4.81	0.005	0	0.63
Eu	µg/kg	3.1	133	803	0.18	0	133
Gd	mg/kg	0.01	0.59	3.66	0.005	0	0.59
Tb	µg/kg	4.01	108	610	0.23	0	108
Dy	mg/kg	0.01	0.44	2.15	0.003	0	0.44
Ho	µg/kg	3.8	104	547	1	0	104
Er	mg/kg	0.06	0.23	0.65	0.003	0	0.23
Tm	µg/kg	8.5	47.5	132	1	0	47.5
Yb	mg/kg	0.04	0.21	0.60	0.002	0	0.21
Lu	µg/kg	7.4	47.6	135	0.04	0	47.6
Hf	mg/kg	0.93	2.8	6.5	0.01	0	2.8
Ta	mg/kg	0.03	0.20	1.09	0.03	0	0.20
W	mg/kg	0.68	2.4	29.5	0.02	0	2.4
Re	µg/kg	3.6	7.9	1336	0.92	0	7.9
Pt	mg/kg	0.04	0.06	0.14	0.01	0	0.06
Au	mg/kg	0.02	0.20	2.76	0.01	0	0.20
Tl	mg/kg	0.05	0.14	1.45	0.01	0	0.14
Pb	mg/kg	5.6	23.5	109	0.01	0	23.5
Bi	mg/kg	0.55	25.0	59.8	0.1	0	25.0
Th	mg/kg	0.26	1.09	7.77	0.01	0	1.09
U	mg/kg	1.12	4.6	18.2	0.01	0	4.6

Median** ignores the values <LOD, Median*** treats values <LOD as 0.

Table S.2.9 Comparison of measured effluent concentrations with previous literature.

Reference	Element	Li	Be	B	Na	Mg	P	K	Ca	Ti
	Units	µg/L	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L
This Study	mean	190	0.2	171	139	7	0.03	15	23	6
	median	93	0.15	156	101	0.08	0.02	15	0	6
	max	3344	0.15	386	337	32	0.3	25	231	6
Vriens et al., 2017	median	5	0.001	52	71	9	0.7	14	42	3
	max	687	0.005	400	159	20	9	135	395	26
Kanton St. Gallen, 2009	mean	6	<0.01	272	94	13		15	82	
	max	24	<0.01	880	292	25		47	108	
Gobeil et al., 2005	mean									
Buzier et al., 2006	mean									
Westerhoff et al., 2015	mean				69	9	0.2	7	24	12
	max				206	29	2	26	74	
Verplanck et al., 2010	mean									
	max									

Reference	Element	V	Cr	Mn	Fe	Ni	Co	Cu
	Units	µg/L	µg/L	µg/L	mg/L	µg/L	µg/L	µg/L
This Study	mean	0.7	0.5	14	0.02	6	0.7	6
	median	0.3	0.3	3	0.01	3	0.5	5
	max	6	2.1	219	0.2	56	1.9	19
Vriens et al., 2017	median	0.2	0.2	4	0.01	3	0.3	4
	max	2	3.6	678	0.9	48	3	52
Kanton St. Gallen, 2009	mean	0.2	0.3	37	0.3	2	0.9	7
	max	0.7	8	296	1.9	33	31	41
Gobeil et al., 2005	mean	0.8 ± 0.5	2.7 ± 3	41 ± 13	0.003 ± 0.002	6.6 ± 1.4	0.3 ± 0.04	8.5 ± 3.9
Buzier et al., 2006	mean							
Westerhoff et al., 2015	mean	0.6	1.8	15	0.08	2	0.3	2
	max			20	0.10			10
Verplanck et al., 2010	mean							
	max							

Table S.2.9, Contd.

Reference	Element	Zn	Ga	As	Se	Rb	Sr	Y	Nb
	Units	µg/L	ng/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
This Study	mean	21	74	0.4	0.1	9	680	0.3	0.03
	median	20	35	0.4	0.1	9	260	0.1	0.01
	max	55	740	2	0.4	16	6929	3	0.19
Vriens et al., 2017	median	22	100	0.3	0.3	10	295	0.006	0.02
	max	59	200	4	3.4	28	945	0.04	0.03
Kanton St. Gallen, 2009	mean	30		0.2	0.1		348		
	max	100		1.4	0.4		1242		
Gobeil et al., 2005	mean	23 ± 7.6		0.7 ± 0.2		1.2 ± 0.2	322 ± 62		
Buzier et al., 2006	mean								
Westerhoff et al., 2015	mean	16	<1000	<2	<18	5	292	<0.006	<0.006
	max	48					942		
Verplanck et al., 2010	mean								
	max								

Reference	Element	Mo	Ag	Cd	Sn	Sb	Cs	Ba
	Units	µg/L	µg/L	ng/L	µg/L	µg/L	µg/L	µg/L
This Study	mean	4	0.004	32	1.6	2	0.2	30
	median	2	0.002	23	0.1	1	0.1	14
	max	46	0.03	264	57.1	7	4	545
Vriens et al., 2017	median	1	0.03	11	0.06	0.6	0.1	13
	max	12	0.2	365	9	8	7	38
Kanton St. Gallen, 2009	mean	2	<0.35	20	<0.05	0.3		17
	max	32	<0.35	130	1.38	3		32
Gobeil et al., 2005	mean	8.6 ± 1.3	0.0001 ± 0.00004	240 ± 321			0.05 ± 0.02	21 ± 2.9
Buzier et al., 2006	mean							
Westerhoff et al., 2015	mean	2	<0.2	<500	0.1	0.3	0.05	8
	max	3				0.6		74
Verplanck et al., 2010	mean							
	max							

Table S.2.9, Contd.

This Study	Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho
	Units	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
This Study	mean	42	15	4	9	4	1	112	3	5	3
	median	3	8	2	4	2	0.6	111	0.8	2	1
	max	1352	63	59	42	40	10	286	58	43	57
Vriens et al., 2017	median	1	2	0.3	1	8	4	204	0.2	0.4	0.3
	max	137	65	7	31	79	11	838	0.8	7	1.5
Kanton St. Gallen, 2009	mean										
	max										
Gobeil et al., 2005	mean	3.3	6.3	1.3	5.5	1.5	0.4	308	0.4	3	0.8
Buzier et al., 2006	mean	<30	<50	<30	<6	20	0.01	30	<10	<10	<10
	max					70		300			
Westerhoff et al., 2015	mean	5	10	1.5	6	1.7	0.2	159	0.3	2	0.6
	max	8	27	2	7	2.1	1	239	0.6	3	0.9

Reference	Element	Er	Tm	Yb	Lu	Re	Pt	Au	Pb
	Units	ng/L	ng/L	ng/L	ng/L	ng/L	µg/L	ng/L	µg/L
This Study	mean	5	3	27	3	153	0.02	47	1.0
	median	2	1	3	1	8	0.004	16	0.6
	max	40	57	882	59	5083	0.5	634	4
Vriens et al., 2017	median	0.4	0.2	3	0.3	6	0.006	22	0.06
	max	13	2.5	61	3.8	18	0.5	233	1.9
Kanton St. Gallen, 2009	mean						0		<0.05
	max						0		1.5
Gobeil et al., 2005	mean					3.1 ± 0.5			0.5 ± 0.2
Buzier et al., 2006	mean	3	0.3	7	0.8		0		
Westerhoff et al., 2015	mean	<10	<10	<20	<10	<20	<0.012	80	0.1
	max					60			
Verplanck et al., 2010	mean	2	0.5	3	0.2				
	max	3	0.9	5	1				

Table S.2.9, Contd.

Reference	Element	Bi	U	Zr	W	Tl	Th	Hf	Pd	Te
	Units	ng/L	ng/L	ng/L	µg/L	µg/L	ng/L	ng/L	µg/L	ng/L
This Study	mean	50	237	46	0.2	0.04	72	15	0.46	13
	median	25	170	33	0.1	0.02	27	6	0.11	8
	max	401	1329	177	2	0.6	359	81	6.38	100
Vriens et al., 2017	median	8	400							
	max	49	2300							
Kanton St. Gallen, 2009	mean	<40	700							
	max	220	1600							
Gobeil et al., 2005	mean	5.6 ± 4.0	307 ± 172	22 ± 7.8	0.09 ± 0.03		2.3 ± 2.4			
Buzier et al., 2006	mean									
Westerhoff et al., 2015	mean		200							
	max		900							
Verplanck et al., 2010	mean									
	max									

Table S.2.10 Comparison of Measured Sludge Concentrations with Previous Literature.

	Element	Li	Be	B	Na	Mg	Al	Si	P	S
Reference	Units	mg/kg	mg/kg	mg/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg
This Study	mean	84	0.2	40	5	5	27	6	27	12
	median	63	0.2	35	4	5	15	6	28	10
	max	426	2	106	21	13	79	7	56	70
Vriens et al., 2017	median	3	0.2	18	2	3	10	3	50	3
	max	29	0.5	137	18	10	51	5	76	17
FOEN, 1999	median			4	2	4	13		30	
	max			13	3	10	20		44	
Erikson, 2001	median	4	<0.6	32	3	3	39	40	27	9
	max	13	0.6	390	30	6	92	150	55	26
Kanton St. Gallen, 2009	mean									
Gao, 2012	mean									
Zhang et al., 2002	median	31			10	16	57		2	
	max	44			17	28	85		5	
Stevens, 2010	median				1	4	11		19	
Westerhoff et al., 2015	mean				3	6	17		21	
Verplanck et al., 2010	median									
	max									
Kawasaki, 1998	median		0.4							
	max		0.8							
Shamuyarira & Gumbo,2014	median									
	max									
Mtshali et al., 2014	median			65	1	1	5	0.2		
	max			135	53	10	14	1.2		
Wang et al., 2005	median								11	
Sterritt & Lester, 1980	median									
	max									
Healy et al., 2016	median									
Liu & Sun, 2013	mean				54	2			21	
Ščančar et al., 2000	mean									
Biganzoli et al., 2012	mean									
	max									
Filipović et al., 2013	mean									
Li et al., 2015	mean									
Carletti et al., 2008	mean						9			

Table S.2.10, Contd.

	Element	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni
Reference	Units	g/kg	g/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	g/kg	mg/kg
This Study	mean	4	35	2	370	56	53	385	41	40
	median	3	32	1	188	19	43	307	26	24
	max	7	112	4	5303	654	152	1509	125	280
Vriens et al., 2017	median	3	42	5	152	31	46	326	54	13
	max	11	79	14	233	111	267	1092	124	67
FOEN, 1999	median	3	57	1	138	11	36	427	65	23
	max	8	103	2	240	65	419	916	115	77
Erikson, 2001	median	4	19	3	1400	15	31	230	45	15
	max	12	190	9	4600	44	83	1100	150	168
Kanton St. Gallen, 2009	mean						35			20
Gao, 2012	mean						53	769	47	33
Zhang et al., 2002	median	14	27	13	2592	74	252	565	39	87
	max	23	45	17	3476	103	1317	881	63	279
Stevens, 2010	median		28		87	14	35	433	16	24
Westerhoff et al., 2015	mean	5	38	2	777	35	92	8716	25	41
Verplanck et al., 2010	median									
	max									
Kawasaki, 1998	median									
	max									
Shamuyarira & Gumbo,2014	median						59			35
	max						135			51
Mtshali et al., 2014	median	1	7				429		22	48
	max	5	15				543		37	327
Wang et al., 2005	median	7					317			68
Sterritt & Lester, 1980	median						364	376		110
	max						5190	6120		2020
Healy et al., 2016	median						51		32	25
Liu & Sun, 2013	mean	15	50				222	397	12	79
Ščančar et al., 2000	mean						856		24	621
Biganzoli et al., 2012	mean						25			12
	max						115			27
Filipović et al., 2013	mean						26			28
Li et al., 2015	mean						182			101
Carletti et al., 2008	mean						160		25	50

Table S.2.10, Contd.

	Element	Co	Cu	Zn	Ga	Ge	As	Se	Rb	Sr
Reference	Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
This Study	mean	7	591	800	5	2	5	2	8	321
	median	6	527	656	5	2	4	2	7	212
	max	23	1680	4897	14	11	11	7	28	2117
Vriens et al., 2017	median	7	301	0.8	3	2	3	3	10	251
	max	43	1963	2	6	4	82	16	25	1287
FOEN, 1999	median	12	283	1					5	299
	max	34	507	1.8					11	430
Erikson, 2001	median	5	330	0.5	<1.1	<1.1	4	1	12	110
	max	32	1800	2.3	20	48	14	3	53	1200
Kanton St. Gallen, 2009	mean	11	263	0.6						
Gao, 2012	mean		51	0.2						
Zhang et al., 2002	median	15	279	1.6	19				60	247
	max	17	1002	4.6	29				122	404
Stevens, 2010	median	5	468	0.8			5			
Westerhoff et al., 2015	mean	7	481	1.5	14		8		13	278
Verplanck et al., 2010	median									
	max									
Kawasaki, 1998	median						10			
	max						40			
Shamuyarira & Gumbo,2014	median		351	1.1						
	max		626	1.7						
Mtshali et al., 2014	median	79	208	0.7			12			
	max	163	696	2.3			134			
Wang et al., 2005	median		524	1.8						
Sterritt & Lester, 1980	median	37	565	1.1						
	max	2490	2080	9.2						
Healy et al., 2016	median		640	1.3			<100	3		162
Liu & Sun, 2013	mean		533	1.3						
Ščančar et al., 2000	mean		433	2						
Biganzoli et al., 2012	mean		138	0.4			8	1		
	max		377	1			22	2		
Filipović et al., 2013	mean	3	928	1.1			8			
Li et al., 2015	mean		322	0.9			26			
Carletti et al., 2008	mean		320	2.2			8			

Table S.2.10, Contd.

	Element	Y	Zr	Nb	Mo	Pd	Ag	Cd	Sn	Sb
Reference	Units	µg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	µg/kg
This Study	mean	3702	129	2	10	0.1	3	1	34	3165
	median	2647	111	2	7	0.04	2	1	28	1476
	max	14740	370	5	39	0.5	9	3	189	36359
Vriens et al., 2017	median	3000	9	2	6	0.03	5	1	23	3000
	max	14000	403	6	18	0.986	105	8	216	27000
FOEN, 1999	median	1000	0.4		4	0.5	2	1	15	2000
	max	5000	0.9		13	0.9	92	3	65	102000
Erikson, 2001	median	8000	31	3	6	0.13	5	1	20	1000
	max	32000	240	19	20	0.56	33	11	40	18000
Kanton St. Gallen, 2009	mean				6			2		
Gao, 2012	mean							11		
Zhang et al., 2002	median	18000		13	1				14	
	max	27000		17	1				213	
Stevens, 2010	median	4000			11		14	2	37	2000
Westerhoff et al., 2015	mean	6000		7	13	0.3	46	123	59	4000
Verplanck et al., 2010	median									
	max									
Kawasaki, 1998	median						17	2		2000
	max						61	3		4000
Shamuyarira & Gumbo,2014	median						8	1		
	max						22	3		
Mtshali et al., 2014	median				5				161	
	max				25				303	
Wang et al., 2005	median							17		
Sterritt & Lester, 1980	median				4			16	15	
	max				214			110	329	
Healy et al., 2016	median				5		11	11	55	20000
Liu & Sun, 2013	mean							7		
Ščančar et al., 2000	mean							3		
Biganzoli et al., 2012	mean							1		
	max							1		
Filipović et al., 2013	mean				<1			3		
Li et al., 2015	mean							3		
Carletti et al., 2008	mean							9		

Table S.2.10, Contd.

	Element	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu
Reference	Units	mg/kg	mg/kg	mg/kg	µg/kg	µg/kg	µg/kg	mg/kg	mg/kg	µg/kg
This Study	mean	0.1	0.5	328	9278	14357	1615	4	1	170
	median	0.04	0.3	296	7387	10859	1094	3	1	133
	max	0.22	2	1598	63719	88866	11789	28	5	803
Vriens et al., 2017	median	0.2	0.5	293	12000	19000	1700	6	1.5	400
	max	0.5	2.6	616	178000	854000	5300	21	16.4	3800
FOEN, 1999	median		0.4	163	1000	2000				
	max		0.9	302	99000	74000				
Erikson, 2001	median	0.1	0.5	290	13000	20000	2500	8	1.3	300
	max	0.8	1.9	650	56000	82000	12000	44	6.4	1000
Kanton St. Gallen, 2009	mean									
Gao, 2012	mean				22000	49000	5500	29	5.1	1300
Zhang et al., 2002	median		4.6	694	24000	62000	5800	22	4.1	1100
	max		9.5	1022	35000	83000	8400	33	6.4	1500
Stevens, 2010	median			431						
Westerhoff et al., 2015	mean		0.6	427	12000	26000	1600	7	1.2	300
Verplanck et al., 2010	median				1000	2000	200	1	0.2	30
	max				13000	15000	1900	8	1.8	400
Kawasaki, 1998	median		0.8		6000	13000	1500	6	1	
	max		1.9		14000	38000	3200	13	1.9	
Shamuyarira & Gumbo,2014	median									
	max									
Mtshali et al., 2014	median									
	max									
Wang et al., 2005	median									
Sterritt & Lester, 1980	median									
	max									
Healy et al., 2016	median									
Liu & Sun, 2013	mean									
Ščančar et al., 2000	mean									
Biganzoli et al., 2012	mean									
	max									
Filipović et al., 2013	mean			177						
Li et al., 2015	mean									
Carletti et al., 2008	mean									

Table S.2.10, Contd.

	Element	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf
Reference	Units	mg/kg	µg/kg	mg/kg	µg/kg	mg/kg	µg/kg	mg/kg	µg/kg	mg/kg
This Study	mean	1	140	1	137	0.2	49	0.2	49	3
	median	1	108	0.4	105	0.2	48	0.2	48	3
	max	4	611	2	547	1	133	1	136	7
Vriens et al., 2017	median	1.5	200	1	200	0.6	0.1	0.7	0.1	0.3
	max	6.3	700	2.9	600	1.6	0.2	2.4	0.3	17.4
FOEN, 1999	median									
	max									
Erikson, 2001	median	1.7	300	1.3	400	0.9	0.2	0.9	0.1	0.8
	max	6.8	1000	6.3	1200	2.9	0.6	3.5	0.5	7.4
Kanton St. Gallen, 2009	mean									
Gao, 2012	mean	6.4	800	3.8	700	2.2	0.3	1.9	0.3	
Zhang et al., 2002	median	4.2	500	2.9	600	1.6	0.2	1.9	0.2	
	max	6.3	800	4.1	800	2.3	0.4	2.6	0.4	
Stevens, 2010	median									
Westerhoff et al., 2015	mean	1.4	100	0.9	200	0.5	0.1	0.5	0.1	1
Verplanck et al., 2010	median	0.2	20	0.1	20	0.1	0.01	0.1		
	max	1.9	300	1.5	300	0.8	0.1	0.7		
Kawasaki, 1998	median	1.1	200	0.9	200	0.5	0.1	0.5	0.1	
	max	2.5	300	1.5	300	0.9	0.1	0.8	0.1	
Shamuyarira & Gumbo,2014	median									
	max									
Mtshali et al., 2014	median									
	max									
Wang et al., 2005	median									
Sterritt & Lester, 1980	median									
	max									
Healy et al., 2016	median									
Liu & Sun, 2013	mean									
Ščančar et al., 2000	mean									
Biganzoli et al., 2012	mean									
	max									
Filipović et al., 2013	mean									
Li et al., 2015	mean									
Carletti et al., 2008	mean									

Table S.2.10, Contd.

	Element	Ta	W	Re	Pt	Au	Tl	Pb	Bi	Th
Reference	Units	mg/kg	mg/kg	µg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
This Study	mean	0.3	4	49	0.08	0.3	0.2	28	26	2
	median	0.2	2	8	0.08	0.2	0.1	24	25	1
	max	1	30	1337	0.2	3	1	109	60	8
Vriens et al., 2017	median	0.3	0.7	2	0.02	0.041	0.2	38	4	1
	max	1.9	18	9	2.117	2.573	4.1	232	15	3
FOEN, 1999	median		0.3					56		
	max		3.6					464		
Erikson, 2001	median	0.7	3.5	<40	<0.04	0.57	0.1	32	1	1
	max	3.1	124	80	0.2	5.2	0.4	110	4	12
Kanton St. Gallen, 2009	mean							39		
Gao, 2012	mean							34		8
Zhang et al., 2002	median	1.9						137	2	9
	max	3						549	7	14
Stevens, 2010	median							49		0.1
Westerhoff et al., 2015	mean		1.3	0	<0.1	0.9	0.1	70		1
Verplanck et al., 2010	median									
	max									
Kawasaki, 1998	median								5	
	max								21	
Shamuyarira & Gumbo,2014	median							43		
	max							172		
Mtshali et al., 2014	median							83		
	max							96		
Wang et al., 2005	median							28		
Sterritt & Lester, 1980	median							299		
	max							4540		
Healy et al., 2016	median							791		
Liu & Sun, 2013	mean							115		
Ščančar et al., 2000	mean							126		
Biganzoli et al., 2012	mean							35		
	max							191		
Filipović et al., 2013	mean							67		
Li et al., 2015	mean							100		
Carletti et al., 2008	mean							21		

Table S.2.11 Comparison of Measured Concentrations with Legal Limits.

	Measured Sample Concentrations				Legal Guidelines*		Number of WWTPs Above Lowest Guideline
Element	Sample	Unit	Median	Max	Ontario	US	
Sb	effluent	µg/L	1.4	6.9	20	206	0
As	effluent	µg/L	0.3	1.7	5	104	0
	sludge	mg/kg	4.1	10.6		75	0
B	effluent	µg/L	155	385	200		0 (10)
Cd	effluent	µg/L	0.02	0.26	0.1-0.5	10.2	0
	sludge	mg/kg	0.8	2.7		85	0
Cr	effluent	µg/L	0.3	2.1	8.9	323	0
	sludge	mg/kg	42.5	152		3000	0
Co	effluent	µg/L	0.5	1.9	0.9	124	0 (9)
Cu	effluent	µg/L	5.4	18.9	1-5	242	0 (22)
	sludge	mg/kg	526	1679		4300	0
Fe	effluent	µg/L	14	153	300		0
Pb	effluent	µg/L	0.6	4.1	1-5	160	0 (2)
	sludge	mg/kg	23	109		840	0
Mo	effluent	µg/L	1.8	46	40		0 (1)
	sludge	mg/kg	7.2	39.1		75	0
Ni	effluent	µg/L	3.0	56.4	25	1450	0 (1)
	sludge	mg/kg	24	280		420	0
P	effluent	µg/L	21	282	10-30		0 (8)
Se	effluent	µg/L	0.15	0.41	100		0
	sludge	mg/kg	1.7	6.7		100	0
Tl	effluent	µg/L	0.02	0.6	0.3		0 (2)
W	effluent	µg/L	0.08	1.85	30		0
U	effluent	µg/L	0.17	1.33	5		0
V	effluent	µg/L	0.27	6.2	6	66.2	0 (1)
Zn	effluent	µg/L	19	55	20	420	0 (19)
	sludge	mg/kg	655	4897		7500	0
Sn	effluent	µg/L	0.09	57		120	0
Ti	effluent	µg/L	5.6	6.3		61.8	0

* In Ontario, wastewater effluent regulations for municipal WWTPs are based on site-specific requirements for the receiving body (Provincial Water Quality Objectives [PWQO]; MOEE, 2016), and therefore ranges are sometimes indicated. Effluent concentration limits for the US were adopted from section 437.42 “The Centralized Waste Treatment Point Source Category” of the Electronic Code of Federal Regulations (USEPA, 2003a). Whereas the indicated US limits represent the maximum monthly average effluent concentrations, the PWQO guidelines are representative of surface water concentrations after dilution and mixing of the WWTP effluent with the receiving surface water. Biosolids concentration limits in Ontario and the US depend on the destination of the generated sludge (e.g., incinerated, landfilled or used as fertilizer). Sewage sludge guidelines used for the US are published by the USEPA in “Regulatory Determinations for Pollutants in Biosolids” (USEPA, 2003b); those for Ontario in the Ontario Nutrient Management Act (Ontario, 2021).

Table S.2.12 Per-capita elemental loads of 59 elements (in mg/person/day).

Element	Median	Mean	Max	Min
Na	47551	72008	204240	6066
Ca	11817	18385	151302	545
K	7610	8486	21340	1564
S	3101	7400	47319	238
Si	6152	6597	20303	2437
Fe	4426	5622	25134	7
Mg	1667	4643	20291	81
P	2983	4214	28061	11
Sr	221	484	4588	40
Li	59	154	2426	7
B	77	113	365	32
Zn	81	113	629	1
Mn	39	88	1326	0.4
Cu	45	79	565	0.3
Ba	42	79	640	3
Zr	12	18	90	0.8
V	2	12	220	0.03
Ni	5	11	72	0.3
Cr	5	8	46	0.08
Sn	3	7	54	0.009
Rb	5	6	17	2
Mo	2	5	40	0.09
Bi	2	4	18	0.006
Pb	2	4	15	0.07
Ce	0.9	2	8	0.001
Sb	0.9	2	9	0.1
Co	0.9	2	9	0.1
As	0.6	1	15	0.05
La	0.7	1	5	0.001
W	0.3	1.0	16	8E-05
U	0.7	0.9	4	0.006
Ga	0.5	0.7	3	0.003
Sc	0.5	0.6	3	0.2
Y	0.4	0.6	3	0.03
Nd	0.2	0.5	3	0.0007
Hf	0.3	0.4	2	0.009
Ge	0.2	0.4	2	0.05
Se	0.3	0.4	2	0.07
Ag	0.2	0.4	2	0.0067

Table S.2.12, Contd.

Element	Median	Mean	Max	Min
Nb	0.1	0.3	2	0.009
Pd	0.077	0.3	4	0.0102
Cs	0.1	0.2	3	0.02
Th	0.2	0.2	0.7	0.004
Gd	0.1	0.2	1	0.007
Pr	0.09	0.2	0.9	0.0002
Cd	0.10	0.2	0.7	0.004
Sm	0.06	0.1	0.7	0.004
Re	0.006	0.1	3	0.0005
Dy	0.04	0.08	0.4	0.0002
Au	0.03	0.05	0.2	0.004
Yb	0.03	0.05	0.3	0.0002
Er	0.03	0.04	0.2	0.0001
Eu	0.01	0.03	0.1	0.0007
Tl	0.01	0.02	0.1	1.5E-05
Ho	0.010	0.02	0.08	7.5E-05
Tb	0.01	0.02	0.08	0.0001
Te	0.01	0.02	0.07	3.2E-05
Pt	0.011	0.02	0.1	0.0012
Lu	0.005	0.010	0.05	6.5E-05
Tm	0.005	0.009	0.05	3.2E-05

Table S.2.13 Comparison of per-capita loads with previous literature.

Element	Unit	This study (median) 42 WWTP	Gobeil et al., 2005 1 WWTP	Vriens et al., 2017 (median) 60 WWTP	Carletti et al., 2008 (min-max) 5 WWTP	Buzier et al., 2006 (mean) 1 WWTP	Karvelas et al., 2003 (mean) 1 WWTP
Cu	mg/capita/day	45	11	30	(9 – 49)	2.7	1.6
Zn	mg/capita/day	81	29	76	(83 – 1896)		14
Pb	mg/capita/day	2	1	3.4	(1.6 – 8.6)	0.15	1.2
Cr	mg/capita/day	5	4	3.7	(9 – 56)	0.7	1.2
Ni	mg/capita/day	5	9	2.6	(4 – 49)	2.4	1.6
Cd	mg/capita/day	0.1	0.4	0.1	(0.1 – 21.8)	0.03	0.1
V	mg/capita/day	2	1	2.5			
Cr	mg/capita/day	5	4	3.7			
Mn	mg/capita/day	39	52	32			
Fe	mg/capita/day	4426	396	3900			
Co	mg/capita/day	1	0.4	0.8			
As	mg/capita/day	1	1	0.4			
Rb	mg/capita/day	5	2	6.5			
Sr	mg/capita/day	221	427	161			
Zr	mg/capita/day	12	0.03	1.4			
Mo	mg/capita/day	2	11	1.1			
Cs	mg/capita/day	0.1	0.1	0.2			
Ba	mg/capita/day	42	28	31			
W	mg/capita/day	0.3	0.1	0.2			
Bi	mg/capita/day	2	0.01	0.4			
Th	mg/capita/day	0.4	0.003	0.08			
U	mg/capita/day	0.2	0.4	0.5			

Table S.2.14 Removal efficiencies [%] of 59 elements in WWTPs (all treatment designations).

Element	Mean	Min	Median	Max	Element	Mean	Min	Median	Max
P (total)	97.0	76.5	99.5	99.95	Cs	41.3	0.6	38.6	80.27
B	6.6	0.1	4.2	29.83	Ba	72.2	0.8	77.4	96.93
Cu	90.7	11.9	94.4	99.61	La	97.4	71.3	99.8	99.97
Fe	97.0	63.6	99.5	99.98	Ce	98.5	79.1	99.6	99.94
Mg	55.4	0.1	80.5	99.22	Pr	96.7	64.8	99.2	99.92
Si	15.9	0.2	11.6	63.17	Nd	97.2	76.6	99.2	99.87
S	50.8	0.5	55.6	98.52	Sm	94.5	58.6	97.7	99.72
Ca	57.1	0.5	78.9	99.35	Eu	91.0	6.8	96.1	99.52
Li	15.9	0.1	11.3	70.25	Gd	55.5	4.6	56.4	96.00
Sc	36.4	0.9	33.2	94.64	Tb	89.9	20.6	96.1	99.47
V	87.4	23.2	94.0	99.04	Dy	92.1	48.8	96.5	99.57
Cr	89.8	10.6	95.6	99.34	Ho	88.2	22.2	93.7	99.51
Mn	84.5	9.1	95.2	99.99	Er	87.8	38.1	93.8	99.05
Co	63.3	3.0	66.2	96.35	Tm	81.7	17.5	90.6	98.91
Ni	56.7	1.6	55.5	96.47	Yb	81.9	13.0	92.3	98.74
Zn	79.0	6.3	83.2	99.25	Lu	76.2	15.6	85.3	98.50
Ga	92.0	35.1	96.2	99.83	Hf	95.6	24.0	99.4	99.97
Ge	80.1	8.7	89.3	99.31	W	99.9	98.7	100.0	100.00
As	64.7	1.2	72.1	95.42	Re	21.9	0.4	9.7	93.93
Se	65.2	4.2	72.0	97.46	Au	63.5	0.4	67.1	99.29
Rb	16.3	0.3	12.8	48.19	Tl	99.7	95.3	99.9	99.99
Sr	14.9	0.1	10.8	63.30	Pb	99.9	97.1	100.0	100.00
Y	70.4	6.4	82.1	98.54	Bi	97.2	49.0	99.1	99.95
Zr	99.5	88.8	99.9	99.99	Th	78.9	1.2	89.3	99.52
Nb	88.8	15.8	95.7	99.67	U	78.3	5.9	88.9	99.97
Mo	45.5	0.8	45.0	97.71	Na	1.4	0.1	1.4	12.53
Cd	80.5	7.9	83.8	98.03	K	6.5	0.1	4.7	43.66
Sn	91.5	3.4	98.2	99.80	Pt	70.2	41.1	79.1	97.8
Sb	23.9	0.2	14.8	78.79	Pd	19.1	5.1	11.3	93.1
Te	48.0	6.1	48.3	100.00	Ag	98.7	90.6	99.4	100.0

Table S.2.15 Average elimination rates in WWTP of different treatment designation (59 elements).

WWTP#	Treatment designation	Average elimination rate for 59 calculated elemental loads (%)	Average elimination rate of each designation (%)
8	tertiary	71	74
9	tertiary	70	
17	tertiary	88	
19	tertiary	66	
22	tertiary	89	
26	tertiary	71	
28	tertiary	76	
32	tertiary	73	
34	tertiary	70	
35	tertiary	64	
36	tertiary	62	
42	tertiary	83	
2	secondary	77	71
3	secondary	87	
4	secondary	74	
37	secondary	78	
41	secondary	76	
10	secondary	59	
11	secondary	72	
12	secondary	75	
14	secondary	80	
15	secondary	68	
16	secondary	63	
27	secondary	77	
38	secondary	71	
21	secondary	28	
5	secondary	65	
29	secondary	84	
33	secondary	70	
1	< secondary	73	65
7	< secondary	42	
39	< secondary	76	
13	< secondary	61	
23	< secondary	76	
18	< secondary	65	

2.7.4 Supporting References

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Chapter 3: Imprints of Wastewater Discharge on Trace Element Dynamics in the Grand River, Ontario

3.1 Abstract

Discharge of treated wastewater effluent can be an important source of contaminants to downstream environments, yet only a handful of specific effluent parameters are regulated and monitored in Canada. Consequently, the importance of effluent discharge for the surface water budgets of trace elements remains poorly understood. Here, we report concentrations of >50 major and trace element in >30 riverine and effluent samples collected in the Grand River catchment, Ontario, in an attempt to assess imprints of effluent discharge on riverine trace element loads. We find that effluent-derived loads of major and trace elements generally outweigh those of tributaries when contrasted to their hydraulic contribution at the point of confluence. In particular, effluent-derived loads of conservative elements (>30-fold the receiving riverine load), but also heavy metals and REE (>10-fold and 2-fold the receiving riverine load, respectively) exerted major controls on trace element dynamics in the Grand River. Yet, multiple elemental tracers suggest that detectable imprints of these trace element inputs remain spatially restricted and limited to the catchment's upper reaches, urban areas, and confluences and effluent inputs with low mixing ratios. This study presents important baseline data for trace elements in this complex riverine system and highlights the need for expanded surface water quality monitoring to disentangle anthropogenic from natural factors affecting trace element budgets.

3.2 Introduction

Population growth, continued industrialization, and climate change impose growing stresses on surface water quality around the world, in severe cases resulting in deleterious effects to these ecosystems and the impairment of drinking water resources (Teng et al., 2011; Lyndall et al., 2010; Jastram et al., 2013). Contamination of surface waters has been causally linked to various point- and non-point sources, both of which can introduce unique types and various amounts of contaminants. Non-point or diffuse sources of contamination to surface waters include atmospheric deposition and urban and agricultural runoff, whereas spatially constrained sources span from industrial effluents (organic compounds, metals) and mining operations (polycyclic aromatic hydrocarbons, metals and acidity) to landfill sites (pathogens, nitrates) and, often importantly, municipal wastewater treatment plants (WWTP) and combined sewage overflows (CSO) (Ritter et al., 2002). Disentangling the origins of contaminants to surface water systems is imperative to implementing effective source reduction and management policies, but remains a challenging feat, particularly in complex catchment areas with a variety of land-uses where a combination of these sources contribute to the riverine loads of aquatic pollutants (Jabbar and Grote, 2019; Paul et al., 2021).

Wastewater treatment facilities often release treated effluent directly into streams, rivers, and lakes, and as a consequence, may constitute important point-sources of surface water contamination. The impacts on the receiving water body can be intensified when mixing rates are low due to increased effluent discharge or episodes of decreased flow. Furthermore, the frequency and impacts of low mixing ratios may become harder to predict as a result of climate change (Li et al., 2016). Treated wastewater effluent has

been found to constitute a possible source of various contaminants, including heavy metals (Oliver and Cosgrove, 1975; Goldstone, 1990; Agoro et al., 2020), trace metals (Westerhoff et al., 2015; Pinter et al., 2021; Turcotte et al., 2022), microbial pathogens (Ajonina et al., 2015), hormones (Phillips et al., 2012), organic pollutants (Ahmaruzzaman, 2009; Dickenson et al., 2011), nutrients (Carey and Migliaccio, 2009; Bali and Gueddari, 2019), pharmaceuticals (Ternes, 2004; Guerra et al., 2019), microplastics (Prata, 2018; Baresel and Olshammar, 2019; Sun et al., 2019), and other chemicals of emerging concern (CEC) (Petrie et al., 2015). Past studies have documented the various impacts of such contaminants on their receiving environments, including threats to drinking water quality, physical habitat properties, and ecosystem health. Examples of effluent-related water quality impairments include eutrophication (Askey, 2007; Akpor and and Muchie, 2011) and oxygen depletion (Akpor and Muchie, 2011; Bai et al., 2019), water temperature variability (Holeton et al., 2011), turbidity changes (Holeton et al., 2011), bacterial contamination (Akpor and Muchie, 2011; Igere et al., 2020), and aquatic toxicity (Petrie et al., 2015). Exposure to wastewater-derived contaminants through drinking water and recreational activities has also been linked to negative effects on human health (Akpor and and Muchie, 2011). The potential negative impacts of WWTP-derived contaminant discharges thus need to be understood to minimize exposure risk and optimize long-term water quality management.

Pinter et al. 2021 and earlier works (Poulton, 1992; Gobeil et al., 2005; Laitta et al., 2014) have shown that WWTP can deliver significant loads of trace elements to surface waters, despite substantial elimination during treatment. Most municipal treatment facilities are designed to remove regulated substances from the aqueous phase before

discharge to the environment, with the removal of other, non-regulated substances (including many emerging contaminants) being a byproduct of the treatment process. Unfortunately, and adding to the relatively thin ecotoxicological knowledge base on trace elements, the scales and impacts of WWTP-derived trace element loads have remained largely enigmatic. This is in part because trace element dynamics in rivers and surface water systems remain poorly understood generally, as they are not commonly part of government surveillance programs, e.g., the Provincial Water Quality Monitoring Network (PWQMN) in Ontario (Ontario Ministry of Environment and Energy, 1994).

To this end, we studied the loads of major and trace elements, as well as other water quality parameters, in WWTP effluents and riverine samples from the Grand River, Ontario, Canada. The Grand River is Southern Ontario's largest watershed and a particularly suitable catchment for this analysis, because i) its water quality is intensively monitored and managed (Liu et al., 2016; Veale and Cooke, 2016; Irvine et al., 2019, Zhang et al., 2021), ii) its hydrometrics are gauged in high resolution, iii) it has a particularly large variety of land-use types including geographically separated urban developments (**Figure 3.1**), and iv) 30 WWTP of various size and treatment technologies are located in its watershed, of which impacts have been previously investigated (Gillis et al., 2014; Lee et al., 2014; Bahamonde et al., 2015; Hayward, 2020). The purpose of this work is to report current trace metal concentrations in the Grand River, determine spatial water quality and trace metal trends, and assess the potential imprint of WWTP effluent on river water quality using mass-balance techniques and elemental tracers.

3.3 Materials and Methods

3.3.1 Surface water sampling

A total of 19 surface water samples from the Grand River and six of its major tributaries were collected over the course of 2 days in August 2021: 13 from the Grand River, and one each from the Conestogo River, Speed River, Nith River, Fair Child Creek, Big Creek, and McKenzie Creek (**Figure 3.1**; coordinates in **Table S.3.1**). The most upstream and downstream of the Grand River samples were taken 216 km and 7.4 km, respectively, from its mouth at Lake Erie: the samples collectively covered a total of 77% of the river length and were spaced <20 km between to allow for a high-resolution assessment of water quality. Tributary sampling locations were selected as close as accessible to their point of confluence with the Grand River (on average 1.6 km) to ensure representation of tributary loads and allow for mixing calculations (**Table S.3.1**). During sampling, temperature was typical for the region, and precipitation was slightly below average, yet well within ranges seen in the area over the previous five years (**Figure S.3.1**).

Surface water samples were collected from the centerline of the river or tributary using a metal-free, 20L LDPE Niskin-type sampling vessel. Immediately upon collection, samples were split into two aliquots: (i) 250 mL was filtered using 0.2 µm PTFE syringe filters (VWR, Canada) and acidified to 1% HNO_3 using ultrapure nitric acid (70%, Sigma Aldrich) for the analysis of total major cation concentrations, and (ii) 250 mL was filtered but not acidified for the analysis of major anions and other physicochemical parameters (see Section 2.3). Both aliquots were stored in pre-cleaned Nalgene sample bottles (TraceCert, Supelco) at 4°C until analysis. The remainder of the collected sample was used to measure electrochemical parameters (pH, Total Dissolved Solids (TDS),

Electrical Conductivity (EC), Dissolved Oxygen (DO), and Temperature) in the field, using HANA HI9813-6 multimeters, Milwaukee MW500 Portable ORP meters, and Extech DO-210 Dissolved Oxygen probes. The sensors were calibrated daily according to manufacturer instructions and all sampling equipment was pre-cleaned with ultrapure HNO_3 and rinsed with de-ionized (DI) water (18.2 MΩ; Millipore Q-pod) before use. Detection limits for these major water quality parameters can be found in **Table S.3.2**. Blanks were collected in the field every n=10 samples to assess potential contamination.

3.3.2 Wastewater effluent sampling

Samples of treated wastewater (effluent) were collected from five wastewater treatment facilities, covering five of the six largest WWTP (Hagan, 2020) that discharge effluent directly into the Grand River (**Figure 3.1**). The purpose of this sampling, concurrent with the surface water sampling detailed above, was to assess spatial rather than temporal trends. Sampling at the WWTP followed the methodology outlined in Pinter et al., (2021), where 500 mL effluent samples (24-hour composite aggregates, on average) were collected once by the WWTP operators, during the same two days in August 2021 that river water samples were collected and shipped to the laboratory by courier. Upon receipt, effluent samples were immediately filtered through 0.2 µm PTFE membrane filters and stored at 4°C in the dark until further processing analysis. A 10 mL aliquot of the filtered wastewater was digested in-bottle with 500 µL ultrapure 67-70% nitric acid (HNO_3; Anachemia) before elemental analysis, while a second 10 mL aliquot of the filtered wastewater was not acidified and used to measure anions and major physical and chemical parameters.

Select parameters of the sampled WWTP can be found in **Table S.3.3**, but the sampled facilities requested to anonymize effluent data otherwise. All facilities are considered municipal WWTP that treat a combination of household wastewater, industrial and commercial effluent, and road runoff, together processing wastewater from ~320,000 people equivalents, roughly 30% of the population in the Grand River watershed (Grand River Conservation Authority, 2022).

3.3.3 Analytical Methodology

Wastewater effluent and surface water samples were analyzed for major and trace elements using an iCAP inductively coupled plasma-optical emission spectrometer (ICP-OES) and an iCAP triple quadrupole-inductively coupled plasma-mass spectrometer (TQ-ICP-MS; both Thermo Scientific). The TQ was operated in two modes based on lowest detection limit: single quadrupole in KED mode (He collision gas) and triple-quadrupole with oxygen as the reaction gas, utilizing mass shifting for select elements. Procedural blanks and in-house and commercial certified aqueous reference materials (AQUA1, SLRS6 and NIST1643f) were measured every n=10 samples, measured values were in agreement with expected values of both aqueous reference materials. A single isotope was used to quantify each element's total concentration (typically the most abundant isotope) and when possible, a secondary isotope was used to confirm the absence of isobaric interference. Elemental detection limits are provided in **Table S.3.2**; further details on the elemental analyses can be found in Pinter et al., (2021). Total dissolved phosphate (PO_4), sulfate (SO_4), chloride (Cl) and ferrous iron (Fe^{+2}), along with alkalinity, EC, and pH of the effluent and surface water samples were measured on a Thermo

Gallery Discrete Analyzer photospectrometer. The Gallery was calibrated daily using calibration and reagent solutions according to manufacturer specification.

3.3.4 Data processing

Quantitative assessments of effluent and tributary (confluence) inputs into the Grand River were done by converting element concentrations to loads, i.e., multiplying measured concentrations with either the annual-average daily flow rate of a tributary at the closest available gauging station (<1 km distance, on average) for river water samples, or with the month-average daily WWTP-effluent discharge rate (m^3/d), according to the equation below:

$$L_X = \left([F]_{sample} \times [X]_{sample}\right) \quad \text{(eq. 1)}$$

where L_x is the load of element *x*, $[F]_{sample}$ is the riverine flow rate or WWTP effluent discharge rate, and $[X]_{sample}$ is the concentration of element *x* in the corresponding sample. Hydrometric data for the Grand River and sampled tributaries were obtained from the Provincial Water Quality Monitoring Network (PWQMN) and the Grand River Conservation Authority (Ontario Ministry of the Environment, Conservation and Parks, 2019; Grand River Conservation Authority, 2021), and WWTP effluent discharge data directly from the sampled facilities. Subsequently, mixing calculations were used to assess mass-balances by comparing upstream- versus downstream elemental loads across a WWTP-effluent discharge or tributary confluence, for all sampled points of confluence as follows:

$$M_X = [([L_X]_{downstream}) - \left([L_X]_{upstream} + [L_X]_{input}\right)] \times 100 \quad \text{(eq. 2)}$$

where M_x is the normalized residual mass-imbalance, $[L_X]_{downstream}$ and $[L_x]_{upstream}$ are the loads of element *X* at the nearest sampled downstream and upstream locations, respectively, from the point of effluent or confluence input, and $[L_X]_{input}$ is the load of element *X* carried by the tributary or WWTP effluent being assessed. Finally, measured total REE concentrations were normalized to REE natural abundance patterns, and the anthropogenic anomaly quantified by examining REE ratios as described in the Supporting Information **Methods M2**.

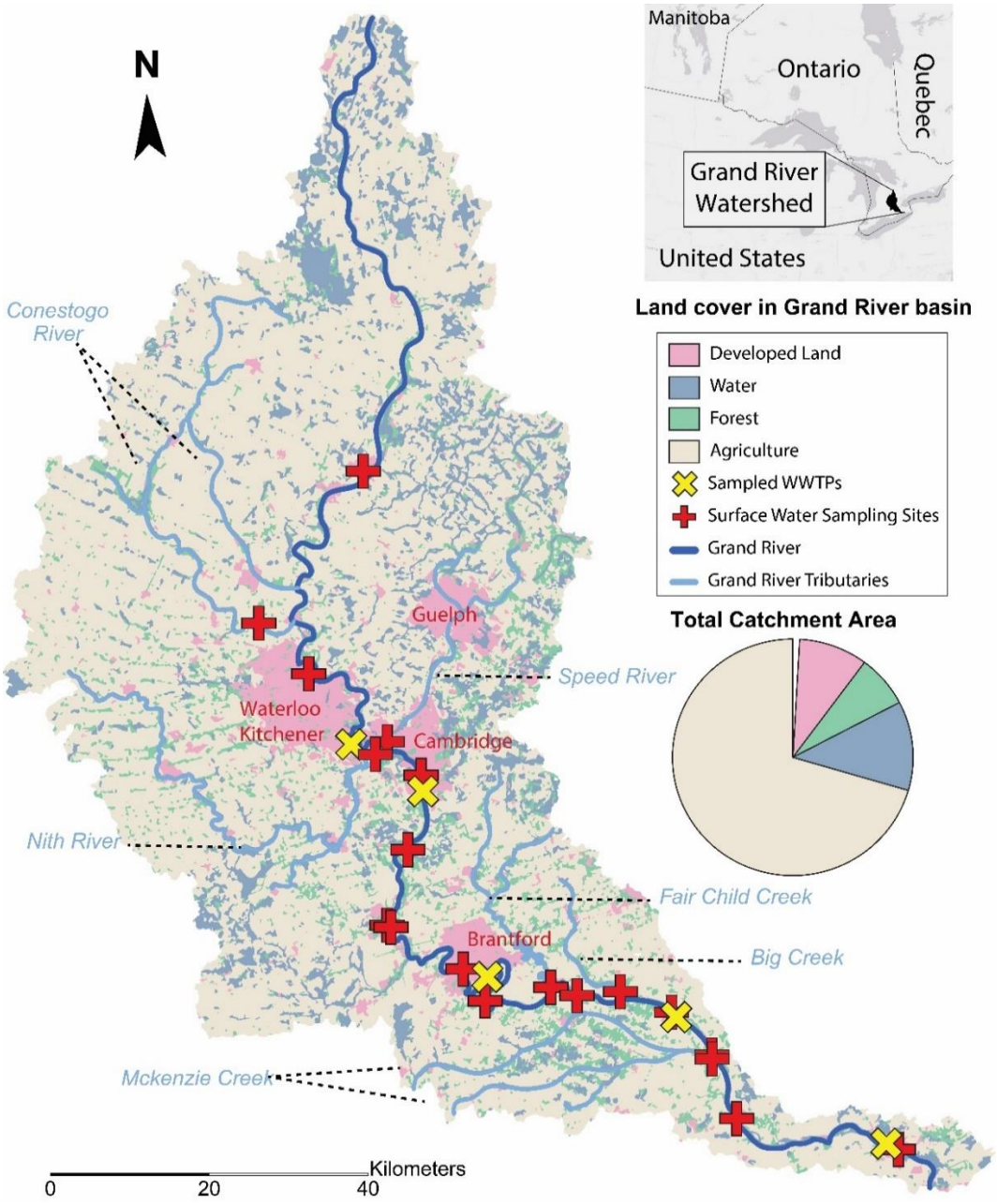

Figure 3.1 *Map of the Grand River catchment, displaying land use, surface water sampling locations, and sampled WWTPs. The map inset at the top right shows the location of the Grand River watershed within the Great Lakes region. The legend describes the symbols used for each feature on the map, with the aggregate relative proportions of developed land, water, forest, and agriculture within the Grand River watershed summarized in the pie chart. A scale is provided in the bottom left.*

3.4 Results and Discussion

3.4.1 Major Water Quality Trends in the Grand River

A selection of major water quality parameters measured in the Grand River, its tributaries and collected effluent samples is plotted in **Figure 3.2**; additional parameters are provided in **Figure S.3.2** and **Table S.3.4.** All river and tributary samples were indicative of well-oxygenated circumneutral freshwater, with median dissolved oxygen and pH values of 6.4 mg/L and 7.7, respectively. Grand River water was generally high in alkalinity (median of 204 mg/L $CaCO_3$), and contained median chloride, sulfate, and phosphate levels of 102 mg/L, 52 mg/L and 33 µg/L respectively. Temperature, pH, alkalinity and DO levels were relatively constant along the river, with maximum relative standard deviations <15% (**Table S.3.4**). In contrast, chloride, sulfate, and EC strongly increased upstream-to-downstream: with chloride increasing 5-fold from ~20 mg/L in the most upstream sample to >100 mg/L in the most downstream sample, sulfate increasing >10-fold from 6.1 mg/L to 90 mg/L, and EC more than doubling from 0.42 mS/cm to 0.87 mS/cm (**Figure 3.2**). While the physicochemical characteristics of the Grand River water thus appeared reasonably consistent upstream-to-downstream in August 2021, the chemical composition of the river and its tributaries varied considerably across the catchment.

A comparison of measured major water quality parameters, as well as major and trace element concentrations with historic data from select stations of the PWQMN in the Grand River as well as previous studies on the Grand River (Rott et al., 1998; Irvine et al., 2019; Jamieson et al., 2013; MacDougall et al., 2012) can be found in **Table S.3.5**. The median values of measured major water quality parameters such as dissolved PO_4, Cl and

alkalinity in this study align well (i.e., within an order of magnitude) with those recorded in the PWQMN (Ontario Ministry of the Environment and Energy, 1994) and abovementioned studies. Minor discrepancies in other parameters (at most a factor of 4) are potentially explained by the fact that most PWQMN measurements are conducted on unfiltered water samples, whereas this study reports dissolved concentrations from filtered aliquots. Thus, while our measurements indicate distinct trends in river water quality across the catchment, the overall dynamics can be considered typical for the long-term traits of this river system.

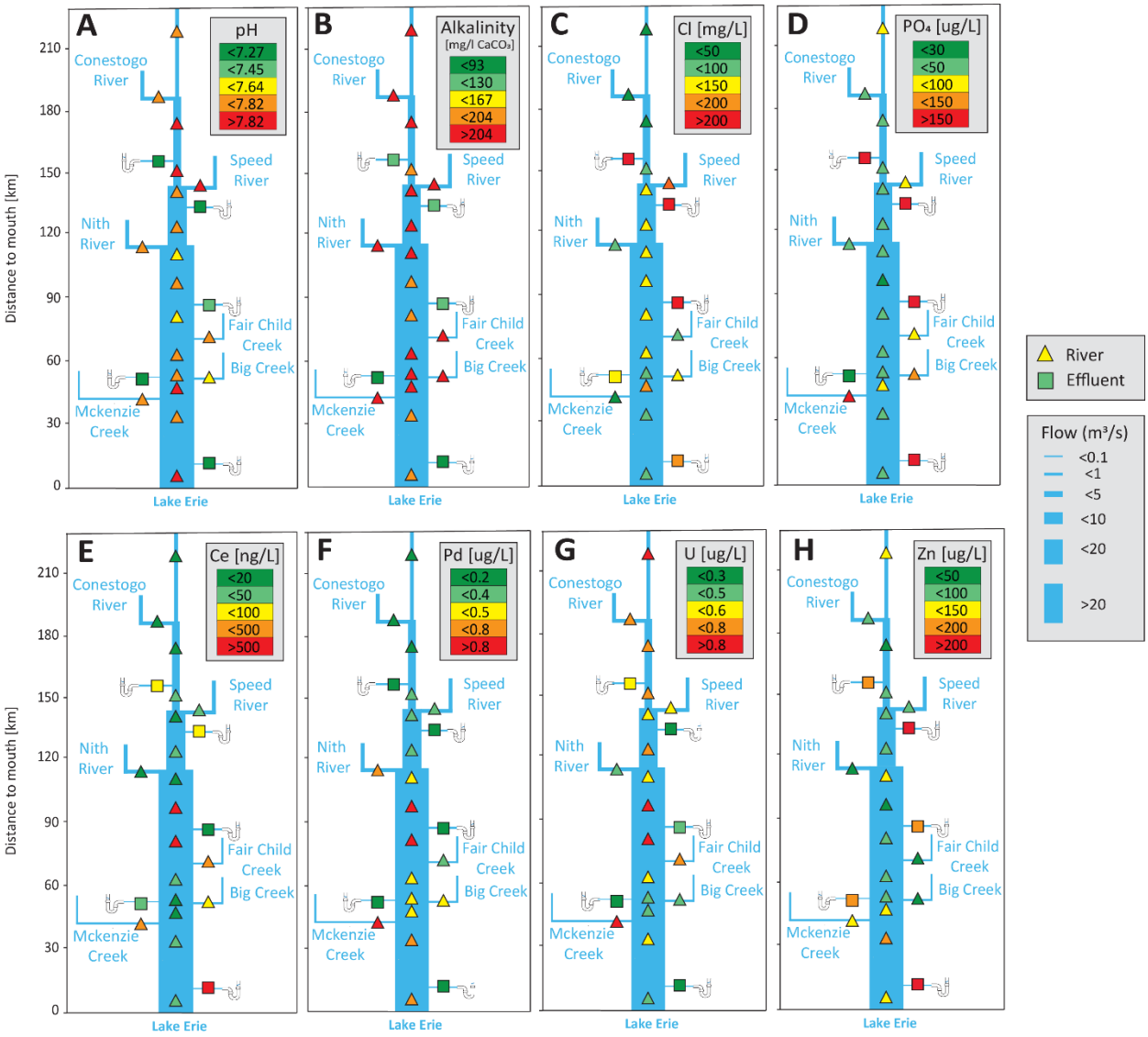

Figure 3.2 *Schematic illustration of major water quality dynamics and trace element concentrations in the Grand River. Plotted are the concentrations of select major physicochemical parameters and trace elements in the Grand River, its tributaries and WWTP effluents (linearized schematically). Legends of color-coding used to visualize concentration are provided in each frame. Approximate flow rates of the rivers and effluents are visualized through the thickness of the streams at each particular point (legend on the right).*

3.4.2 Trace Element Dynamics in the Grand River

Summary statistics on major and trace element concentration ranges measured in the Grand River and its tributary surface water samples can be found in **Table S.3.6**; the spatial trends of a selection of 4 trace elements are plotted in **Figure 3.2**. Overall, the measured elemental concentration ranges in the surface waters reflect typical natural abundance patterns, with major elements such as Na, Ca, Mg, K or S being the most abundant. These and other major element concentrations measured in the Grand River waters also align with available long-term PWQMN monitoring data (**Table S.3.5**). On the other end of the spectrum, least abundant were trace elements such as the rare earth elements (REE), platinum group elements (PGE), and select transition group elements, present at abundances in the order of some µg/L to only a few ng/L (**Table S.3.6**).

Similar to the major water quality trends discussed in Section 3.1, a majority of the analyzed trace elements display a gradual increase in concentration in the Grand River upstream-to-downstream. More than 30 of the measured trace elements showed consistently increasing concentrations, including most of the REE, PGE, Cs, Ga, Ge, Sn, and W (examples in **Figure 3.2E-F**). The average increase in their total aqueous concentration was on the order of +1% to +5% per km, with the exception of a clear, steeper spike in concentrations at sampling locations GR10 and GR11 (Brantford), as discussed below. Another group of elements, including Zr, Ru, Nb, U, and Ag, displayed gradually decreasing concentration upstream-to-downstream (-1.75% per km on average), yet accompanied by the same discernable spikes at GR10 and GR11 mentioned above (example in **Figure 3.2G**). Finally, over 15 other major and trace elements showed a generally increasing concentration trend upstream-to-downstream

(up to +10% per km), without anomalies observed at GR10 and GR11, but often with local enrichment at GR18, a sampling point relatively close (~33 km) to the mouth of the Grand River (**Figure 3.2H**). These elements included Li, As, B, Ba, Bi, Cd, Co, Cr, Mo, Ni, Pb, Se, Tl, V, and Zn; a seemingly diverse group of major and trace elements.

Several localized spikes in select trace element concentrations were observed along the Grand River. Firstly, sampling location GR5, at which several major water quality parameters rapidly changed, as described in Section 3.1, is also the site of significant increases various trace elements. The concentrations of >20 elements increased up to fourfold at GR5 compared to the nearest upstream sampling location GR3 (26 km upstream of GR5), between which one sampled WWTP is located, and no major effluent discharge points or confluences occur. Second, location GR10 within the city of Brantford exhibited relatively elevated concentrations of >20 elements, including most REE and various metalloids and transition metals. These select elemental concentrations at GR10 were at least 60% above those measured at the nearest upstream sample (GR9; 17 km upstream of GR10), in between is the city of Brantford, at least one WWTP and various effluent discharge locations. Finally, relatively elevated trace element concentrations were observed at location GR18 in the town of Cayuga, 33 km from the mouth of the Grand River. At this site, >10 elements displayed concentrations at least 30% above those in the previous sampling location (GR16; 9 km upstream from GR18). As for GR10, potential inputs lie directly upstream from GR18, including the McKenzie Creek (GR17), located 8 km upstream from GR 18, and a WWTP effluent discharge point, located 15 km upstream of GR18. While overall in line with the major water quality trends in terms of gradual salinification of the Grand River water along its flow path, the observed trace

element trends suggest various locations of differently important inputs and/or sinks, in this catchment of otherwise reasonably homogeneous water quality.

3.4.3 Trace Element Concentrations in Wastewater Effluents

Summaries of the measured major and trace element concentration ranges in WWTP effluent samples are provided in **Table S.3.7**. As for the surface water samples, the most abundant elements in effluent samples included major elements such as Na, Ca, S, Mg, K, Si and Sr, with median concentrations ranging from ~1 mg/L up to >150 mg/L, but major element concentrations in effluents were orders-of-magnitude higher than those in surface waters. Trace elements were present at much lower abundances than major elements in WWTP effluent samples: the least abundant elements had median concentrations of <10 ng/L and even as low as <1 ng/L in the effluents, including for many REE, several PGE (Rh, Ru) as well as Re and Ag. Element concentrations in the effluent samples varied by over 9 orders-of-magnitude from most abundant to least abundant and, similar to the major elements, most trace elements exhibited higher concentrations in the effluents compared to the surface waters (i.e., up to 100 ng/L in the effluents versus several ng/L in surface waters). Interestingly, a few elements showed the opposite trend, with surface water samples having up to 5-times higher median concentrations than WWTP effluent samples, e.g., for Ru, Bi, Ir, and Pd (compare **Tables S.3.6–S.3.7**).

The distribution of element concentrations measured in effluents exhibited considerable skew between sampled WWTP, with highest concentrations occurring at >100-times their median, e.g., for Ce, Cr, La, Dy, Ho, Tb and Bi (**Table S.3.7**). Despite this variability in effluent concentrations for certain elements, effluent concentration ranges found in this study otherwise align within an order-of-magnitude with previous

works on trace metals in WWTP effluents (Westerhoff et al., 2015; Vriens et al., 2017; Pinter et al., 2021; Turcotte et al., 2022). Notably, the average effluent concentrations of Ce appear somewhat higher, and Li somewhat lower, in this work than in previous studies, although a general scarcity of data prevents further interpretation of these differences (Pinter et al., 2021).

Measured effluent concentrations are compared with applicable legal surface water guidelines for 18 elements in **Table S.3.8**. Guidelines outlined in the Ontario Provincial Water Quality Objectives (PWQO) apply to surface water concentrations after dilution and mixing of effluent with the receiving surface water body. When considering the dilution of the sampled effluents, none of the measured concentrations exceed the guidelines set by PWQO, and even without dilution, there would be few elements for which at least one WWTP effluent exceeds surface water guideline concentrations at the point of discharge. Effluent concentrations of Cu and P were closest to their applicable surface water guideline limits (although still well-below threshold values), which emphasizes the importance of their continued monitoring considering that effluent concentration ranges in this work only provide a snapshot of the sampled WWTP and not temporal ranges. While the observed adherence to available guidelines indicates that further reduction of at least the regulated trace elements in WWTP is not critical, a lack of guidelines for most other trace elements warrants that the possible impacts of the observed concentration ranges are further examined.

3.4.4 Assessment of Tributary and Effluent Inputs to the Grand River

We first assess the contribution of tributary confluents to trace element loads observed along the Grand River. The contribution of the investigated tributary confluents to loads in the studied sections of the Grand River ranged from >40% (for heavy metals such Pb and Cd from the Conestogo and Speed Rivers), to <2% (for most heavy metals and REE in the Big and MacKenzie Creeks) (**Tables S.3.9**). Across all six sampled tributaries, contributions for most elements correlated well to their hydraulic contributions (well within an order of magnitude), e.g., downstream tributaries such as the McKenzie Creek (hydraulic contribution of 2.4%) contributed ~3.2% to element loads, averaged across all elements analyzed. While major element inputs through confluences contributed to Grand River loads as expected (13% on average for Ca, K, Na, Mg, Na, S and Cl across all six tributaries), those of heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) were considerably higher (23% on average; **Figure 3.3A**). For major elements, the residual mass-imbalances at tributary confluences were low at <30%, averaged across the six sampled tributary confluents (**Figure 3.3B**; **Table S.3.10**), as expected based on their comparatively conservative nature. For trace elements, similarly good closure of confluence mixing was achieved only for a few elements, such as Sn, U and W (all <25% residual), but most other elements could not be mass-balanced across the sampled confluents, with imbalances exceeding 100% (i.e., a factor unit discrepancy between input and output; **Table S.3.10**).

The contributions of WWTP effluent loads to trace element patterns observed along the Grand River are described next, in a similar manner as the tributary load contributions above. Firstly, the hydraulic contribution of the investigated WWTP-effluents to the Grand

River was significantly lower (2.4% on average across all five sampled facilities) than that of the tributaries (13% on average) (**Table S.3.9, Figure 3.3A**). However, due to WWTP effluent concentrations reaching up to 30x those of the Grand River for particular elements, resulting load contributions reached >100%, particularly at sites lower mixing ratios. The significance of effluent-derived input is particularly evident for the major elements (Ca, K, Mg, Na, S and Cl), with an average contribution of >200% across all five sampled WWTP (**Figure 3.3A**). The contribution of the investigated WWTP effluents to the loads of other trace elements in the Grand River ranged vastly from well over 100% for select heavy metals to <0.5% for many REE. Overall, poorly soluble REE had average effluent-derived loading contributions of <5%, but the loads of metalloids and heavy metals were several factors to over an order-of-magnitude higher than the hydraulic contribution of the sampled effluents. Although the effluent loads of conservative elements such as Li and Cl could explain Grand River trends downstream of discharge reasonably well (residual mass-imbalances <33%), many major elements exhibited significantly higher residuals for WWTP inputs, often exceeding 100% (**Figure 3.3B**; **Table S.3.10**). The effluent loads of trace elements could be well-balanced across their discharge points for a few trace elements such as Pd, Cs, and U (<20% residual), but not for most others (e.g., heavy metals at ~100% mass-imbalance, on average). Notably, while the mass-balance agreement for most trace elements was comparable between the studied tributary confluences and WWTP effluent discharges, the conservative element inputs from tributary confluences could be far better balanced than those from WWTP effluents (**Figure 3.3B**).

For both effluent and confluence inputs, the contributions of major and trace elements generally decreased upstream-to-downstream, in line with increased mixing ratios between the effluent/confluence and river flow rates (**Table S.3.1**): the smaller contributions of these inputs relative to the generally growing Grand River loads also correspond to generally lower mass-imbalances calculated over these inputs (i.e., lesser *weight* of the input factor). It may also be hypothesized that a larger distance between the up- and downstream sampling locations considered in these mixing calculations increases the mass-balance residual, due to a higher probability of other unaccounted inputs contributing to the riverine load (baseflow, atmospheric deposition), as well as longer travel times and therefore effects of (bio)geochemical scavenging on aqueous concentrations. We therefore plot the mass-balance residuals for all investigated elements for the n=6 studied confluences and n=5 studied WWTP (n=619 values total; **Figure 3.3C**) as a function of the distance between sampling locations used in these mixing calculations. As expected, mass-balance residuals decrease with decreasing distance between nearest sampling points when aggregated across all elements but, following the variable degrees of achieved mass-balance for the mixing of particular groups of elements as discussed above, no distinct patterns for distinct trace elements groups (e.g., REE versus PGE) were evident. The observed trends suggest that a sampling resolution of at least 1 per 10 km (i.e., <5 km upstream and downstream of an input) is required to achieve a trace element mass-imbalance below 100%, but interpolation of the implied envelopes to lower mass-balance residuals (e.g., <10%) is complicated by the differing trends across confluents versus effluents and a lack of distinct patterns for particular groups of elements.

Overall, these results suggest that both confluence and effluent-derived inputs control trace element dynamics in the Grand River, but that they are challenging to constrain for reactive as well as more conservative elements, regardless of their size. The loading rates derived in this work will differ significantly on longer timescales due to variance in effluent concentrations and discharge, i.e., on the order of hours (Writer et al., 2013) to seasons: flow rates of the Grand River and its tributaries can be twice as high in November-April compared to May-October (Loomer and Cooke, 2011). Despite this variance in trace element loads and the fact that trace element loads specifically are well-below those of major elements, WWTP inputs of select elements appear overall high enough to impact the Grand River, particularly at locations with low mixing ratios, and even at locations where inputs of major elements are low (**Table S.3.10**).

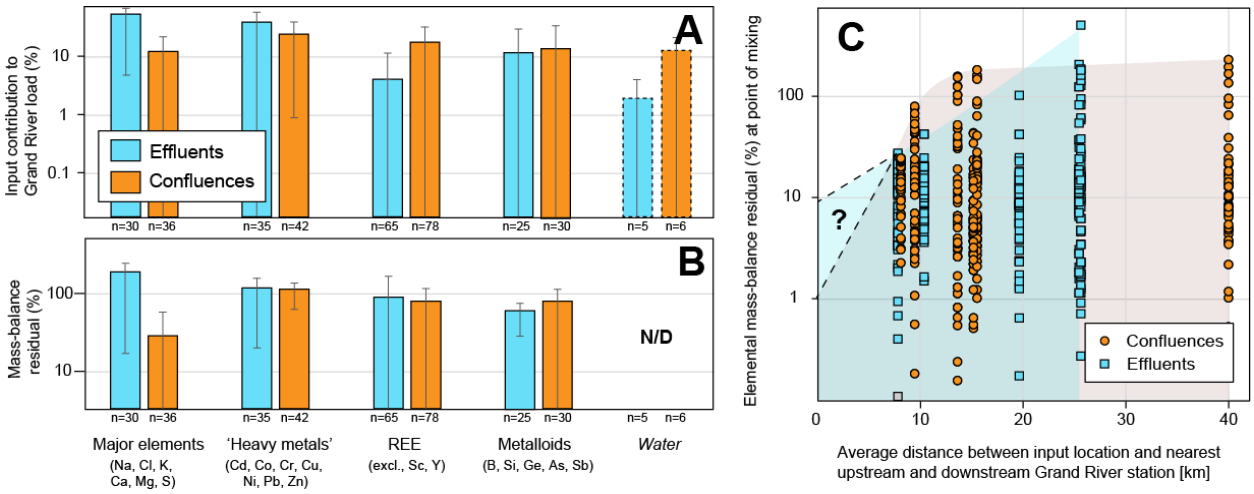

Figure 3.3 *Calculated average contributions of tributary and WWTP effluent inputs to trace element loads observed in the Grand River (**A**); average mass-balance residuals calculated for the mixing of trace element inputs to the Grand River (**B**), and the relationship between sampling resolution (distance between locations considered in the*

*mixing calculations) and mass-imbalance across all studied elements (**C**). The top of the blue and orange bars in panels A and B represent the average input contribution (panel A) or mass-balance residual (panel B) of the corresponding element groups and error bars represent the respective standard deviations in those groupings. Log scales are used in all three panels to account for multiplicative factors. The shading of the envelopes on panel C are for illustrative purposes only.*

3.4.5 Estimation of Human Imprints through Elemental Tracers

Various elements enriched in or specific to WWTP effluents have previously been used to quantify and track effluent-sourced inputs, including Na, K, B, the Rb/Sr ratio, and the anthropogenic fraction of REE, primarily Gd (Smith et al., 2021; Dang et al., 2022). In the Grand River, Na and K levels were highest in the most downstream sampling locations but did not appear to increase in the downstream vicinity of effluent discharge sites except downstream of the Kitchener-Waterloo region, ~150 km upstream of the river mouth (**Figure 3.4**), despite the fact that Na and K concentrations in effluent were up to an order-of-magnitude higher than surface water samples. The various sampled Grand River tributaries carried Na and K concentrations lower than most Grand River samples, but exhibited distinct chemical signatures (lower pH and DIC) that may deplete Ca relative to Na and K. However, except for a slight increase in the Ca/Na ratio downstream of the Nith River confluence (mixing ratio ~ 9:1), no major impacts of confluence inputs, even at lower mixing ratios, could be discerned (**Figure 3.4**). The assessment of Na or K anomalies, based on the regression with Ca, thus does not appear to constitute an appropriate tracer to discern WWTP effluent inputs form the variety of geochemical tributary signatures in this complex watershed.

Similarly, B concentrations in the Grand River were also highest close to the mouth of the river and tributary confluences did not appear to imprint the Grand River dynamics because of generally similar concentrations (**Figure 3.4, Table S.3.6**). The measured B concentrations in the WWTP effluent were slightly above those in the Grand River surface waters (up to 3-fold; **Table S.3.6** and **S.3.7**), but apparently insufficiently enriched given the effluent mixing ratios to be over-imprinted by the geochemical background. This finding aligns with previous observations that municipal effluent in Canada is unlikely to be a major source of B because of low B concentrations previously measured in effluents (Canadian Council of Ministers of the Environment, 2009), with the exception of specific locations (Pinter et al., 2021).

Thirdly, Rb may be enriched relative to Sr in municipal wastewater (Smith et al., 2021), and Rb and Sr behave relatively conservatively (Andersson, 1994), making the Rb/Sr ratio a viable conservative tracer for effluent near WWTPs that discharge into surface waters with naturally low Rb/Sr background levels. However, while the Rb/Sr ratios in the Grand River consistently decreased upstream-to-downstream, with highest values recorded in the upper reaches of the catchment (**Figure 3.4**), background ratios were >0.01 except for the most downstream 50 km of the catchment. While Rb/Sr ratios in the investigated effluents were ~0.01 on average also (data not shown), no distinct anomalies could be traced to WWTP effluents, particularly on the spatial scales of this study that were quite large compared to previous works (Smith et al., 2021). Finally, we assessed the spatial distribution of total dissolved Gd and its anthropogenic fraction, isolated from extrapolation of natural REE enrichment patterns (Section 2.4). Total Gd levels were generally higher at further downstream sampling locations compared to lower levels

measured upstream, with the exception of a decrease in Gd concentrations recorded between Caledonia, York and Cayuga (60-30 km upstream of the Grand River mouth) possibly due to dilution (**Figure 3.4**). However, isolation of the anthropogenic from the total Gd fraction revealed segments of the Grand River with particularly significant proportions of anthropogenic Gd, including downstream of the Kitchener-Waterloo region and city of Cambridge (>75% anthropogenic), as well as near Caledonia (>50% anthropogenic). Overall, a majority of sampled Grand River locations downstream of WWTP effluent inputs exhibited high proportions of anthropogenic Gd, which appeared to be sustained for ~30 km, depending on in-mixing of confluents (**Figure 3.4**). While variability in the relative contributions of this signal could be related to WWTP treatment technologies, the biogeochemistry of Gd, or other factors intrinsic to the local population, e.g., the frequency of Gd use in medical imaging, the anthropogenic Gd tracer appears to capture WWTP effluent discharges more successfully than aforementioned tracers. Overall, the variable suitability of the above elemental tracers indicates that a more complete appreciation of the potential imprints of tributary and effluent inputs in this catchment requires quantitative assessment of the geological imprint on the Grand River, e.g., through additional monitoring of its trace element signature, as well as consideration of relevant land use and industry characteristics. Future work in this catchment may look to compare trace element patterns and their partitioning (Gagnon and Saulnier, 2003) with alternative established tracer compounds that could include *e.coli* (Pongmala et al., 2015), isotopes (McCance et al., 2018) or persistent organic compounds (Glassmeyer, 2005).

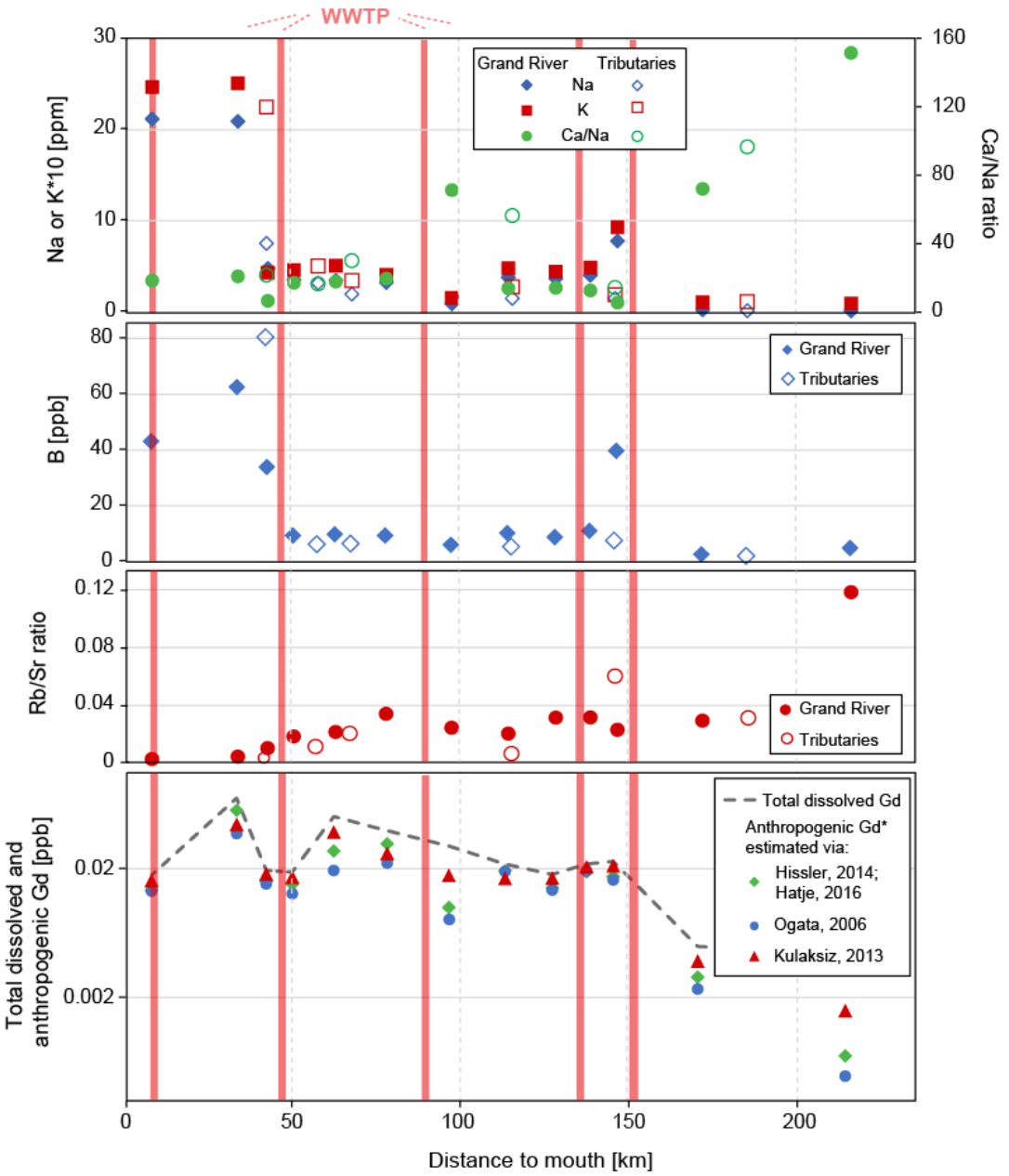

Figure 3.4 *Upstream-to-downstream trends of potential elemental tracers of WWTP-effluent inputs in the Grand River. Locations of the sampled WWTP are represented by vertical red lines on each panel. Legends at the top right of each individual panel separate the values for the 13 Grand River samples from those of the 6 tributary samples. Note the secondary y-axis on the top panel, different units, and the logarithmic scale used in the bottom panel.*

3.5 Conclusions

This study presented new data on the concentration ranges of >50 major and trace elements in surface water and WWTP effluent samples from the Grand River, Ontario. From our trace-level geochemical analyses, subsequent geospatial analyses, and mixing calculations, we conclude that:

- physicochemical characteristics of the Grand River are consistent with existing monitoring data but trace element concentrations reveal distinct spatial trends of accumulation or dilution, with notable anomalies throughout the catchment;
- average trace element concentrations in effluents exceed those of surface waters, and effluent-derived loads of trace elements as well as major elements consequently outweighed tributary confluences in relation to their hydraulic contribution;
- localized inputs from tributaries or effluents appear significant enough to impact select trace elements patterns in the Grand River, particularly at locations with low mixing ratios, even at locations with average major element inputs;
- the anthropogenic Gd fraction in surface water samples appears to capture imprints of WWTP effluent discharge more so than alternative elemental tracers.

Even though this study provides an instantaneous snapshot of current site conditions and is not representative of longer-term trends, our results shows that trace element dynamics in the Grand River system are governed by a complex interplay of natural and anthropogenic sources. Future monitoring is required to better constrain the various (non-)point sources of trace element loads in the Grand River and to quantitatively assess the spatiotemporal scales with which these inputs imprint water quality, thereby allowing improved management and preservation of water quality.

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Conflicts of interest

The authors declare no conflicts of interest.

Supplementary Information

Supplementary Information (Methods M2, Figure S.3.1-S.3.3 and Tables S.3.1-S.3.10 contains additional methodology (calculation of anthropogenic REE anomalies, details on analytical settings and quality control results), and additional results (statistics on observed concentrations, calculated element-specific loads and mass-imbalances).

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3.7 Supporting Information

3.7.1 Supporting Methods

M2 Quantification of anthropogenic REE anomalies.

For quantification of the anthropogenic Gd anomaly in riverine and effluent samples, measured REE concentrations were first normalized to the Post Archean Australian Shale reference standard (Taylor and McIennan, 2009) (**Figure S.3.3**), and the following REE pattern-filling equations were then used to isolate the anthropogenic Gd component from the total Gd concentrations in the aqueous samples:

5. $\frac{Gd}{Gd^*} = \frac{Gd_{SN}}{(0.33Sm_{SN}+0.67Tb_{SN})}$ (Hissler et al., 2014; Hatje et al., 2016)

6. $\log\ Gd^*_{SN} = \frac{(4logEu_{SN} - logNd_{SN})}{3}$ (Kulaksiz & Bau, 2013)

7. $\log\ Gd^*_{SN} = 0.5(logSm_{SN} + logDy_{SN})$ (Ogata, 2006)

where the subscript SN indicates the shale-normalized concentrations and the asterisk Gd* indicates the natural (geogenic) Gd component (total = anthropogenic + geogenic). All four methods yielded very similar anthropogenic Gd fractions (<10% discrepancy; data not shown), of which the average was taken. For the above calculations, aqueous concentrations below analytical detection limits were not further considered.

3.7.2 Supporting Figures

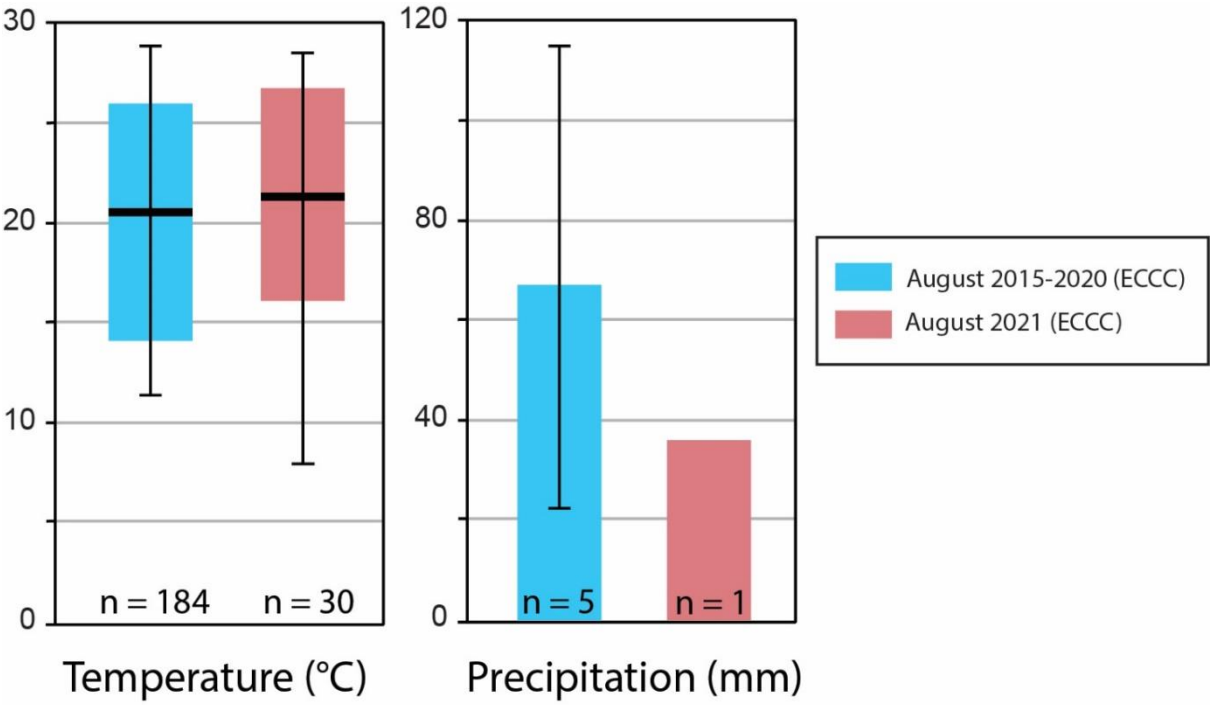

Figure S.3.1 Weather conditions at Brantford Airport (climate ID 614092) during the month of August 2021 versus average weather conditions during the Augusts of 2015-2020 at the same location, via Government of Canada (Environment and Climate Control Canada, 2021). This location was chosen as it is roughly halfway from both the top and bottom of the Grand River. For the temperature chart, thick black bars represent the average monthly temperatures, the bottom and top of the blue and red boxes represent the average minimum and average maximum monthly temperatures, respectively, and the thin black error bars represent the absolute minimum and maximum temperatures over the respective time periods. For the precipitation chart, the red bar represents the total precipitation in August 2021 and the blue bar represents the average monthly precipitation for the month of August from 2015-2020, with the error bar representing the lowest and highest monthly precipitation over 2015-2020. Precipitation data in 2019 for the month of August was missing, therefore n=5 (months) of precipitation data compared to n=184 days (6 months) for temperature during 2015-2020.

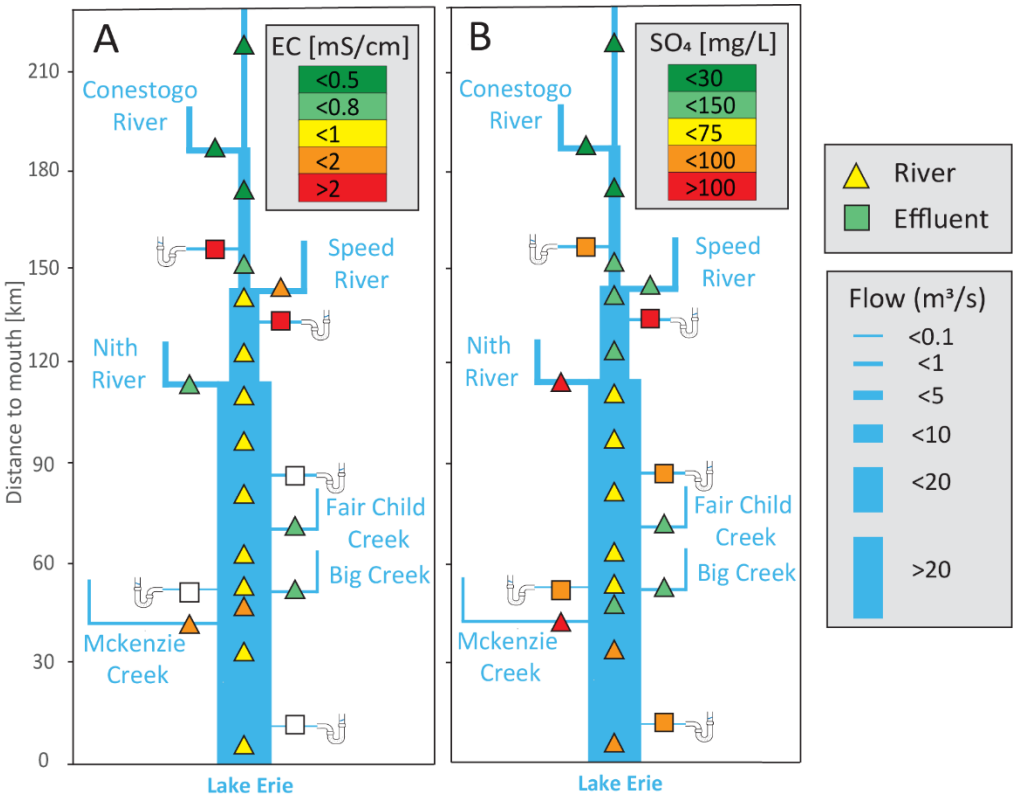

Figure S.3.2 Schematic illustration of select major water quality trends in the Grand River. Plotted are the concentrations of electrical conductivity (EC) (panel A) and sulfate (panel B) in the Grand River, its tributaries and WWTP effluents (legends of color-coding provided in each frame). Approximate flow rates of the rivers and effluents are visualized through the thickness of the streams at each particular point (legend on the right).

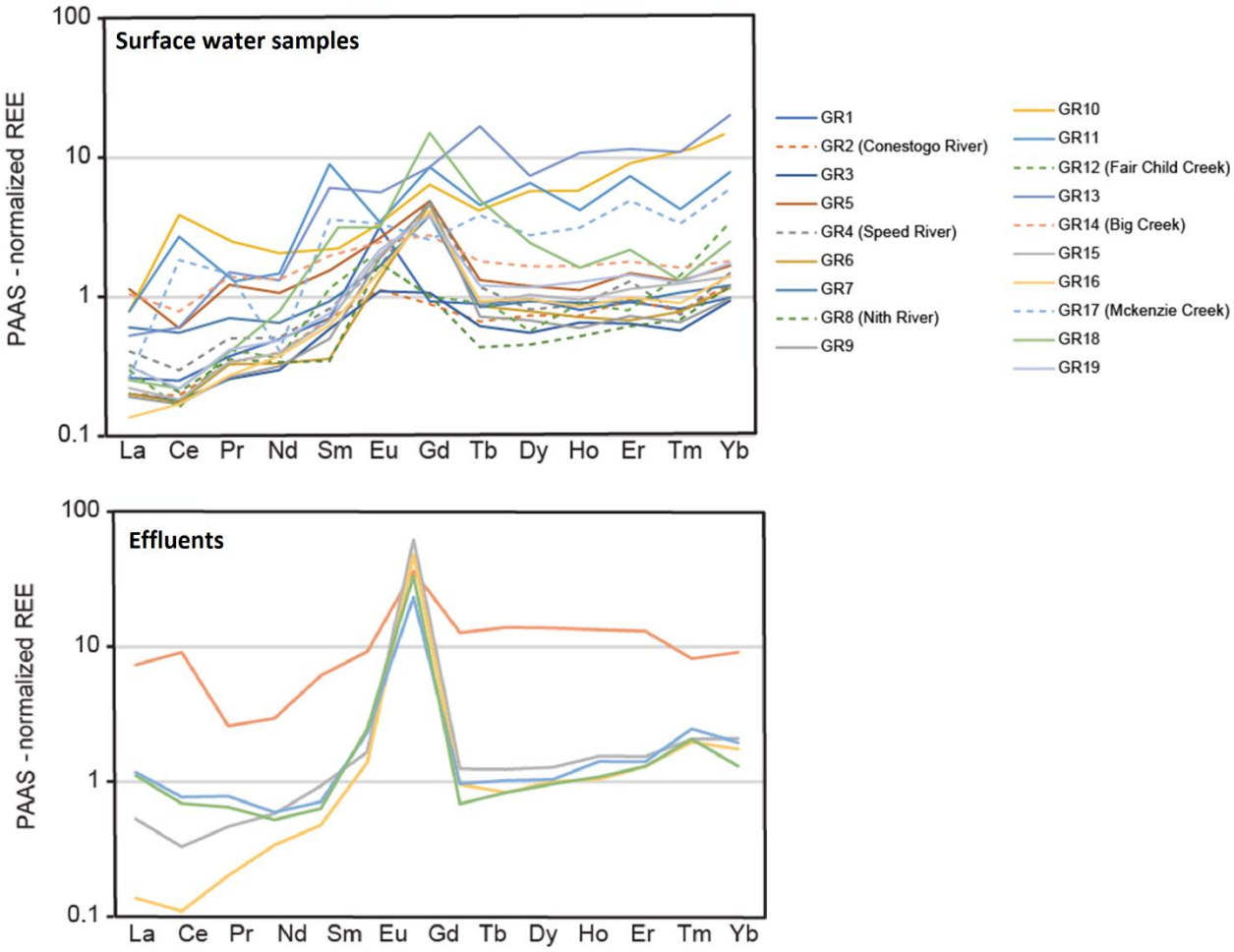

Figure S.3.3 Post-Archean Australian Shale-normalized (Taylor and McIennan, 2009) REE patterns in 13 Grand River surface water samples and 6 Grand River tributary samples (top), as well as in 5 WWTP effluent samples (bottom; anonymized).

3.7.3 Supporting Tables

Table S.3.1 Sampling locations of surface water samples in the Grand River catchment.

Sample ID	River	Location	Lat	Long	Flow Rate (m^3/s)	Mixing Ratio (Grand River: Tributary)	Distance from mouth of Grand River (km)	Distance to conjunction of Tributary with Grand River(km)
GR1	Grand	Fergus, ON	43.71	-80.38	4.62	-	216	-
GR2	Conestogo River	St. Jacobs, ON	43.54	-80.55	3.12	2:1	185	5.6
GR3	Grand	Kitchener, ON	43.48	-80.48	9.01	-	172	-
GR4	Speed River	Blair, ON	43.40	-80.37	2.87	3:1	146	1.4
GR5	Grand	Blair, ON	43.39	-80.38	9.09	-	146	-
GR6	Grand	Cambridge, ON	43.36	-80.32	11.13	-	138	-
GR7	Grand	Glen Morris, ON	43.28	-80.34	19.51	-	128	-
GR8	Nith River	Paris, ON	43.19	-80.38	2.18	9:1	115	1
GR9	Grand	Paris, ON	43.19	-80.38	21.69	-	114	-
GR10	Grand	Brantford, ON	43.14	-80.27	21.70	-	97	-
GR11	Grand	Brantford, ON	43.10	-80.24	21.71	-	77	-
GR12	Fair Child Creek	Onondaga, ON	43.11	-80.14	0.42	52:1	67	0.5
GR13	Grand	Onondaga, ON	43.10	-80.10	22.11	-	62	-
GR14	Big Creek	Caledonia, ON	43.10	-80.03	0.25	87:1	57	1.1
GR15	Grand	Caledonia, ON	43.07	-79.95	22.37	-	50	-
GR16	Grand	York, ON	43.02	-79.90	22.81	-	42	-
GR17	McKenzie Creek	York, ON	43.02	-79.90	0.54	41:1	41	0.2
GR18	Grand	Cayuga, ON	42.95	-79.86	22.91	-	33	-
GR19	Grand	Dunnville, ON	42.90	-79.62	23.10	-	7	-

Table S.3.2 Overview of analytical detection limits for water quality analyses.

Parameter	Unit	LOD	Instrument used	Parameter	Unit	LOD	Instrument used
Ag	µg/L	0.002	TQ-ICP-MS	Nb	µg/L	0.009	TQ-ICP-MS
Al	µg/L	0.8	ICP-OES	Nd	µg/L	0.001	TQ-ICP-MS
Alkalinity	mg/L $CaCO_3$	1.2	photospectrometer	Ni	µg/L	0.02	TQ-ICP-MS
As	µg/L	0.02	TQ-ICP-MS	ORP	mV	1	Field probe
Au	µg/L	0.004	TQ-ICP-MS	P	µg/L	13	ICP-OES
B	µg/L	0.5	TQ-ICP-MS	Pb	µg/L	0.002	TQ-ICP-MS
Ba	µg/L	0.2	TQ-ICP-MS	Pd	µg/L	0.002	TQ-ICP-MS
Be	µg/L	0.09	TQ-ICP-MS	PO_4	µg/L	3	photospectrometer
Bi	µg/L	0.001	TQ-ICP-MS	Pr	µg/L	0.0004	TQ-ICP-MS
Ca	µg/L	7	ICP-OES	Pt	µg/L	0.001	TQ-ICP-MS
Cd	µg/L	0.004	TQ-ICP-MS	Rb	µg/L	0.005	TQ-ICP-MS
Ce	µg/L	0.002	TQ-ICP-MS	Re	µg/L	0.001	TQ-ICP-MS
Cl	mg/L	0.4	photospectrometer	Rh	µg/L	0.002	TQ-ICP-MS
Co	µg/L	0.004	TQ-ICP-MS	Ru	µg/L	0.03	TQ-ICP-MS
Cr	µg/L	0.02	TQ-ICP-MS	S	µg/L	30	ICP-OES
Cs	µg/L	0.003	TQ-ICP-MS	Sb	µg/L	0.005	TQ-ICP-MS
Cu	µg/L	0.02	TQ-ICP-MS	Sc	µg/L	0.03	TQ-ICP-MS
Dy	µg/L	0.0004	TQ-ICP-MS	Se	µg/L	0.02	TQ-ICP-MS
EC	mS/cm	0.0007	Field probe	Si	µg/L	2	ICP-OES
Er	µg/L	0.0003	TQ-ICP-MS	Sm	µg/L	0.0004	TQ-ICP-MS
Eu	µg/L	0.0002	TQ-ICP-MS	Sn	µg/L	0.007	TQ-ICP-MS
Fe	µg/L	1	ICP-OES	SO_4	mg/L	1	photospectrometer
Fe^{2+}	mg/L	0.04	photospectrometer	Sr	µg/L	0.02	ICP-OES
Ga	µg/L	0.004	TQ-ICP-MS	Ta	µg/L	0.006	TQ-ICP-MS
Gd	µg/L	0.0003	TQ-ICP-MS	Tb	µg/L	0.0002	TQ-ICP-MS
Ge	µg/L	0.008	TQ-ICP-MS	TDS	mg/L	1	Field probe
Hf	µg/L	0.003	TQ-ICP-MS	Te	µg/L	0.01	TQ-ICP-MS
Ho	µg/L	0.0003	TQ-ICP-MS	Temp	°C	0.1	Field probe
In	µg/L	0.005	TQ-ICP-MS	Ti	µg/L	0.4	ICP-OES
Ir	µg/L	0.002	TQ-ICP-MS	Tl	µg/L	0.001	TQ-ICP-MS
K	µg/L	0.8	ICP-OES	Tm	µg/L	0.0002	TQ-ICP-MS
La	µg/L	0.003	TQ-ICP-MS	U	µg/L	0.0003	TQ-ICP-MS
Li	µg/L	0.06	TQ-ICP-MS	V	µg/L	0.02	TQ-ICP-MS
Lu	µg/L	0.0003	TQ-ICP-MS	W	µg/L	0.01	TQ-ICP-MS
Mg	µg/L	7	ICP-OES	Y	µg/L	0.002	TQ-ICP-MS
Mn	µg/L	0.09	ICP-OES	Yb	µg/L	0.0002	TQ-ICP-MS
Mo	µg/L	0.02	TQ-ICP-MS	Zn	µg/L	0.4	ICP-OES
Na	µg/L	1	ICP-OES	Zr	µg/L	0.005	TQ-ICP-MS

Table S.3.3 Selected parameters of sampled wastewater treatment facilities.

WWTP	Altitude (m)	Distance to River Mouth (km)	Population Equivalents	Average Daily Flow (m^3/day)	Mixing Ratio (Grand River: WWTP Daily Flow)
Kitchener	77	152	148,464	68,794	10:1
Galt	80	136	61,495	22,879	42:1
Brantford	200	89	94,400	31,002	60:1
Caledonia	329	48	9,674	2,850	678:1
Dunnville	256	9.5	5,759	4,890	445:1

Table S.3.4 Major water quality parameters in Grand River surface water samples, tributary surface water samples, and wastewater effluent samples.

Grand River Surface Water Samples (n=13)						
Parameter*	Unit	Min	Median	Max	Skew	RSD (%)
Alkalinity	mg/L $CaCO_3$	199	204	222	1.5	4
Chloride	mg/L	20	102	185	-0.4	39
DO	mg/L	4.9	6.4	7.5	-0.3	12
EC	mS/cm	0.4	0.8	1.1	-1.1	23
Fe^{2+}	mg/L	0.01	0.03	0.1	1.4	36
ORP	mV	173	184	210	0.9	6
pH	unitless	7.6	7.7	8	0.8	2
PO_4	µg/L	30	33	100	2.8	50
SO_4	mg/L	6	52	91	-0.3	47
TDS	mg/L	311	572	609	-2	19
Temperature	°C	22	26	27	-0.7	6
Tributary Surface Water Samples (n=6)						
Parameter*	Unit	Min	Median	Max	Skew	RSD (%)
Alkalinity	mg/L $CaCO_3$	204	216	241	1.1	6
Chloride	mg/L	30	60	184	1.4	71
DO	mg/L	4.5	6.3	7.9	-0.2	19
EC	mS/cm	0.4	0.8	1.1	-0.3	31
Fe^{2+}	mg/L	0.03	0.03	0.04	1.9	8
ORP	mV	186	193	201	0.5	2.5
pH	unitless	7.6	7.7	8	1.0	2
PO_4	µg/L	30	65	159	0.9	64
SO_4	mg/L	16	39	252	1.7	108
TDS	ppm	308	538	748	-0.1	30
Temperature	°C	23	25	27	-0.3	6.9
Wastewater Effluent Samples (n=5)						
Parameter*	Unit	Min	Median	Max	Skew	RSD (%)
Alkalinity	mg/L $CaCO_3$	56	97	128	-0.2	33
Chloride	mg/L	115	296	370	-1	41
EC	mS/cm	0.8	1.7	2.7	0.04	49
Fe^{2+}	mg/L	0.02	0.03	0.1	1.1	58
pH	unitless	7.1	7.2	7.4	0.6	2
PO_4	µg/L	30	214	668	0.7	83
SO_4	mg/L	87	92	173	2.2	34

*Where EC is electrical conductivity, TDS is total dissolved solids, ORP is oxidation-reduction potential and DO is dissolved oxygen. TDS, ORP, DO and temperature were measured in the field directly after sample collection and therefore were not measured in the wastewater effluent samples.

Table S.3.5 Comparison of measured Grand River sample water chemistry with that of four Provincial Water Quality Monitoring Network (PWQMN) stations of the Grand River.

		Grand River Surface Water Samples, August 2021 (n=13)					PWQMN Grand River Surface Water Samples, August 2016-2019 (n=16)				
Parameter	Unit	Min	Median	Max	Skew	RSD(%)	Min	Median	Max	Skew	RSD(%)
Al	µg/L	1	2.1	24	2.2	121	20	44	107	0.5	52
Alk	mg/l $CaCO_3$	199	204	222	1.5	4	139	161	176	-0.5	7
Ba	µg/L	1.4	3.5	105	2.9	157	17	26	41	0.4	25
Be	µg/L	0.02	0.04	1.8	2.2	188	0.01	0.1	0.2	1.1	62
Bi	µg/L	0.002	0.006	1.4	2.1	228	0.2	1.2	5.0	1	89
Ca	mg/L	17	44	54	2.1	124	47	54	76	1.1	14
Cd	µg/L	0.01	0.01	0.8	1.6	177	0.1	0.4	0.8	0.5	43
Cl	mg/l	20	102	185	-0.4	39	26	86	116	-0.6	40
Co	µg/L	0.1	0.3	3.6	2.4	166	0.4	0.5	0.8	0.3	26
Cr	µg/L	0.08	0.1	2.7	2.2	180	0.02	0.3	1.8	1.3	104
Cu	µg/L	0.6	1	4.7	2.6	72	0.8	1.6	2.7	0.3	30
DO	mg/L	4.9	6.4	7.5	-0.26	12	6.8	10	14	0.05	17
EC	mS/cm	0.4	0.8	1.1	-1.1	23	0.7	0.4	0.9	-0.5	20
Fe	µg/L	5.4	11	39	2	69	58	91	296	1.3	55
K	mg/L	0.1	0.5	2.5	1.9	96	2.3	3.4	3.8	-0.9	15
Li	µg/L	0.1	0.4	5.3	1.7	111	0.8	4.9	14	0.9	68
Mg	mg/L	4	20	30	2.1	147	17	20	26	0.5	14
Mn	µg/L	1.2	4.2	17	1.1	86	7.2	14	45	1.1	59
Mo	µg/L	0.1	0.5	14	3.3	199	0.1	0.6	1.6	0.3	63
Na	mg/L	1	4	21	1.8	99	16	49	70	-0.5	41
Ni	µg/L	0.2	0.8	9.3	2.2	124	0.02	0.5	1.0	0.1	66
Pb	µg/L	0.2	0.5	2.2	2.4	213	1	3.9	6.1	-0.3	45
pH	unitless	7.6	7.7	8	0.8	2	8.5	8.2	8.8	1.1	2
PO_4	µg/L	30	33	100	2.8	50	3.5	6.7	20	3.5	64
Sr	mg/L	0.01	0.1	0.9	2.1	133	0.2	0.3	0.6	1.1	34
Temp	°C	22	26	27	-0.7	6	23	17	26	-0.7	13
U	µg/L	0.5	0.6	0.8	0.6	22	0.9	4.4	6.6	-0.6	44
V	µg/L	0.3	0.7	5.9	2.9	135	0.4	0.7	1.0	-0.03	24
Zn	µg/L	1.6	4.2	19	2.5	83	4.1	14	40	2.2	54
Zr	ng/L	7.5	13	60	1.2	78	18	85	169	0.2	59

Data from 2016-2019 for the month of August was taken from four different PQWMN stations for comparison. The four stations used were the Grand River at Crosscut Bridge Brantford (ID: 16018402702), at Glenn Morris (ID: 16018401002), at Fountain St S (ID: 16018401202), and at Bridge St Bridgeport (ID: 16018401502) (Ontario Ministry of the Environment, Conservation and Parks, 2019).

Table S.3.5, Cont'd.

		Grand River Surface Water Samples, August 2021 (n=13)					MacDougall et al., Aug 2004 (n=40)			Rott et al., Jun-Aug 1994 (n=60)	
Parameter	Unit	Min	Median	Max	Skew	RSD (%)	Min	Median	Max	Min	Max
Cl	mg/l	20	102	185	-0.4	39	23	75	120	12	47
DO	mg/L	4.9	6.4	7.5	-0.26	12	5.7		19		
pH	unitless	7.6	7.7	8	0.8	2	7.2	8	8.7	7.4	8.3
PO_4	µg/L	30	33	100	2.8	50	20	80	380	1	34
Temp	°C	22	26	27	-0.7	6	20		27	19	25

		Grand River Surface Water Samples, August 2021 (n=13)					Irvine et al., Oct-Sept 2013-2016 (n=369)			Jamieson et al., May-Aug 2004-2005 (n=59)				
Parameter	Unit	Min	Median	Max	Skew	RSD (%)	Min	Median	Max	Min	Median	Max	Skew	RSD (%)
Cl	mg/l	20	102	185	-0.4	39								
DO	mg/L	4.9	6.4	7.5	-0.26	12				1	6	12	-0.2	37
pH	unitless	7.6	7.7	8	0.8	2								
PO_4	µg/L	30	33	100	2.8	50	~10	~40	~250					
Temp	°C	22	26	27	-0.7	6								

Comparison of concentration data for this study with concentration data from several previous studies on the Grand River including (Irvine et al., 2019; Rott et al., 1998; Jamieson et al., 2013; MacDougall et al., 2012).

Table S.3.6 Total elemental concentration ranges in the Grand River and tributary surface water samples.

Concentration ranges in surface water samples (n=19)								
Element	Unit	Min	Median**	Max	Skew	RSD(%)	#<LOD	Median***
Ag	ng/L	0.7	4.1	121	1.5	151	0	4.1
Al	µg/L	1	3.3	24	2.7	116	0	3.3
As	µg/L	0.2	0.5	9.3	3.6	169	0	0.5
Au	µg/L	0.002	0.01	0.1	2.2	179	14	0
B	µg/L	2	9.4	80	1.8	118	0	9.4
Ba	µg/L	1.4	3.5	105	2.9	179	0	3.5
Be	µg/L	0.02	0.04	1.8	2.9	199	2	0.04
Bi	µg/L	0.002	0.01	1.4	2.7	212	0	0.01
Ca	mg/L	15	52	91	2.9	175	0	52
Cd	µg/L	0.01	0.01	0.8	2	172	0	0.01
Ce	ng/L	14	20	756	2.8	193	0	20
Co	µg/L	0.1	0.3	3.6	3	157	0	0.3
Cr	µg/L	0.08	0.1	2.7	2.8	165	0	0.1
Cs	ng/L	7.5	14	393	2.5	185	0	14
Cu	µg/L	0.5	1.0	4.7	2.5	70	0	1.0
Dy	ng/L	2.1	4.9	40	3.4	171	0	4.9
Er	ng/L	1.5	2.7	11	3.9	226	0	2.7
Eu	ng/L	1.2	2.4	31	3.9	221	0	2.4
Fe	µg/L	5.1	11	39	2	68	0	11
Ga	ng/L	7.5	17	138	2	115	0	17
Gd	ng/L	4.2	19	116	2.3	101	0	19
Ge	ng/L	11	25	111	2.5	75	3	23
Hf	µg/L	0.003	0.01	0.1	2.5	170	11	0
Ho	ng/L	1.1	1.7	10	3.2	235	6	1.3
Ir	ng/L	0.3	5	10	2.2	180	14	0
K	mg/L	0.1	0.4	2.5	1.8	114	0	0.4
La	ng/L	5.2	12	115	3.1	116	0	12
Li	µg/L	0.1	0.4	6.6	2	149	0	0.4
Lu	ng/L	0.4	0.6	12	3.9	314	0	0.6
Mg	mg/L	4	20	30	2.1	176	0	20
Mn	µg/L	1.2	5.7	76	3.1	147	0	5.7
Mo	µg/L	0.1	0.5	14	3.9	218	0	0.5
Na	mg/L	1	3	21	2.2	123	0	3
Nb	ng/L	1.1	2.7	124	4.1	267	1	2.7
Nd	ng/L	10	17	125	2.4	95	0	17
Ni	µg/L	0.2	0.8	9.3	2.8	146	0	0.8

Median** ignores the values <LOD, Median*** treats values <LOD as 0

Table S.3.6, Contd.

Concentration ranges in surface water samples (n=19)								
Element	Unit	Min	Median**	Max	Skew	RSD(%)	#<LOD	Median***
P	µg/L	17	32	95	2.4	54	0	32
Pb	µg/L	0.2	0.5	2.2	3	195	0	0.5
Pd	µg/L	0.1	0.4	1.7	2.2	77	0	0.4
Pr	ng/L	2.3	3.7	12	2.2	162	0	3.7
Pt	µg/L	0.01	0.01	0.1	2.2	158	14	0
Rb	µg/L	0.5	1.6	4.0	1.4	49	0	1.6
Re	ng/L	3.2	5.2	221	3	197	0	5.2
Rh	ng/L	0.2	0.7	94	3.7	249	2	0.7
Ru	ng/L	2.9	11	323	2.1	180	3	8.1
S	mg/L	1.9	16	126	3	111	0	16
Sb	µg/L	0.04	0.1	8.0	3.9	256	0	0.1
Sc	µg/L	0.1	0.1	0.6	2.1	79	0	0.1
Se	µg/L	0.1	0.1	1.3	2.4	125	1	0.1
Si	mg/L	1.8	5.5	13	0.9	58	2	3.8
Sm	ng/L	1.9	4.6	13	1.8	150	0	4.6
Sn	ng/L	14	31	133	2.3	79	0	31
Sr	mg/L	0.1	0.1	2.4	3.3	211	0	0.1
Ta	ng/L	0.4	1.1	104	3.5	261	6	0.7
Tb	ng/L	0.3	0.9	14	3.9	284	0	0.9
Te	µg/L	0.01	0.03	0.2	1.6	86	0	0.03
Ti	µg/L	0.3	0.4	1.2	2.3	40	0	0.4
Tl	µg/L	0.001	0.004	0.9	2.9	249	0	0.004
Tm	ng/L	0.2	0.5	15	3.9	309	0	0.5
U	µg/L	0.4	0.6	0.9	0.3	25	0	0.6
V	µg/L	0.3	0.7	5.9	3.0	125	0	0.7
W	ng/L	4.3	18	124	2.6	112	0	18
Y	µg/L	0.02	0.1	0.2	2.2	72	0	0.1
Yb	ng/L	1.6	3.0	107	4.3	269	0	3.0
Zn	µg/L	1.2	3.3	19	2.7	88	0	3.3
Zr	ng/L	7.5	15	113	2.4	99	1	14

Median** ignores the values <LOD, Median*** treats values <LOD as 0

Table S.3.7 Summary of measured concentrations in WWTP effluent samples.

Concentration ranges in effluent samples (n=5)								
Element	Unit	Min	Median**	Max	Skew	RSD(%)	#<LOD	Median***
Ag	ng/L	0.5	0.5	0.5	-	-	4	0
Al	µg/L	25	126	199	-0.1	75	1	61
As	µg/L	0.2	0.6	0.8	-0.7	49	0	0.6
Au	µg/L	0.005	0.01	0.01	1.7	36	2	0.005
B	µg/L	10.6	23.3	38.1	-0.2	42	0	23.3
Ba	µg/L	19	33.1	42	-0.3	34	0	33
Be	µg/L	0.03	0.03	0.03	-	-	4	0
Bi	µg/L	0.003	0.004	0.1	0.6	117	0	0.004
Ca	mg/L	69	102	112	-0.5	21	0	102
Cd	µg/L	0.01	0.03	0.04	-0.5	41	0	0.03
Ce	ng/L	6	52	2488	2.2	209	0	52
Co	µg/L	0.2	0.5	1.2	1.7	69	0	0.5
Cr	µg/L	0.3	0.7	25	0.6	130	0	0.7
Cs	ng/L	57	85	172	1	43	0	85
Cu	µg/L	3.2	7.9	8.4	-2.1	31	0	7.9
Dy	ng/L	3.1	4.6	66	2.2	166	0	4.6
Er	ng/L	2.4	3.9	38	2.2	151	0	3.9
Eu	ng/L	1.2	2.4	16	2.2	130	0	2.4
Fe	µg/L	12	52	216	0.5	94	0	52
Ga	ng/L	9.6	68	437	1.0	109	0	68
Gd	ng/L	111	175	303	0.6	37	0	175
Ge	ng/L	11	80	198	0.6	90	0	80
Hf	µg/L	0.01	0.03	0.03	-0.3	55	0	0.03
Ho	ng/L	0.8	1.0	14	2.2	162	0	1
Ir	ng/L	0.3	0.5	1	1.7	63	0	0.5
K	mg/L	17	23	38	1.6	32	0	23
La	ng/L	3.6	41	958	2.2	196	0	41
Li	µg/L	4.9	6.0	24	2.2	86	0	6
Lu	ng/L	0.5	0.8	3.6	2.2	99	0	0.8
Mg	mg/L	15	25	32	-0.4	28	0	25
Mn	µg/L	0.9	8.1	35	1.1	108	0	8.1
Mo	µg/L	1.9	4.3	6.0	-0.1	43	0	4.3
Na	mg/L	103	191	277	-0.05	40	0	191
Nb	ng/L	16	23	38	1.1	37	0	23
Nd	ng/L	8.5	19	67	2	90	0	19
Ni	µg/L	2.2	5.0	20	0.6	86	0	5

Median** ignores the values <LOD, Median*** treats values <LOD as 0. Values which could not be calculated due to a high number of samples <LOD appear as "-".

Table S.3.7, Contd.

Concentration ranges in effluent samples (n=5)								
Element	Unit	Min	Median**	Max	Skew	RSD(%)	#<LOD	Median***
Ni	µg/L	2.2	5.0	20	0.6	86	0	5
P	µg/L	20	115	303	1.1	87	0	115
Pb	µg/L	0.1	0.2	0.7	0.5	91	0	0.2
Pd	µg/L	0.02	0.04	0.1	1.7	60	0	0.04
Pr	ng/L	1.3	5.5	15	1.5	82	0	5.5
Pt	µg/L	0.04	0.04	0.1	-	27	3	0
Rb	µg/L	10	11	12	-0.9	7	0	11
Re	ng/L	4.9	6.7	21	0.7	66	0	6.7
Rh	ng/L	0.6	1.3	3.1	1.7	67	0	1.3
Ru	ng/L	0.8	0.9	0.9	-	10	3	0.8
S	mg/L	26	30	52	2	30	0	30
Sb	µg/L	0.4	3.1	3.7	-0.7	64	0	3.1
Sc	µg/L	0.1	0.2	0.6	0.6	75	0	0.2
Se	µg/L	0.1	0.1	0.2	0.2	35	0	0.1
Si	mg/L	0.8	2.7	5.5	0.2	72	0	2.7
Sm	ng/L	2.0	3.8	34	2.2	142	0	3.8
Sn	ng/L	133	174	251	1.2	25	0	174
Sr	mg/L	0.6	1	3.4	1.8	79	0	1
Ta	ng/L	13	19	26	-0.1	26	0	19
Tb	ng/L	0.5	0.7	10	2.2	163	0	0.7
Te	µg/L	0.02	0.02	0.03	-0.3	35	2	0.02
Tl	µg/L	0.002	0.005	0.01	0.4	52	0	0.005
Tm	ng/L	0.4	0.6	5.3	2.2	145	0	0.6
U	µg/L	0.2	0.3	0.5	0.9	44	0	0.3
V	µg/L	0.1	0.3	1.6	2.1	118	0	0.3
W	ng/L	29	47	109	0.5	59	0	47
Y	µg/L	0.03	0.04	0.3	1.5	99	0	0.04
Yb	ng/L	4.6	5.7	21	2.2	78	0	5.7
Zn	µg/L	14	29	54	0.3	55	0	29
Zr	ng/L	23	47	78	0.1	40	0	47

Median** ignores the values <LOD, Median*** treats values <LOD as 0. Values which could not be calculated due to a high number of samples <LOD appear as "-".

Table S.3.8 Comparison of measured effluent concentrations with surface water guidelines.

		Measured Effluent Concentrations				Ontario PWQO Guidelines
		With Dilution*		Without Dilution		
Element	Unit	Median	Max	Median	Max	
As	µg/L	0.004	0.07	0.6	0.8	5
B	µg/L	2.5	22	233	381	200
Cd	µg/L	0.0003	0.001	0.03	0.04	0.1-0.5
Co	µg/L	0.01	0.05	0.5	1.2	0.9
Cr	µg/L	0.01	2.4	0.7	25	8.9
Cu	µg/L	0.1	0.8	7.9	8.4	1-5
Fe	µg/L	0.9	21	52	216	300
Mo	µg/L	0.08	0.4	4.3	6.0	40
Ni	µg/L	0.08	1.7	5	20	25
P	µg/L	3.7	5	115	303	10-30
Pb	µg/L	0.001	0.07	0.2	0.7	1-5
Sb	µg/L	0.03	0.05	3.1	3.7	20
Se	µg/L	0.002	0.01	0.1	0.2	100
Tl	µg/L	0.0001	0.0002	0.005	0.01	0.3
U	µg/L	0.005	0.05	0.3	0.5	5
V	µg/L	0.002	0.04	0.3	1.6	6
W	µg/L	0.001	0.003	0.05	0.1	30
Zn	µg/L	0.3	1.4	29	54	20

* In Ontario, wastewater effluent regulations for municipal WWTPs are based on site-specific requirements for the receiving body, and therefore ranges are provided (Ontario Ministry of the Environment and Energy, 1994). Although the PWQO guidelines are not intended to be applied directly to wastewater effluents, they are applicable to surface water concentrations after dilution and mixing of the WWTP effluent with the receiving surface water. The median and maximum concentrations of the five sampled WWTP in this study are given in both non-diluted and diluted concentrations, calculated using the appropriate average dilution factor provided in **Table S.3.3**.

Table S.3.9 Elemental load contributions (%) from sampled tributaries and WWTP.

	Hydraulic Contribution	Major Elements (Ca, K, Mg, Na, S, Cl)	REE (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y, Yb)	Heavy Metals (Cd, Co, Cr, Cu, Ni, Pb, Zn)	Metalloids (B, Si, Ge, As, Sb)	Others (Al, Ba, Bi, Cs, Fe, Ga, Li, Mn, Mo, Nb, P, Pd, Rb, Re, Rh, Se, Sn, Sr, Te, Tl, U, V, W, Zr)
Conestogo River	35	29	40	47	37	37
Speed River	26	25	36	47	29	26
Nith River	10	11	10	12	15	11
Fair Child Creek	2	1	7	5	4	6
Big Creek	1	1	2	2	1	2
McKenzie Creek	2	3	4	<1	3	7
Tributary Average	**13**	**12**	**16**	**23**	**15**	**15**
Kitchener WWTP	8.8	119	15	145	31	44
Galt WWTP	1.4	137	2.5	69	7.6	15
Brant WWTP	1.7	130	1	4.3	14	5.4
Caledonia WWTP	0.1	9	0.4	0.5	0.6	0.9
Dunnville WWTP	0.2	4	5	0.8	1.6	1.5
WWTP Average	**2.4**	**79**	**5**	**44**	**11**	**13**

Table S.3.10 Elemental mass-imbalances (%) from sampled tributaries and WWTP.

	Major Elements (Ca, K, Mg, Na, S, Cl)	REE (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y, Yb)	Heavy Metals (Cd, Co, Cr, Cu, Ni, Pb, Zn)	Metalloids (B, Si, Ge, As, Sb)	Others (Al, Ba, Bi, Cs, Fe, Ga, Li, Mn, Mo, Nb, P, Pd, Rb, Re, Rh, Se, Sn, Sr, Te, Tl, U, V, W, Zr)
Conestogo River	35	18	121	114	441
Speed River	35	131	151	134	250
Nith River	8	65	125	138	193
Fair Child Creek	12	119	129	17	181
Big Creek	7	138	38	26	20
McKenzie Creek	77	52	88	54	54
Tributary Average	**29**	**87**	**109**	**81**	**190**
Kitchener WWTP	269	283	239	109	72
Galt WWTP	224	56	58	41	38
Brantford WWTP	200	35	34	36	53
Caledonia WWTP	30	22	40	53	59
Dunnville WWTP	7	54	199	52	515
WWTP Average	**226**	**90**	**114**	**58**	**147**

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Chapter 4: Conclusions and Recommendations for Future Research

4.1 General Thesis Summary

The research presented in this thesis investigated the role of wastewater treatment plants in affecting the occurrence of trace metals in surface water environments at different scales; in the Laurentian Great Lakes and the Grand River catchment. Municipal wastewater treatment systems are used around the world and have been shown to be a major source of deleterious levels of nutrients, organic contaminants and various emerging contaminants to freshwater systems, that have been linked to negative effects on human and ecosystem health (Carey & Migliaccio, 2009; Holeton et al., 2011). Comparable information on large-scale trace element sources and loads to and from wastewater treatment systems has been scarce. On the broadest level, the research presented in this thesis has advanced our understanding of current wastewater concentration ranges of trace elements typically not considered in governmental monitoring programs and regulation, their behavior during treatment, and potential impacts once discharged via effluent.

Chapter 2 provides new insights into the concentration ranges, loading rates, and removal efficiencies of trace elements in a representative selection of wastewater treatment plants in the Great Lakes basin. It was found that concentration ranges in both effluents and biosolids, as well as the resulting calculated average per-person trace element loads, mostly follow natural abundance patterns and are reasonably similar to values reported in the few available previous studies in other regions. Concern regarding trace metals in wastewater and sewage sludge may be low overall, because few

anomalously high concentrations or loads were observed in this large selection of >40 facilities. Despite only a handful of anomalously high concentrations and loads in WWTP samples, effects of the recorded values can not be ruled out due to the lack of toxicological data on these elements, particularly at locations where the mixing ratio of effluent with receiving waters is low. Although a wide variety of facilities were sampled in terms of treatment type, size, location, and catchment statistics, concentrations and loading rates only provide a snapshot view and were not used to evaluate temporal trends. In chapter 2, it was also concluded that conservative major elements, phosphorous, most transition metals, PGE, and REE, are all effectively eliminated at a rate of >90% during wastewater treatment, and that facilities with tertiary treatment technologies achieved better elimination for all element groups when compared to facilities with primary and secondary treatment technologies. This does not necessarily mean that every facility should have tertiary treatment technologies, as tertiary treatment is often implemented to target a specific type of contaminant that is known to have increased levels in that facility's influent, such as emerging micro-pollutants, pathogens, and organic matter (Frontistis et al., 2011), antimicrobial resistant bacteria (Guardabassi et al., 2002), as well as nitrogen and phosphorous (Chevalier et al., 2000), among others. Lastly, chapter 2 investigated various attributes of the sewersheds of sampled wastewater treatment plants to contextualize trends in trace metal loads and explore potential source pathways. This approach was successful for previously determined relationships, such as the number of hospital beds in the sewershed and the gadolinium load entering the facility (Reynolds et al., 2000), as well as a point sourced rhenium anomaly in a sewershed containing a rhenium recycling plant. Weaker correlations were observed

when exploring other potential sourcing pathways with results being more inconclusive for platinum, palladium, and rhodium WWTP loads in relation to sewershed road density and arsenic WWTP concentrations in relation to arsenic drinking water concentrations in the respective sewershed.

Chapter 3 presents new data on the concentration ranges of major and trace elements in wastewater and surface water samples from the Grand River watershed, i.e., at a smaller scale but higher resolution than the basin-wide screening in chapter 2. Trace metal concentrations in the Grand River revealed distinct spatial trends of accumulation and dilution, as well as notable anomalies throughout the catchment. Investigation of element concentrations in tributary confluents and wastewater effluent determined that effluent-derived loads of both major and trace elements often outweighed tributary confluences in relation to their hydraulic contribution. Furthermore, localized inputs from tributaries or effluents appear significant enough to impact select trace element patterns in the Grand River, particularly at locations with low mixing ratios, and even at locations with average major element inputs. After testing several elemental tracers in an attempt to quantify human imprints on trace metal trends in the river, it was found that the anthropogenic Gd fraction appears to capture imprints of WWTP effluent discharge in the Grand River better than concentrations of Na, K, B, or the Rb/Sr ratio. Our results in chapter 3 show that trace element dynamics in the Grand River system are governed by a complex interplay of natural and anthropogenic sources, and particularly upstream, where mixing ratios of wastewater effluent with the river are low, wastewater does seem to imprint water quality on the Grand river.

Overall, this thesis demonstrates the effectiveness of wastewater surveillance for quantification of anthropogenic and geogenic trace element emissions and its value to improving the general understanding of the sourcing of emerging trace element contaminants and their behavior during wastewater treatment. Although the recorded trace element concentration ranges do not appear to warrant direct modification of existing monitoring programs, additional monitoring of select sites (i.e. those with expected low mixing ratios or catchments with known (industrial) use and/or effluent discharge) and select elements may help better constrain their controls on surface water loads.

4.2 Recommendations for Future Work

The following is a list of recommendations for future research regarding trace elements in wastewater treatment plants in the Laurentian Great Lakes and the Grand River, Ontario:

- To account for seasonal variation in element concentrations, which is known to be the case for major water quality parameters and as a function of discharge rate variability (Xu et al., 2019), wastewater treatment plants could be sampled once in each of the four seasons.
- Wastewater treatment facilities as well as surface water study areas could be sampled over a longer period of time (e.g., for 5-10 years), to get a better understanding of the potential temporal changes (and the resulting weather related changes) in trace element concentrations. Although the results of this paper do not indicate a large-scale cause for concern regarding trace element concentrations in wastewater

treatment plants, this could change if their concentrations are increasing at significant rates.

- To better determine the differences in elimination rates of particular elements or element groups across wastewater treatment plants with different treatment technologies, the facilities could be grouped by specific treatment technologies they employ, such as aerobic digestion, ultraviolet disinfection, chlorine disinfection, etc., instead of their broader treatment classifications of primary, secondary and tertiary. Furthermore, to help determine where within the treatment process the most significant elimination takes place, and therefore where it could be improved if necessary, monitoring of concentrations and loads within WWTP (i.e., between each treatment stage) should be done.
- To get a more complete analysis of trace element point sources in WWTP sewersheds, particularly when analyzing parameters such as Pt and their relationship to road density, an understanding of the related sewer system (combined sewers versus separated sewers) should be explored.
- To get a better understanding of element concentrations and loads in both WWTP and surface waters, monitoring should not only include analysis of dissolved concentrations (as done in this paper), but also particulate concentrations.
- To achieve a more complete understanding of the potential imprints of tributary and effluent trace element inputs in the Grand River, further assessment of the geological signature of the Grand River, e.g., through additional monitoring of its trace element signature in secondary or tertiary tributaries and consideration of other non-point sources such as soil erosion, land use, agricultural runoff, industry, and geology of the

basin, among others, should be done. Analysis of non-point sources could be done through the Soil & Water Assessment Tool (SWAT, 2022), as there is likely sufficient hydrometric stations and published data for the Grand River (Environment, Conservation and Parks, 2019; Grand River Conservation authority, 2022). Studies in the past have done similar work for the Grand river (Loomer & Cooke, 2011; Lee et al., 2014), as well as the Maumee River (Cipoletti et al., 2020; Singh et al., 2017) but were not all encompassing, only focusing on a few contaminants and sources.

- Sampling of all 30 wastewater treatment facilities within the Grand River watershed would provide a more complete understanding of potential imprints. This also translates to other watersheds, particularly urban catchments, where as all WWTP within the watershed should be sampled to obtain the most accurate analysis and complete understanding of potential imprints.
- Due to the land application of sludge, consideration of element concentrations in sewage sludge from sampled WWTP in the Grand River could potentially act as a source to river concentrations through runoff and should be considered in future research. To complete this, the volume and location of land applied sludge would need to be retrieved either directly from the WWTP or from local reports such as (Hagan et al., 2020), although the location of land applied sludge is not normally reported. Additionally, the length of time for the contaminants in sludge to reach the surface water in the catchment would need to be considered (Ghirardini and Verlicchi, 2019; Tyrrel and Quinton, 2003).
- Alternate established wastewater tracer compounds such as *e.coli* (Pongmala et al., 2015), isotopes (McCance et al., 2018), or persistent organic compounds

(Glassmeyer et al., 2005) could be used to assess trace element patterns and the impact of WWTP effluent the Grand River.

- Understanding and analysis of trace element partitioning in the Grand River is another factor that should be considered in future research regarding the systems trace element dynamics. Once introduced to water, many trace elements will not be conservative but in fact reactive and bind to dissolved particulates (mineral and organic), and many could also be actively scavenged by biota (Förstner and Salomons, 1983; Wangersky, 1986). For this scavenging/partitioning to be important, one would need to consider the average residence time of water in the catchment, with longer travel times associated with higher chances of uptake or removal (Wangersky, 1986).
- Lastly, as many of the above recommendations pertain to the Grand River, other well characterized river systems with variable land use types and contaminant sources could also benefit from trace element input analysis, such as the Mississippi River or the Rhine River. This approach could also be extrapolated into a model for total trace element inputs from riverine systems into oceans.

4.3 References

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