EMERGING CONTAMINANTS IN OLD LANDFILLS AND STREAM IMPACTS

CONTAMINANTS OF EMERGING CONCERN IN GROUNDWATER POLLUTED BY HISTORIC LANDFILLS: LEACHATE SURVEY AND STREAM IMPACT ASSESSMENT

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Master of Science

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TITLE: Contaminants of Emerging Concern in Groundwater Polluted by Historic Landfills: Leachate Survey and Stream Impact Assessment

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Lay Abstract

Historic landfills are a known source of groundwater contamination. This study investigated whether these landfills contain new groups of chemicals, called contaminants of emerging concern (CECs), which are suspected to pose serious environmental and human health risks. This study found many CECs at high concentrations in most of the 20 historic landfill sites investigated, even those closed up to 60 years. A full-year investigation at one historic landfill site showed that organisms living in the sediments of a nearby stream are exposed to high concentrations all year long. Concentrations in the stream increased as it flowed past the landfill, and may be higher in winter and after rains, times monitoring is rarely done. The elevated concentrations of harmful contaminants in this water are potentially threatening the stream ecosystem. Operators of historic sites should consider testing for CECs and ensure that monitoring strategies accurately evaluate the risk posed to the environment.

Abstract

Many types of contaminants of emerging concern (CECs), including per- and poly-fluoroalkyl substances (PFAS), have been found in leachate of operating municipal landfills. However, information on CECs in leachate of historic landfills (≥ 3 decades since closure, often lacking engineered liners or leachate collection systems) and the related risk posed from groundwater plumes discharging to nearby aquatic ecosystems is limited. In this study, 48 samples of leachate-impacted groundwater were collected from 20 historic landfills in Ontario, Canada. The CECs measured included artificial sweeteners (ASs), PFAS, organophosphate esters (OPE), pharmaceuticals, bisphenols, sulfamic acid, perchlorate, and substituted phenols. Several landfills, including ones closed in the 1960s, had total PFAS concentrations similar to those previously measured at modern landfills, with a maximum observed here of 12.7 µg/L. Notably elevated concentrations of several OPE, cotinine, and bisphenols A and S were found at many 30-60 year-old landfills. There was little indication of declining concentrations with landfill age, suggesting historic landfills can be long-term sources of CECs to groundwater. A full-year field study was performed on a 0.5-km reach of an urban stream receiving contaminated groundwater from nearby historic landfills. Elevated concentrations of ammonium, the AS saccharin, an indicator of old landfill leachate, and CECs (e.g., maximum total PFAS of 31 μ g/L) in the shallow discharging groundwater were relatively stable across the seasons but were spatially restricted by hyporheic exchange and discharge of other groundwater. This indicates a patchy but long-term exposure for endobenthic organisms, which are rarely monitored. Stream water concentrations were more dilute, but increased markedly across the landfill stretch, and showed signs of increases in winter and after rain/snowmelt events. These findings provide guidance on which CECs may require monitoring at historic landfill sites and suggest how landfill monitoring programs could be improved to fully capture the risk to receiving water bodies.

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List of Abbreviations

AFFF	Aqueous film forming foam				
AS	Artificial sweeteners				
BP	Bisphenols				
CEC	Contaminant of emerging concern				
Cl	Chloride				
DO	Dissolved oxygen				
EC	Electrical conductivity / specific conductance				
ECCC	Environment and Climate Change Canada				
ESI	Electrospray ionization				
ET	Evapotranspiration				
FLUX-LM	FLUX in Layered Media				
GW-SW	Groundwater-surface water				
IC	Ion chromatography				
LC	Liquid chromatography				
LCS	Leachate containment system				
mdl	Minimum detection limit				
MS	Mass spectrometer				
MSW	Municipal solid waste				
OPE	Organophosphate esters				
PFAA	Perfluoroalkyl acids				
PFAS	Per- and polyfluoroalkyl substances				
PFCA	Perfluoroalkyl carboxylic acid				
PFSA	Perfluoroalkyl sulfonic acid				
PFECA	Perfluoroalkyl ether carboxylic acids				
PFESA	Polyfluoroalkyl ether sulphonic acids				
RMSE	Root mean square error				
SPE	Solid phase extraction				
SRP	Soluble reactive phosphate				
UHPLC	Ultra high performance liquid chromatography				
USGS	United States Geological Survey				
VFLUX2	Vertical Fluid [Heat] Transport Solver 2				
VOC	Volatile organic compound				
WAX	Weak-anion exchange				
WWTP	Wastewater treatment plant				
XOC	Xenobiotic organic compounds				
Compound Names					
BPA	Bisphenol A				
BPS	Bisphenol S				
BTEX	Benzene, toluene, ethyl-benzene, xylenes				
PFBA	Perfluorobutanoic acid				
PFPeA	Perfluoropentanoic acid				

PFHxA	Perfluorohexanoic acid
PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnA	Perfluoroundecanoic acid
PFDoDA	Perfluorododecanoic acid
PFTriDA	Perfluorotridecanoic acid
PFTeDA	Perfluorotetradecanoic acid
PFHxDA	Perfluorohexadecanoic acid
PFBS	Perfluorobutanesulfonate
PFPeS	Perfluoropentanesulfonate
PFHxS	Perfluorohexanesulfonate
PFHpS	Perfluoroheptanesulfonate
PFOS	Perfluorooctanesulfonate
PFDS	Perfluorodecanesulfonate
PFDoDS	Perfluorododecanesulfonate
PFECHS	Perfloroethylcyclohexanesulfonate
FBSA	Perfluorobutylsulphonamide
FOSA	Perfluorooctanesulfonamide
HFPO-DA	Hexafluoropropylene oxide dimer acid (GenX)
ADONA	3H-perfloro-3-(3-methoxypropoxy)propanoic acid
9-C1-PF3ONS	6:2 chlorinated polyfluoroalkyl ether sulfonate
11-Cl-PFOUdS	8:2 chlorinated polyfluoroalkyl ether sulfonate
8C1-PFOS	Sodium 8-chloroperfluoro-1-octanesulfonate
TEP	Triethylphosphate
TBPO	Tributylphosphine oxide
TPrP	Tripropyl phosphate
TnBP	Tributylphosphate
TiBP	Tri-isobutylphosphate
TPPO	Triphenylphosphine oxide
TEEDP	Tetraethyl ethylenediphosphonate
TCEP	Tris(2-chloroethyl)phosphate
TCPP	Tris(2-chloroisopropyl) phosphate
TDCPP	Tris(1,3-dichloro-2-propyl)phosphate
TPHP	Triphenylphosphate
EHDPP	2-ethylhexyl diphenyl phosphate
TOTP	Tritolyl phosphate
IDDPP	Isodecyl diphenyl phosphate
TBOEP	Tris(2-butoxyethyl) phosphate
TEHP	Tris(2-ethylhexyl)phosphate
TBPDPP	Tert-butylphenyl diphenyl phosphate

DPIPP	Diphenyl-3-isopropylphenyl phosphate
TXP	Tris-xylenyl phosphate
T35DMPP	Tris(3,5-dimethylphenyl)phosphate
DTBPPP	Di-tert-butylphenyl phenylphosphate
T2IPP	Tris(2-isopropylphenyl)phosphate
TTBPP	Tris(p-tert-Butylphenyl) phosphate
TDBPP	Tris(2,3-dibromo propyl) phosphate
DOPP	Dioctylphenyl phosphonate

List of Symbols

q	Specific discharge (groundwater flux)
Κ	Hydraulic conductivity
i	Hydraulic gradient
Q	Discharge
А	Area
λ	Bulk thermal conductivity
Т	Temperature
t	Time
ρ, ρ_w, ρ_s	Bulk, fluid, sediment density
c, c_w, c_s	Bulk, fluid, sediment specific heat
Z	Distance along flow direction
η	Porosity
v	Groundwater velocity
λ_{e}	Effective thermal conductivity
α*	Thermal dispersivity
κ _e	Effective thermal diffusivity
β	Thermal Peclet number
L	Characteristic length
d	Total thickness

Declaration of Academic Achievement

I am the sole author of this thesis. I was the main contributor for the co-authored articles, composing Chapters 3 and 4, as outlined below.

Article 1: Located in Chapter 3

Propp, V.R., A.O. De Silva, C. Spencer, S. Brown, S. Catingan, J.E. Smith, J.W. Roy. Organic contaminants of emerging concern in leachate of historic municipal landfills. Environmental Pollution (in press)

I, Victoria R. Propp, was the primary author. I wrote the first draft of this manuscript and actively participated in manuscript revisions with Dr James Roy. I worked with Dr. James Roy to design the experiments. I coordinated with landfill operators for site access and led field activities. I collected essentially all field data with assistance from field technicians. I performed the data analysis and interpretation with feedback from coauthors. Amila O. De Silva, of Environment and Climate Change Canada, conducted chemical analysis on samples for contaminants of emerging concern (CECs), assisted in the interpretation of those CEC data, and reviewed and edited the draft manuscript. Christine Spencer, of Environment and Climate Change Canada, performed laboratory analysis of water samples for CECs. Susan J. Brown, of Environment and Climate Change Canada, contributed analysis tools for artificial sweeteners and reviewed the draft manuscript. Sara D. Catingan provided laboratory assistance to C. Spencer and A. O. De Silva. James E. Smith, of McMaster University, provided supervision and financial support to the candidate, and reviewed and edited the draft manuscript. James W. Roy, of Environment and Climate Change Canada, was the principle investigator for the project, provided initial motivation and experimental design, supervised field data collection, provided insight and suggestions for data analysis and interpretation, drafted figures in their final format, reviewed the manuscript draft and led revisions from journal reviews.

Article 2: Located in Chapter 4 (in preparation for publication)

I, Victoria R. Propp, was the primary author. I wrote the first draft of this manuscript. I worked with Dr. James Roy to design the experiments. I led field activities and collected essentially all field data with assistance from field technicians. I performed the data analysis and interpretation with feedback from Dr. James Roy. James E. Smith, of McMaster University, provided supervision and financial support to the candidate and reviewed the draft manuscript. James W. Roy, of Environment and Climate Change Canada, was the principle investigator for the project, provided initial motivation and experimental design, supervised field data collection, provided insight and suggestions for data analysis and interpretation, and reviewed and edited the manuscript draft.

Chapter 1: Introduction

1.1 Background

Municipal solid waste (MSW) landfills are a well-known source of pollution to the environment, often through groundwater contaminant transport of landfill leachate. Historic landfills may pose a greater risk to the environment than modern, active landfills because of less stringent documentation and regulation, less infrastructure to prevent plume migration and leachate formation, and frequent close proximity to surface water bodies (Lisk 1991; Environmental Commissioner of Ontario 2010). Closed, old landfills are not always adequately monitored; in Ontario, it is common for many publicly owned landfills to be monitored annually, although older (pre-1970s) landfill sites may not be subject to such regulations. This monitoring varies between sites, but often includes the collection of samples from leachate or groundwater wells and, if applicable, nearby surface water samples that are analyzed for common leachate constituents such as hydrocarbons and volatile organic solvents, and inorganics, including salts, nutrients, and heavy metals.

Landfill operators throughout North America are not currently required to test for contaminants of emerging concern (CECs), which are compounds that were previously not considered of concern and/or were not detectable in environmental matrices with past analytical capabilities, but are now known or suspected to pose a widespread and longlasting risk to human and/or ecological health (Qi et al. 2018). Per- and polyfluoroalkyl substances (PFAS) are an example of a class of CEC compounds that have received a great deal of global attention due to their extreme persistence, bioaccumulative

tendencies, current health concerns, and ubiquitous detections worldwide (Sunderland et al. 2019). Some PFAS and compounds within other CEC classes, such as organophosphate esters and pharmaceuticals, have been detected in landfill leachate at modern, active landfills (Busch et al. 2010; Regnery et al. 2011; Masoner et al. 2014; Lang et al. 2017); however, few studies have investigated CEC presence in leachate of old, closed landfills and only in a few (max. 7) landfill sites per study (see, e.g., Barnes et al. 2004; Buszka et al. 2009; Gallen et al. 2016; Hepburn et al. 2019). Thus, there is a knowledge gap surrounding the prevalence of CECs in landfill leachate-impacted waters in a broad range of historic, closed landfills.

Due to the proximity of many historic landfills to surface water bodies, there is a strong likelihood of leachate-impacted groundwater interacting with surface waters, which has been observed numerous times in previous work (e.g., Borden and Yanoschak 1990; Yusol et al. 2009; Maqbool et al. 2011; Milosevic et al. 2012; Thomsen et al. 2012; Gooddy et al. 2014; Fitzgerald et al. 2015; Stefania et al. 2019). However, previous work has not investigated CECs such as PFAS in leachate-impacted groundwaters discharging to surface water. These studies also have taken a strongly hydrogeologic viewpoint and not rigorously considered the potential ecological threat posed. As leachate-impacted groundwater discharges to surface water, the risk may be extreme for endobenthic organisms living in the shallow sediments of discharge zones that experience undiluted concentrations of groundwater contaminants prior to mixing with the surface water. The exposure for epibenthic zone organisms living on the sediment bed varies based on timing and location of groundwater flux and contaminant concentrations. Mass loading of

contaminants to the stream can also impact surface water quality for pelagic organisms, though with greater dilution expected, and in the case of streams, contaminants can impact downgradient receptors such as lakes or drinking water supplies. The processes of groundwater-surface water (GW-SW) interaction must be understood to evaluate the risk of leachate-impacted groundwater exposure (Conant et al. 2019). Current landfill plume monitoring programs may not adequately examine the temporal and spatial variability of GW-SW interaction, thereby poorly evaluating the surface water exposure to leachate-impacted groundwater from historical MSW landfills.

1.2 Project Overview and Research Objectives

This thesis is part of a larger project by Environment and Climate Change Canada, funded by the Ministry of the Environment, Conservation and Parks, with an overall goal to evaluate landfills within Ontario as a potential source of harmful contamination to the Great Lakes waters. Historic landfills within Ontario were recognized as being forgotten polluters that potentially lack adequate regulations to protect the surrounding environment and surface waters (Environmental Commissioner of Ontario 2010). Therefore, the motivation behind this project was to evaluate the potential for historic landfills to impact surface waters, through a survey of the contaminants in leachate-impacted groundwater and detailed investigations of leachate plumes interacting with surface waters (both a stream and a pond) through hydrogeological, chemical, and ecotoxicological assessments.

The portions of the project covered in this thesis are the leachate survey and the hydrogeological/ chemical assessments of a leachate plume discharging to a stream. Three main objectives were developed for this thesis, the first of which was to assess the prevalence of CECs in leachate-impacted groundwater from closed, historical MSW landfills that may pose an environmental risk. Based on those findings, the next objective was to evaluate the potential risk posed to aquatic organisms of leachate-impacted groundwater discharging to a stream. A special focus was placed on PFAS for both aforementioned objectives due to the heightened global concern associated with their extreme environmental persistence and the current associated health concerns for these compounds (Sunderland et al. 2019). Finally, this study aims to investigate the spatial and temporal variability of leachate-impacted groundwater as it discharges to a stream, with consideration of the different ecosystem compartments (i.e., endobenthic, epibenthic, pelagic zones, plus downstream ecosystems).

A two-part study was completed in order to investigate these objectives and is presented here as a "sandwich" style thesis. A breakdown of each chapter is as follows:

- Chapter 1 briefly introduces the research topic, establishes the motivation of the overall project, and outlines the research objectives and overall structure of the thesis.
- Chapter 2 provides a literature review to inform the reader on the topic and provide a review of the current state of research on this subject. Note that some information from this chapter may overlap with content in the introduction sections of Chapter 3 and 4.

- Chapter 3 is a leachate survey investigating 20 historic MSW landfills from across Ontario, Canada, for 81 CECs and 122 common leachate constituents. Chapter 3 was accepted on November 29th, 2020 for publication in the journal Environmental Pollution. The supplemental information included with this journal article is included as Appendix A. The candidate was the main contributor for this article, responsible for field data collection, data analysis and interpretation, and completion of the article draft. Contributions for this co-authored article are fully outlined above in the Declaration of Academic Achievement.
- Chapter 4 is a full-year field study on a 0.5 km reach of an urban stream receiving contaminated groundwater from a set of three nearby historic landfills. At this site, detailed investigations of the hydrogeological controls and the contaminant conditions were performed at two stream stretches, with surface water impacts investigated more broadly. Additional information associated with this chapter is included in Appendix B. The candidate was the main contributor for this article, responsible for field data collection, data analysis and interpretation, and completion of the article draft. Contributions for this co-authored article are fully outlined above in the Declaration of Academic Achievement.
- Chapter 5 summarizes the main conclusions and implications of Chapter 3 and 4, connecting these chapters to the overall project goal and describing the contribution of the thesis to the advancement of the state of knowledge on this topic.

Chapter 2: Literature review

2.1 Municipal Landfills

For centuries landfilling has, and continues to be, one of the leading methods for waste disposal worldwide. Garbage is buried or piled on the ground and may be subject to compaction or cover. Landfill leachate is the liquid that develops over time as moisture within the garbage or precipitation that is able to percolate into the landfill travels through the waste. Depending on the groundwater flow system, leachate plumes may transport harmful contamination >1 km off site (see Table 3.1 in Christensen et al. 2001). This leachate-impacted groundwater can affect surface waters receiving groundwater discharge, drinking or irrigation water wells, sublevel dwellings (via vapour intrusion), and possibly terrestrial phreatophytes.

Currently many developed countries strictly regulate and engineer landfilling processes, designating municipal waste landfilling sites for the disposal of non-hazardous household/ commercial material, whereas hazardous and industrial waste materials are disposed of at sites specially designed for these higher-risk substances. Landfilling, however, greatly predates these modern definitions and stringent regulations. Throughout the 20th century, as waste production increased, alongside the increasing concerns of open-pit burning, the focus shifted to sanitary landfilling methods of waste disposal (Lisk 1991). Dumps, open pits, and garbage piles were a trademark in almost every community across North America in the early 1900s and continue to be the norm for some developing countries. From a Canadian standpoint, 'historic' landfills are defined in this thesis as landfilling sites that have been closed ≥30 years (i.e., closed by the mid-1990s).

These sites lack some of the infrastructure and design considerations now common in modern and active landfills, and predate stringent regulations, as discussed in further detail below. Historic landfill sites pose a risk to the surrounding environment due to the many unknowns surrounding their location, design, and waste and leachate composition (Environmental Commissioner of Ontario 2010).

Older landfill sites were often located in close proximity to communities for ease of access (Lisk 1991). As communities grew around them, these landfills frequently became located at the centre of modern towns. Development restrictions on closed landfills has resulted in many historic sites being repurposed into recreational sports fields and parkland. Those that remained on the fringes of towns are often repurposed as waste transfer stations after their closure. Historic landfills were frequently situated on valley bottoms or floodplains because the thick soils typically present were useful for cover material, while low grades allowed easy equipment access (Lisk 1991); furthermore, these areas were often too wet for other development. As a result, old historic landfills are often located near surface water bodies. Therefore, historic landfills often have the potential to adversely affect human health due to their close proximity to urban centres and surface waters that could allow leachate plumes to interact with drinking water sources. Numerous studies have investigated landfill leachate plumes interacting with surface water bodies (e.g., Borden and Yanoschak 1990; Yusol et al. 2009; Maqbool et al. 2011; Milosevic et al. 2012; Thomsen et al. 2012; Gooddy et al. 2014; Fitzgerald et al. 2015). Coakley (1989) looked at landfill sites located close to the shores of the Great Lakes in Ontario and found that shoreline erosion causes direct

interaction between buried waste and surface water. Landfills located near surface water bodies have shorter flow paths for leachate-impacted groundwater to discharge resulting in less attenuation of chemical constituents entering the surface water (Coakley 1989).

Interaction between leachate and the surrounding environment at historic landfill sites is due in part to the lack of advanced waste and leachate management strategies available at the time of operation. As knowledge about groundwater flow regimes increased, landfill operators were able to target either discharge or recharge zones appropriate for their management technique. In discharge zones, leachate would need to be collected on site as groundwater moved up through the waste (Lisk 1991). Recharge zones carried leachate impacted water away from the surface, but leachate could potentially travel off site and impact surrounding receptors. Targeting areas of low permeability slowed transport allowing for more time for attenuation processes; however, too slow of permeability would cause precipitation to saturate the waste (Lisk 1991). Therefore, clay covers were placed over the waste to reduce percolation of precipitation. There is a great deal of variability in the design of old historic landfills, causing their current leachate composition to vary drastically. In 1998, Ontario introduced O. Reg 232/98 (Landfilling Sites) under the Environmental Protection Act that requires new and expanding landfill sites to undergo hydrogeological assessments prior to landfilling and assess groundwater, surface water and gas emissions; therefore, modern operational landfills should be in ideal hydrogeological settings with infrastructure installed that reduces the potential harm to the environment. This can include synthetic liners and covers added to clay liners, leachate collection systems underneath the landfill which

typically pump leachate to a nearby wastewater treatment plant (WWTP), and reactive barriers to assist in the degradation of leachate plumes. Therefore, modern operational sites are less likely to have leachate plumes that are transported off site.

Older closed landfills that did not fall under O.Reg. 232/98 were less regulated resulting in many unknowns surrounding their location, waste composition and leachate concentrations. Data provided by the Ministry of the Environment, Conservation and Parks (MECP), last updated in September 2017, reports that in Ontario there are currently 670 active municipal landfills, 23 inactive but not yet capped landfills, 1705 closed landfills that were issued Environmental Compliance Approvals, and an estimated 1495 historic sites which closed prior to the formation of the Ministry in 1970. The exact number of historic landfills is unknown, as many older landfills may not have been declared and have since been forgotten (Environmental Commissioner of Ontario 2010). Newer landfills are required to monitor leachate usually at minimum once per year. Older sites which predate monitoring legislation are sometimes not required to sample annually, increasing the likelihood that details such as the waste composition and location are forgotten. Modern municipal landfills strictly monitor the waste that is accepted; however, at older sites unregulated disposal often occurred which could have resulted in more than just non-hazardous domestic waste entering landfills. These landfills, and many other poorly regulated sites worldwide, pose an unspecified threat to groundwater and surface water due to the unknown chemicals that could be present in the leachate.

Differences in leachate composition between landfills of different ages is also dependent on the history of chemical use in the region. After a compound is invented and

becomes widely manufactured, it may be found in landfills for many years, but likely will not be in landfills that closed before the compound's widespread use. This means that even if very old historic landfills accepted hazardous waste, they may not contain the same wide range of chemicals that existed at a later time. Older sites may, however, have accepted waste containing chemicals that were later banned from use. This would cause a different leachate composition compared to modern landfills because these older landfill sites will contain waste products from before these substances were banned and may even contain concentrated industrial wastes related to the production of those chemicals. After a compound is banned, for a period of time there will still be waste entering the landfill as products containing that compound may have a lifetime of use before they are disposed of. Chemical use and restrictions can vary drastically between regions, potentially adding to spatial variations in landfill leachate composition.

Overall, considering all the points above, the risk posed to groundwater and surface waters near old historic landfills may be similar to that of younger and operational municipal landfill sites. Although greater amounts of time have passed, allowing for degradation and attenuation of leachate plumes, there is a much higher risk of leachate-impacted water travelling off site. Sites that are unlined may still be transporting leachate offsite, while those that were lined may be reaching an age where the liner is starting to fail. Due to the poor documentation of many historic sites, there is a knowledge gap surrounding the exact composition of these leachate plumes, especially for emerging contaminants that have only recently been recognized as potential long-term pollutants (discussed further in section 2.2).

Municipal landfill leachate is typically composed of dissolved organic matter, inorganic components, heavy metals, and synthetic compounds such as halogenated and aromatic hydrocarbons. The exact concentrations of each component can vary greatly both between and within landfills. Factors affecting concentrations include the stage of decomposition, age of landfill, landfill infrastructure technology, composition of waste, site hydrogeology, and seasonal and climatic variation (Kjeldsen et al. 2002). Therefore, individual leachate samples from a landfill may not be representative of other landfills or even other areas within the same landfill. Multiple samples should be considered in order to determine a range of typical leachate concentrations. Table 2-1 summarizes typical concentrations of common municipal leachate constituents reported in the literature. The large ranges seen for most compounds, often over multiple orders of magnitude, represents the heterogeneous nature of municipal landfills due to the factors listed above.

The concentrations of constituents such as ammonium, chloride, sodium and potassium do not change substantially across decomposition stages (Kjeldsen et al. 2002). Ammonium concentrations are believed to remain steady for many years under methanogenic conditions, making this compound an effective tracer (discussed further in section 2.4.1). Organic compounds not found in nature are commonly called synthetic compounds or xenobiotic organic compounds (XOC). Table 2-1 includes a few common XOC, and Table 1 in Slack et al. (2005) provides an extensive list of XOC that can be found in household waste. The list of XOC in landfill leachate will always be changing as new compounds are created and others banned. Section 2.2 below discusses contaminants of emerging concern, many of which are classified as XOC.

Literature Citation	Kjeldsen et al.	Lisk 1991	Kjeldsen and	Renou et al. 2008
	2002		Christophersen 2001	
Description of	Literature review	15 landfills in	106 small, closed	Review of old
landfills in study	of mostly newer	UK	landfills in Denmark	landfills (age >10
	landfills			years)
pH []	4.5-9	6.2-7.4	(7.0)	7-11.5
EC (μ S cm ⁻¹)	2500-35000		(3000)	
Ammonium-	50-2200			
Nitrogen				
Ammonia-N		5-730	(110)	0.2-1600
Chloride	150-4500	70-2800	(360)	
Sulphate	8-7800	55-460	(150)	
Sodium	70-7700	43-2500	(210)	
Potassium	50-3700	20-650	(140)	
Calcium	10-7200	165-1150	(280)	
Magnesium	30-15000	12-480	(60)	
Iron	3-5500	0.09-380	(76)	4.1-26
Manganese	0.03-1400	0.32-27	(3.5)	0.13-15.5
Arsenic	0.01-1		(0.016)	
Cadmium	0.0001-0.4	< 0.005-0.01	(0.0068)	
Chromium	0.02-1.5	< 0.05-0.14	(0.076)	
Copper	0.005-10	< 0.01-0.15	(0.070)	0.005-0.031
Lead	0.001-5	< 0.05-0.22	(0.070)	
Nickle	0.015-13	< 0.05-0.16	(0.13)	
Zinc	0.03-1000	< 0.05-0.95	(0.67)	
Benzene	0.0002-1.6		<0.001-0.40	
Toluene	0.001-12.3		<0.001-0.90	
Ethylbenzene	0.2		<0.1	
Xylenes	0.0008-3.5		<0.001-2.4	
Trichloroethylene	0.00005-0.75		<0.0001-0.024	
Tetrachloroethylene	0.00001-0.25		<0.0001-0.005	

Table 2-1: Typical concentrations (mg/L unless otherwise stated) of common municipal landfill leachate constituents reported in the literature; average values shown in brackets.

2.2 Contaminants of Emerging Concern

Contaminants of emerging concern (CECs) are defined here as synthetic or natural compounds that are not frequently tested for in environmental matrices, but are known or suspected to pose a widespread and long-lasting risk to human and/or ecological health (Qi et al. 2018). CECs are typically present in the environment at trace concentrations (on the ng·L⁻¹ – μ g·L⁻¹ scale) yet are still able to cause adverse effects at these levels. CECs can be newly invented compounds, or compounds which have existed for decades but can only now be detected in the environment due to recent advances in analytical methodology. The classes of CECs that are discussed in greater detail in the subsequent sections are per- and polyfluoroalkyl substances (PFAS), organophosphate esters (OPE), and bisphenols (BP). Many more groups of compounds are also CECs, including those which are mobile, and therefore important, in groundwater such as pharmaceuticals and personal care products, phenols and substituted phenols, pesticides, and artificial sweeteners (discussed further in section 2.4).

Part of the concern surrounding CECs is the fact that many have multiple of the following properties: persistent and ubiquitous in the environment, bioaccumulative, and negative human and ecological health effects. Persistent compounds do not readily break down, and as a result are transported throughout the environment for many decades. Ubiquitous substances are found in many environmental matrices all over the world, typically as a result of widespread usage. Bioaccumlative compounds accumulate within living organisms because they are absorbed quicker than they are broken down and excreted. Although research into many of these contaminant classes is relatively recent and inconclusive, most CECs have suspected adverse human and/or ecological health effects. Lack of conclusive research means many of these compounds have not been sufficiently regulated in consumer products, food, or drinking water.

2.2.1 Per- and Polyfluoroalkyl Substances

Fluorinated compounds are a general class of substances that contain at least one fluorine atom (F) (Buck et al. 2011). PFAS are a subclass of synthetic aliphatic

compounds defined by the presence of at least one perfluoroalkyl moiety ($-C_nF_{2n}$ -), that is at least one carbon atom where all of the H atoms in the nonfluorinated analogues from which they are notionally derived have been replaced by F atoms (Buck et al. 2011; Nakayama et al. 2019). Where all H atoms have been replaced by F atoms in the alkyl chain (i.e., not in the functional groups) the compound is called a perfluoroalkyl substance. Polyfluoroalkyl substances have all of the H atoms on at least one, but not all, carbon atoms in the alkyl chain replaced by F (Buck et al. 2011).

While there are thousands of PFAS chemicals, perfluoroalkyl acids (PFAA), which includes both perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), have been the focus of most work on PFAS in the literature, especially for landfill leachate (Hamid et al. 2018). Figure 2-1 below shows the general structure of PFCAs and PFSAs, which only differ by their respective functional group. Perfluorooctanesulfonate (PFOS), one of the most widely used and studied PFAS chemicals, is a PFSA with 8 perfluoroalkyl moieties (n=8) and 8 carbon atoms (C8). Perfluorooctanoic acid (PFOA), another widely used and studied chemical, is a C8 PFCA; however, due to the carbon atom in the functional group, it only has 7 perfluoroalkyl moieties (n=7). Literature often classifies PFAS as long-chained or shortchained, depending on the length of the alkyl chain. Long-chained PFAS are defined as PFCAs with 8 or more carbon atoms (n \geq 7) or PFSAs with 6 or more carbons (n \geq 6) (Buck et al. 2011). For further information on the other PFAS compounds and groups, including precursor compounds, see Table 1 in Nakayama et al. (2019).



Figure 2-1: (A) General structure of PFSAs; (B) General structure of PFCAs; n represents the number of perfluoroalkyl moieties; adapted from Nakayama et al. (2019).

PFAS, termed the "forever chemicals", are considered extremely persistent with multiple compounds listed for immediate elimination or restriction by the Stockholm Convention on Persistent Organic Pollutants. PFAS contaminated sites are very difficult to remediate, though a recent study has reported PFAS biodegradation for the first time (Huang and Jaffé 2019). In particular, PFOS and PFOA are ubiquitous in the environment, both due to their widespread use and the degradation of precursors (Gobelius et al. 2018). Although PFAS compounds have a range of toxicity effects and tendencies to bioaccumulate, many are considered to have additive adverse effects on human health, causing a push for PFAS to be regulated as an entire class of compounds (Ahrens and Bundschuh 2014; Sunderland et al. 2019). PFAS compounds have been shown to cause adverse health effects in both animals and humans, including carcinogenic, immunotoxic, and metabolic effects (Sunderland et al. 2019). Most water quality guidelines are for the better-studied compounds PFOA and PFOS, although some jurisdictions have released guidelines for other PFAS (see table A-7 in Appendix A for more information on drinking water and aquatic life guidelines). For most regions, these guidelines are not enforceable and do not even begin to cover the 4000+ known PFAS compounds due to a lack of definitive research findings for most compounds.

The most notable sites contaminated by PFAS are those with past use of aqueous film-forming foams (AFFF) for fire-fighting (e.g., airports, military bases, fire-training areas). Maximum groundwater concentrations of PFOS, PFOA, and other C4-C8 PFAS have typically been 10s-100s μ g/L (e.g., Moody et al. 2003, Banzhaf et al. 2014, Anderson et al. 2016) but for PFOS reaching 2910 μ g/L at a fire-fighting training area in Sweden (Wennberg and Fridlund 2015) and 4300 μ g/L at a U.S. military base (Anderson et al. 2016). The other main uses of PFAS are in stain- and water-proof coatings on various products including clothing, upholstery, carpet and paper, food packaging, non-stick coatings on cookware, cosmetics, electronic and photography equipment, and dental floss. Many of these products are disposed of in landfills, contributing to PFAS in landfill leachate (Hamid et al. 2018). Use of PFAS in consumer products began in the 1950s, but since the 2000s the use of PFOA, PFOS, and their precursors compounds have been banned and restricted in many countries (Buck et al. 2011; Longpré et al. 2020).

2.2.2 Organophosphate Esters

Organophosphate esters (OPE) and congeners are often used as plasticizers, flame retardants, anti-wear and anti-foaming agents, laquers, hydraulic fluids, floor polishes, in products such as plastics, rubber, lubricants, electronics, polyurethane foams, textiles, etc. (Wei et al. 2015; Qi et al. 2019). As an additive to these products, rather than being chemically bonded, OPE are more easily able to enter the environment when these products are disposed (Wei et al. 2015; Qi et al. 2019). OPE can be classified as alkyl, aryl or chlorinated, depending on the attached R groups. Chlorinated OPE, such as tris(2chloroethyl)phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP) and tris(1,3dichloro-2-propyl)phosphate (TDCPP) became widely used as flame retardants due to the phasing out of polybrominated flame retardants (Blum et al. 2019).

Due to their wide range of physicochemical properties, OPE compounds can have a large range of toxicity, persistence and bioaccumulative tendencies. Health effects for many compounds are still widely unknown, although preliminary work suggests that OPE, especially chlorinated OPE, may be carcinogenic and neurotoxic, adversely affecting human health and posing a toxicity risk to wildlife (van der Veen and de Boer 2012; Pantelaki and Voutsa 2019; Wei et al. 2015). Various OPE compounds have been found in many environmental matrices at elevated levels (Pantelaki and Voutsa 2019; Wei et al. 2015) and countries have begun to restrict the use of some OPE in children's products and furniture (Blum et al. 2019). There are currently no water quality standards in place for OPE compounds, although assessments of risk to human health and the environment have been made for some of these compounds under the Canadian Environmental Protection Act (Government of Canada, 2020).

2.2.3 Bisphenols

Bisphenols are a group of compounds characterized by two phenol groups and are frequently used as monomers in the production of polycarbonate plastics, epoxy resins, and in lacquers/paints, thermal paper, adhesives, and brake fluid. Bisphenol A (BPA) is the most widely used and well-studied compound in this group. It is a high production volume chemical and its widespread abundance in consumer products has resulted in high

exposure to humans and the environment (Chen et al. 2016). BPA is a known endocrine distributor, and evidence suggests BPA causes neurological, immune response, reproductive and developmental defects, particularly in children (Inadera 2015; Careghini et al. 2015). Therefore, gradual restrictions have been put in place over the last few decades to reduce the amount of BPA in consumer products. Production of analogs of BPA have resultingly increased to meet the demand for BPA-free products. However, research into the health effects of BPA analogs has discovered that the risk of adverse effects to humans and the environment may not be reduced. In the case of bisphenol AF and bisphenol B, studies have found higher estrogenic activity than BPA (Inadera 2015). Bisphenol S (BPS) has a similar structure to BPA and has been increasingly used in epoxy resins and thermal receipt paper. BPS tends to persist longer in the environment than BPA, and since the restriction of BPA its production has increased so much so that it is considered ubiquitous in some countries (Oui et al. 2019; Inadera 2015). Preliminary evidence shows BPS has similar neurotoxicity and immunotoxicity, similar or lower endocrine disruption, and lower acute toxicity, reproductive and developmental effects than BPA; yet with higher environmental persistence, BPS can be considered to pose a similar risk of BPA and is not a safer alternative (Qui et al. 2019).

2.3 CECs in Municipal Landfill Leachate

Municipal landfills have been recognized as a major source of CECs to the environment (Eggen et al. 2010; Masoner et al. 2014). The different source pathways for CECs entering landfills are depicted in Figure 2-2. The main pathway, labelled (1) in
Figure 2-2, represents municipal solid waste containing CECs or precursors that is buried directly into the landfill. Household waste can contain products that are directly hazardous to the environment (e.g., paints, batteries, pharmaceuticals); however, non-hazardous substances may also transform or degrade to harmful CEC compounds (Slack et al. 2005). The second pathway, labelled (2), represents industrial waste materials entering municipal landfills, which may have occurred at poorly regulated historic sites.

Another source of CECs to both the environment and landfills is through wastewater. Domestic wastewater contains a wide variety of CECs from human excretions, substances being washed down drains, and from coatings in pipes and other infrastructure. Persistent CECs, such as PFAS, are not removed at WWTPs (Schultz et al. 2006). PFOA concentrations have been shown to increase throughout treatment due to the breakdown of precursor compounds (Schultz et al. 2006). Therefore, the liquid effluent that is used for irrigation, discharged to surface water, or sometimes further treated to be pumped back to the consumer, will still contain elevated concentrations of CECs. CECs may also be present in the WWTP biosolids that are frequently disposed of at landfills (pathway (3) on Figure 2-2; Masoner et al. 2014). Municipal landfills with leachate containment systems often pump excess leachate to WWTPs (see pathway labelled (4) on Figure 2-2; Masoner et al. 2014; Allred et al. 2014; Hamid et al. 2018). This adds to the amount of CEC mass already at the WWTP, increasing the CEC volumes entering the environment, or returning to a landfill in WWTP biosolids.

Both in Ontario and worldwide, there are no regulations that mandate the testing of most CECs in landfill leachate. Considering that many CECs are toxic at trace levels,

and municipal landfill leachate frequently travels off-site and interacts with environmental receptors, the risk and environmental impact of CECs in municipal landfill leachate should not be underestimated. This has spurred collaboration between scientific researchers and landfill operators to investigate CECs in municipal landfill leachate (see Table 2-2 and reviews by Slack et al 2005; Ramakrishnan et al. 2015; Hamid et al. 2018; Qi et al. 2018). Most of the literature has focused on newer municipal landfills (<3 decades since closure), leaving a knowledge gap surrounding CEC concentration ranges expected in older historic sites.



Figure 2-2: Flow chart illustrating the CEC inputs and pathways between landfills and other components of the wastewater and environmental systems

Table 2-2. Past studies that measured some of the same contaminants of concern (CEC) as in this study in leachate or leachate-impacted groundwater from historic (\geq 3 decades since closure) and modern municipal landfills; LCS = leachate containment system

Study	No. historic /	Sample type	Country	CECs included	
	modern				
	landfills				
Holm et al. 1995	1/-	Wells in plume	Denmark	Pharmaceuticals	
Paxeus, 2000	1/2	LCS	Sweden	Bisphenols, substituted phenols, OPE	
Schwarzbauer et al. 2002	-/1	Seep under landfill	Germany	Pharmaceuticals, OPE, BPA	
Baun et al. 2004	4/6	Wells in landfill	Denmark	Substituted phenols	
Barnes et al. 2004	1 /-	Wells in plume	USA	Phenols, pharmaceuticals	
Buszka et al. 2009	1/-	Wells in plume	United States	Pharmaceuticals, OPE, phenols	
Busch et al. 2010	3/19	LCS	Germany	PFAS	
Eggen et al. 2010	0.5/2.5	Well in plume	Norway	Pharmaceuticals	
Huset et al. 2011	1/3	LCS	USA	PFAS	
Andrews et al.	1 /1	Wells in landfill (1) and	United	Pharmaceuticals, select	
2012		plume	States	OPE, phenols	
Benskin et al. 2012	-/2	LCS	Canada	PFAS	
Li et al. 2012	28	Leachate (type / age not stated)	Canada	PFAS	
Allred et al. 2014	-/6	Wells in landfill and leachate pond	USA	PFAS	
Masoner et al. 2014	-/19	LCS	USA	Pharmaceuticals, phenols, OPE	
Peng et al. 2014	-/2	Drinking wells downgradient	China	Pharmaceuticals, phenols	
Clarke et al. 2015	-/5	Leachate (type not stated)	USA	Select PFAS and pharmaceuticals	
Yan et al. 2015	-/5	LCS	China	PFAS	
Gallen et al. 2016	7/6	LCS and leachate pond	Australia	PFAS	
Masoner et al. 2016	4/18	Wells in plume	USA	Pharmaceuticals, BPA, OPE, substituted phenols	
Fuertes et al. 2017	-/4	LCS	Spain	PFAS	
Gallen et al. 2017	1/26	Leachate ponds, LCS and wells in landfill	Australia	PFAS	
Lang et al. 2017	-/18	LCS and wells in landfill	USA	PFAS	
Deng et al. 2018	-/1	LCS	China	OPE	
Cristale et al.	-/1	Leachate pond and wells	Brazil	OPE	
2019		in plume			
Harrad et al. 2019	-/40	LCS and wells in landfill	Ireland	PFAS	
Hepburn et al. 2019	7/-	Wells in landfill and plumes	Australia	PFAS	
Qi et al. 2019	-/6	LCS	China	OPE	

2.4 Artificial Sweeteners as Landfill Leachate Tracers

2.4.1 Traditional Tracers

For a substance to be considered a good tracer, it should have a low tendency to biodegrade, it should move conservatively in groundwater, its presence should be widespread and specific for the contaminant source it represents, and its concentrations in that source should be distinguishable from background environmental concentration levels. For landfill leachate, traditional tracers such as ammonium and chloride have been used because of their frequently elevated levels in landfill leachate (Kjeldsen et al. 2002). While leachate constituent concentrations typically decline as landfills age, ammonium is especially known to persist even in closed landfills for many decades to centuries (Christensen et al. 2001; Kjeldsen et al. 2002). For landfills < 25 years old, ammonium was reported at a range of 50-2200 mg-N/L in the review by Christensen et al. (2001), making it a useful tracer for both operating and closed landfills. Chloride concentrations can be elevated in the environment due to other sources such as road salt or wastewater, and ammonium may be elevated from degrading organic matter within stream sediments, fertilizers, or wastewater. This complicates the identification of landfill leachate plumes in both urban and rural environments through the analysis of only one tracer compound.

2.4.2 Artificial Sweeteners

Artificial sweeteners (AS) are a class of CEC that have been extensively used in consumer products; however, they have only been considered in the environment over the last couple of decades (Lange et al. 2012). Although they are generally considered safe to

humans and wildlife at typical environmental concentrations, Luo et al. (2019) suggest that sub-lethal and synergistic effects on organisms have not been adequately assessed. The four AS commonly analyzed are acesulfame, sucralose, saccharin, and cyclamate (for more information on chemical properties see Table 1 in Lange et al. 2012). Acesulfame and sucralose are persistent and tend not to biodegrade in WWTPs, making them effective tracers for wastewater (Buerge et al. 2009; Van Stempvoort et al. 2011; Lange et al. 2012). Conversely, saccharin and cyclamate concentrations are reduced in WWTP effluent (Buerge et al. 2009; Van Stempvoort et al. 2012).

Roy et al (2014) proposed the use of artificial sweeteners as tracers for landfill leachate, given their common detection in samples of leachate or leachate-impacted groundwater from 15 active and closed landfills across Canada. Sources of artificial sweeteners to municipal waste landfills include food and drink waste, oral personal care products (e.g., mouthwashes, toothpastes), pharmaceuticals, and biosolids from WWTPs. Roy et al (2014) found that acesulfame and sucralose, which were introduced to the Canadian market in the late 1980s, were detected in active and recently closed landfills; however, they found that only saccharin and cyclamate were detected at appreciable concentrations at the 7 older (i.e., pre-1990) landfills. Of these two sweeteners, saccharin was more dominant, with detection at 13 of the 15 total sites, in comparison to only 6 sites for cyclamate. Saccharin did not show any correlation to the age of the landfill, despite being de-listed as a food additive in the 1970s (Roy et al. 2014). Thus, for old landfills (pre-1990), the detection of saccharin alone or with only cyclamate indicates a sample impacted by leachate, whereas the additional presence of acesulfame and/or sucralose would indicate a conflicting source, likely from modern wastewater. This is important because wastewater contains many of the same CECs as landfill leachate, and sometimes ammonium and chloride, making the delineation of contaminant plumes difficult in urban or other multi-source environments. Saccharin does have other sources to the environment, including as a herbicide metabolite, an additive to pig feed, a nickel electroplating brightener, chemical intermediate, and anaerobic adhesive accelerator; however, these sources are not considered to be extensive especially in comparison to the use of saccharin as an AS (Roy et al. 2014).

2.5 Groundwater-Surface Water Interaction

Groundwater-surface water (GW-SW) interaction has become a growing area of research, linking what had often been considered two separate resources into one complex system. As groundwater discharges to a surface water body, whether that be a stream, lake, pond, or wetland, it can be either beneficial or harmful to water quality and ecosystem health. Groundwater discharge maintains base flow during the dry season and can provide ideal temperature and biogeochemical conditions for organisms living within the discharge zone, such as cooler temperatures for fish nesting habitat (Briggs et al. 2020). Conversely, when contaminants are being transported with discharging groundwater, it can cause adverse conditions for those same organisms and the overall water quality of the stream. The same can be said for surface water recharging the groundwater system; aquifers can be replenished, however if surface water contains contaminants they will be transported into the subsurface where they can be difficult to remove, possibly impacting drinking water or irrigation wells. Therefore, the importance of understanding and measuring GW-SW interactions cannot be underestimated.

In the simplest conceptual model, GW-SW interaction can either be discharging, where flow is from the groundwater system into the surface water body, or recharging, where flow is from the surface water into the subsurface. When the surface water body is a stream, this is known as a gaining or a losing stream, respectively. Figure 2-3 shows a simplistic diagram of a gaining stream receiving groundwater. Both these conditions can occur simultaneously, for example in flow-through streams where at one bank groundwater is discharging to the stream while at the other bank the stream is recharging the subsurface. A single stream can also have reaches of gaining, losing, and flow-through conditions. These reaches can vary across meters to centimeters (Conant 2004), adding a great deal of complexity to the basic conceptual model of GW-SW interaction.



Figure 2-3: Simplistic diagram of groundwater discharging to a stream, with different ecological and hydrogeological zones labelled.

Hyporheic zones, originally defined as areas underneath or adjacent to a stream that either contain a percentage of stream water or have been altered by the infiltration of stream water (White 1993), exist at many scales in flowing streams. Exact definition and delineation of hyporheic zones differ between disciplines; however, from a hydrogeology perspective hyporheic zones are taken to be localized zones of stream water recharge into the surrounding sediments, subsurface flow parallel to that of the stream, and then subsequent discharge from the sediments. Hyporheic flow is caused due to changes in streambed topography and morphology (Conant et al. 2019). Temporal changes in hyporheic exchange can occur on daily and seasonal scales, as well as during precipitation events (Malzone et al. 2016; Ren et al. 2019). It should be noted that this is different from bank storage, groundwater ridging, and overbank flooding, which are caused by transient changes between the height of the water table and the stream level. Bank storage occurs when surface water levels suddenly rise higher than surrounding water table levels, causing water to flow horizontally into the surrounding sediments until the stream levels have lowered and the gradient is reversed, releasing the water back into the stream (Conant et al. 2019). Conversely, groundwater ridging occurs in banks with a large capillary fringe where precipitation can cause sudden increases in water table height disproportionate to increases in stream level, resulting in bank discharge into the stream (Conant et al. 2019). Overbank flooding occurs when stream stage rises above the height of the banks causing stream water to spill onto the shores where it infiltrates and directly mixes with riparian groundwater (Ledford et al. 2016). Another distinctly different term, 'transition zone' defines the area underneath and adjacent to a surface water body where

GW-SW interactions take place and conditions change from groundwater dominant to surface water dominant (Conant et al. 2019). The GW-SW interface is taken to be the boundary between the streambed sediment and the open water column.

Conant (2004) mapped a 60 m stretch of stream in Ontario, Canada using multiple methods and found there to be five distinct types of GW-SW exchange occurring on the site. This indicates the amount of spatial variability possible in streams, and the requirement for spatially detailed data to adequately describe GW-SW interactions as needed in the context of the research question, or management objective at hand. Conant et al. (2019) developed a framework for the evaluation of GW-SW interactions which includes all fundamental processes and factors. This comprehensive guide considers biological, biogeochemical, and climatic processes along with flow processes to determine water quality, quantity, and ecosystem impacts. An important step in the framework, and in understanding the GW-SW interaction at a site, is to determine the magnitude and direction of groundwater flux across the interface. Both often change temporally and spatially, which complicates the accurate quantification of groundwater flux. Knowing the groundwater flux provides useful information about the system, including the contribution of groundwater to the surface water body (or conversely the contribution of surface water in recharging an aquifer). For water quality and ecosystem evaluations, groundwater fluxes coupled with information on contaminant concentrations can be used to determine mass fluxes of contaminants between the waters. An accurate estimation of groundwater flux is important in many disciplines, including contaminant hydrogeology, water resource management, ecotoxicology, and agriculture.

2.5.1 Methods of Measuring Groundwater Flux

Due to the complex and frequent changes in groundwater-surface water interactions, it is necessary that a method to estimate groundwater flux must be robust, fast, and affordable. Various methods have been developed that can estimate groundwater flux, each with their own sets of limitations, assumptions, and system requirements (see review by Kalbus et al. 2006).

Darcian approaches, based off of Darcy's Law (middle of Eq. 2.1), require the accurate measure of hydraulic conductivity (K) and hydraulic gradient (i) to determine groundwater flux (q, specific discharge). Traditionally, these values can be obtained

$$q = -K \ i = Q/A \tag{2.1}$$

using piezometers within or near a stream to quantify vertical gradient. Hydraulic conductivity can be estimated if soil properties are known or quantified in the field through various techniques (e.g., slug test, pump test). Piezometers provide accurate measurements of groundwater discharge or recharge, as long as hydraulic conductivity is accurately estimated. Piezometers can be difficult to install in some sediments, and crossconnection between the surface water and the screen must be avoided. Due to the difficulty of moving piezometers between locations, they tend to be used as longer-term measurement points.

Seepage meters can be used to directly measure groundwater discharge to a stream over a certain area (Lee and Cherry 1978). An open bottom cylinder, resembling the top of a barrel, is placed on the streambed capturing discharging groundwater in a bag connected to the top of the cylinder. Seepage meters allow for affordable flux measurements that can easily be taken at multiple locations. They do not require information on sediment properties, as they provide direct discharge (Q) measures over a known area (A) of the seepage meter (right side of Eq. 2.1). Seepage meters can be difficult to properly install, especially in cobbly or gravel sediments. In areas of low discharge, it can take a long time to fill the bag, and if installed for weeks-months the seepage meter can be covered in sediment or debris in a fast-flowing stream.

Stream gauging methods, such as chemical tracing methods where a known concentration of a tracer is added into the stream and then the concentration is measured downstream, provide estimates of groundwater discharge on the reach scale. Dilution of the tracer due to mixing with the stream is determined, and any further dilution is considered to be the result of input from groundwater discharge. This method assumes that the stream is gaining across its entire study length and that no other losses (e.g., evapotranspiration or adsorption of tracer) are occurring. Other mass balance methods, such as gauging stream discharge at two points along the stream with the difference representing water loss or gain, require that the change in flow be due to groundwater flux, not evapotranspiration, precipitation, overland flow or pipe inputs. Therefore, these methods are more accurate on smaller spatial and time scales and will not work for very large or non-flowing streams.

Temperature tracing methods to measure groundwater flux have been understood for many decades, and recent advances in modelling applications have made them accessible for many researchers investigating a wide range of groundwater systems. Temperature is an ideal tracer as it is ubiquitous, easy and cost-effective to measure

accurately, and does not require specific skills to measure. It can be used as a substitute for hydraulic head, often being easier to measure (Anderson 2005). It is a multidirectional method, as it can measure the direction of groundwater flux to differentiate between recharge and discharge. Temperature tracing methods can be applied in a variety of situations to measure groundwater flux, including across streambeds, across confining layers, for percolation in the vadose zone, fracture flow, and recharge to deep aquifers. The following will outline the main methods of using temperature to measure groundwater flux, along with their assumptions and limitations, particularly for streams under discharge conditions.

2.6 Heat as a Tracer

A great deal of advancement in the use of temperature to determine groundwater flux occurred due to pioneering work published in the 1960s (Suzuki 1960; Bredehoeft and Papadopulos, 1965; Stallman 1965). By this time, it was well established that differences in temperature exist between groundwater and surface water due to diurnal and seasonal fluctuations, and that these temperatures were influenced by the interaction between groundwater and surface water. Solutions that use temperature to solve for fluid flux are based on the one-dimensional heat transport equation (Suzuki 1960):

$$\frac{\lambda}{c\rho}\frac{\partial^2 T}{\partial z^2} - \frac{qc_w\rho_w}{c\rho} \left[\frac{\partial(T)}{\partial z}\right] = \frac{\partial T}{\partial t}$$
(2.2)

where λ is the bulk thermal conductivity, T is temperature, t is time, respectively ρ and ρ_w are the bulk and fluid density, respectively *c* and *c*_w are the bulk and fluid specific heat values, z is distance along the direction of flow assumed to be vertical, and q is the

specific discharge. Downward groundwater flow, or recharge, is taken to be positive and depth is positive and increases downwards. Equation 2.2 assumes that there is no horizontal groundwater or heat flow, i.e. only 1D vertical fluxes, homogeneous and isotropic fluid and media properties, incompressible fluid, and fully saturated media. It is assumed that local thermal equilibriums exist between all phases, meaning temperatures at the boundary between soil and fluid must be equal (Rau et al. 2014). The heat transport equation represents heat flow at a macroscopic scale, requiring a representative elementary volume that is large enough that thermal properties can be adequately volume averaged (Rau et al. 2014).

The form of Equation 2.2 is very similar to the solute transport equations used to describe solute transport in groundwater flow systems (Anderson 2005). Without the movement of groundwater, heat is transported through only conduction along thermal gradients, comparable to solute transport through diffusion along concentration gradients. When groundwater flow occurs, heat is also transported by advection, as represented in the second term in Equation 2.2. The first term represents heat transport through conduction, or conduction and thermal dispersion, depending on the variables used. The effective thermal conductivity λ_e , can be used instead of λ to factor in both thermal conduction and thermal dispersion through the thermal dispersivity term (α^*) (Eq. 2.3).

$$\kappa_e = \frac{\lambda_e}{c\rho} = \frac{\lambda}{c\rho} + \alpha^* |v| \tag{2.3}$$

The variable *v* is the groundwater velocity. The effective thermal conductivity divided by the bulk heat capacity is defined as the effective thermal diffusivity κ_e . The $\lambda/c\rho$ term is comparable to the diffusion coefficient in the solute transport equation (Anderson 2005).

There are differing opinions in the literature about the necessity of considering thermal dispersion in heat transport equations. Some authors assume thermal dispersion to be negligible in comparison to thermal conduction (Irvine et al. 2017; Keery et al. 2007), contrary to solute transport where dispersion often dominates over diffusion. Thermal conduction is generally greater than solute diffusion under the same groundwater flow conditions because heat conducts through both solids and fluids, whereas solute transport is limited to the pore spaces. In addition, the thermal advective front velocity is retarded by the thermal properties of the medium (Rau et al. 2012). Other authors have advocated for the use of thermal dispersion in heat tracing methods. Hatch et al. (2006) discusses how, although thermal dispersivity is more difficult to measure than thermal conductivity, studies that have measured thermal dispersivity show it can be comparable in magnitude to solute dispersivity and is also strongly scale dependent. In contrast, Rau et al. (2014) found thermal dispersivity to be orders of magnitude less and less scale dependent than solute dispersivity. Ignoring heat dispersion has shown to cause more error in streambed flux measurements when discharge is high, as can be understood simply from Equation 2.3 (Hatch et al. 2006). Rau et al. (2012) reviewed the use of thermal dispersion in detail and found that for most groundwater studies the value is negligible; however, groundwater flux across a streambed can be significantly larger than usual values and the effects of longitudinal dispersion may need to be considered.

The thermal Peclet number (β) is used to quantify the relative amount of advective heat flux to conductive heat flux (Kurylyk et al. 2019; Anderson 2005), as shown in Equation 2.4, where L is the characteristic length. This term is comparable to

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$$\beta = \frac{qc_w \rho_w L}{\lambda} \tag{2.4}$$

the Peclet number used in solute transport; however, since thermal conduction is greater than solute diffusion, thermal Peclet numbers differ orders of magnitude from solute Peclet numbers for the same groundwater flow conditions (Rau et al. 2012). It is generally accepted that when $\beta >1$ heat transport is dominated by thermal advection, and when $\beta <1$ there is a greater influence of conduction (Rau et al. 2014).

Various analytical and numerical solutions have been developed to solve Equation 2.2 to determine groundwater flux, all of which find their origins in either the Bredehoeft and Papadopulos (1965) steady-state temperature depth-method or the Stallman (1965) transient temperature-time method. The following sections describe the theory behind each of these pioneering papers and provides a brief review of some of the more recent advancements to these methods.

2.6.1 Temperature-Time Methods

Diurnal temperature variations are the daily heating and cooling which occurs at the Earth's surface. These daily fluctuations resemble a sine curve, with the amplitude representing the difference between the daily peak and daily average temperatures. The diurnal signal travels into the subsurface where it is quickly attenuated. This means the temperature-time sine curve at a depth beneath the surface will have a lower amplitude than at the surface. It will also take time for the peak temperature to reach a certain depth beneath the surface, so there is a delay in peak temperature experienced with depth compared to at the surface. This delay in peak temperature, known as the phase shift, and

the attenuation of the amplitude can be used to determine groundwater flux, as shown in the seminal work of Suzuki (1960) and Stallman (1965). The amount and rate of the amplitude attenuation and phase shift with depth into the subsurface depends on soil and fluid properties, as well as the movement of groundwater.

Suzuki (1960) first developed a mathematical solution to the heat transport equation (Eq. 2.2) using the daily fluctuations observed in irrigated rice paddies to quantify percolation rates in the fields. The solution included a sine curve as an upper boundary to account for the diurnal temperature signal. Stallman (1965) corrected and improved this solution, encouraging its applicability to various shallow systems. The method required that temperature be measured continuously at two depths to determine amplitude attenuation and phase shift, which through type curves can be used to determine groundwater velocities (Stallman 1965).

Over the past 60 years, these papers were fundamental in the development of more recent modeling advancements (e.g., Keery et al. 2007; Hatch et al. 2006; see reviews by Irvine et al. 2017; Rau et al. 2014). Various automated and semi-automated solutions have been developed to reduce the computational effort required of the user and facilitating the analysis of larger data sets. Two notable solutions were developed by Hatch et al. (2006) and Keery et al. (2007). Both studies developed solutions to the heat transport equation that use either the amplitude or phase shift between pairs of temperature sensors. All solutions can be used to determine the magnitude of groundwater flux; however, because phase shift is caused by both upward and downward groundwater movement, and the square root in the expression does not allow for

determination of sign, only the amplitude methods can be used to determine direction of groundwater flux (Hatch et al. 2006; Keery et al. 2007; Irvine et al. 2015). These solutions require the user to input system properties, such as the thermal conductivity, and their accuracy is limited by the accurate estimation of thermal properties (see section 2.6.3 below). The main difference between Hatch et al. (2006) and Keery et al. (2007) is that the former requires that the user provides an estimate of thermal dispersivity (i.e., α^* in Equation 2.3) whereas the latter assumes dispersivity to be zero. VFLUX2 (Vertical Fluid [Heat] Transport Solver 2; Gordon et al. 2012; Irvine et al. 2015) is a MATLAB based program that determines 1D vertical fluid flow using the solutions developed by Hatch et al. (2006) and Keery et al. (2007). The key assumptions for VFLUX2 are that the system has only 1D vertical groundwater and heat fluxes, homogeneous and isotropic fluid and media properties, and discernible sinusoidal temperature variations. The user is required to input temperature time series data for a minimum of two depths, along with the physical and thermal properties of the system.

The extinction depth is defined as the depth to which the diurnal signal can still be distinguished by the employed data logger; past this depth the signal is too attenuated to be measured (Briggs et al. 2014). In recharge areas, the diurnal heat signal is transported downwards through both conduction and advection and can reach 0.5 m depth; however, in discharge zones heat is only transported downwards through conduction, and the signal is often attenuated by 0.2 m (Briggs et al. 2014; Irvine et al. 2017). Diurnal temperature-time methods for solving for the groundwater flux require that temperature be measured over time at a minimum of two depths in order to compare the amplitude and phase shifts

between the two depths. By not using the actual depth and rather the spacing between sensors, the effects of streambed scour or sedimentation are reduced (Hatch et al. 2006). To reduce filtering edge effects, it is recommended that months of continuous data be used in the analysis as the first and last few days of the temperature data are not as accurate (Hatch et al. 2006).

2.6.2 Temperature-Depth Methods

A steady-state solution, published by Bredehoeft and Papadopulos (1965), became the foundation for using temperature-depth profiles to determine groundwater flux. The right-side storage term in Equation 2.2 is taken to be zero, representing heat transport for a steady-state thermal regime; it should be noted that steady-state refers to the change in temperature with time and that the groundwater regime is considered to be constant throughout all solutions (Kurylyk et al. 2019). An important requirement for this solution, which stems from the steady state assumption, is that at the depths analyzed the system must not be affected by diurnal temperature fluctuations. As mentioned above, this typically occurs by a depth of 0.2 m in streams with groundwater discharge (Briggs et al. 2014). Bredehoeft and Papadopulos (1965) produced a series of type curves to determine values of β , which can be used to calculate q (Equation 2.4). The authors show that linear temperature-depth profiles represent conduction only conditions, convex upwards represents discharge, and concave upwards represents recharge. The greater the amount of groundwater flow, the greater the curvature of the profile and the assigned absolute value of β . Recharge is given a positive value of β and discharge is negative.

Since the foundational work in the 1960s, there has been a great deal of advancement in the use of temperature-depth profiles. Many numerical and analytical models have been developed to solve for groundwater and thermal transport equations, which have unique initial and boundary conditions and sets of assumptions that differ from the original Bredehoeft and Papadopulos (1965) solution, but allow for this theory to be applied to a variety of scenarios (for a thorough review of other applications see reviews by Kurylyk et al. 2019; Anderson 2005). An analytical solution and spreadsheet tool were presented by Kurylyk et al. (2017) to solve for vertical fluid flux. The authors adapted a solution by Shan and Bodvarsson (2004), which used heat methods to quantify percolation in the vadose zone. A key advancement offered by these solutions is the ability to factor in horizontal heterogeneous layers, whereas previous work had assumed homogenous soil properties. Consequently, it is a requirement that the thermal properties for each layer, specifically the thermal conductivity, and the depth of each layer must be known. As different assumptions are made, equations for the analytical solution become more complex, but also more diverse in that systems that previously did not fit the simplistic assumptions can now be accurately analyzed. The use of these more complex solutions is facilitated by graphical user interfaces that provide easy-to-use setups for researchers to apply the solution to their data. Kurylyk et al. (2017) provide a free access spreadsheet program, FLUX-LM (FLUX in Layered Media) with their paper that allows for groundwater flux to be calculated in a system with 1-4 layers. The only requirements of the user are the temperature- depth data, and the thermal properties and depths of the layers. The analytical model works by plotting the given temperature-depth profile and

matching a calculated profile by adjusting values of q to minimize the root mean squared error between the given and calculated profiles (Kurylyk et al. 2017). This method can distinguish between recharge and discharge, however, usually requires \geq 5 steady state data points for an accurate estimate of q (Kurylyk et al. 2019). Therefore, attention should be placed on ensuring enough data is collected beneath the extinction depth where there is little influence of the diurnal signal. This is more easily achieved in the winter months when the diurnal signal is weaker and ice cover may reduce the signal even further (Kurylyk et al. 2019).

2.6.3 Limitations of Temperature Methods

Many of the partial differential equations used to describe heat flux assume only 1D vertical flow. Conductive heat flow in the subsurface is primarily vertical, due to geothermal and surface temperature fluxes (Kurylyk et al. 2017). This can be violated in some environments, for example where there are adjacent areas of different land cover or steep elevation changes causing stronger horizontal temperature gradients. In environments with horizontal groundwater flow, there could also be an advective component to the horizontal heat flux. This can cause error in both temperature-time and temperature-depth methods for estimating q. There has been debate over how much horizontal groundwater flow would make the analytical solutions invalid; studies have reported that solutions are invalid when the ratio of horizontal to vertical flow is over 10% (Lu and Ge 1996), whereas others have said that 1D solutions are valid when horizontal flow is up to 1000% vertical flow (Irvine et al. 2016). At these high horizontal flow locations, there are solutions that account for horizontal flow in temperature-depth analyses by adding a sink/source term which includes the horizontal groundwater flux and the horizontal thermal gradient (Lu and Ge 1996). For most streambed analyses, the horizontal heat fluxes are negligible, except for strong hyporheic flow areas.

For all solutions, the thermal properties of the media and the fluids, such as heat capacities or thermal conductivities, need to be measured or estimated. Irvine et al. (2015) and Fitzgerald et al. (2015) provide a table of common ranges of values for thermal properties. Typical values for various sediment types are reported in the literature, and therefore if not measured directly, can be estimated if the soil type is known. Some models are also able to fit thermal parameters and test for how accurate they are (see Luce et al. 2013). Uncertainty in groundwater fluxes due to errors in estimating thermal properties are greater for systems that are conduction dominant (Rau et al. 2014).

Hydraulic conductivity, which is needed to determine q when using the piezometer method (Eq. 2.1), can vary on many more orders of magnitude than bulk thermal conductivity, which is better constrained between different soil textures (Rau et al. 2014). Therefore, the potential for errors in estimation of thermal conductivity are generally smaller than for hydraulic conductivity. There needs to be significant difference between layers for a heterogeneous temperature model to be required, so in many cases the homogeneous assumption is valid (Kurylyk et al. 2017). Rau et al. (2014) discussed the range and factors that affect thermal conductivity and further investigates the effects of heterogeneity and averaging thermal properties on the calculation of groundwater flux.

Chapter 3: Organic contaminants of emerging concern in leachate of historic municipal landfills

Propp, V.R., A.O. De Silva, C. Spencer, S. Brown, S. Catingan, J.E. Smith, J.W. Roy. Organic contaminants of emerging concern in leachate of historic municipal landfills. Environmental Pollution (in press)

3.1 Introduction

Municipal solid waste (MSW) landfills are a known source of groundwater contamination, with leachate-impacted plumes that may extend > 1 km (Christensen et al. 2001). Such contaminated groundwater can affect drinking or irrigation water wells, sublevel dwellings via vapour intrusion, surface waters receiving groundwater discharge, and possibly terrestrial phreatophytes. Leachate or leachate-affected groundwater captured by on-site engineered collection systems is commonly sent to wastewater treatment plants (WWTPs) and may have higher concentrations of some compounds than typical WWTP influent (e.g., Masoner et al. 2020). Those leachate chemicals that are not adequately removed by WWTPs may then pose a risk to surface waters receiving the treated effluent.

Over the past two decades, various new contaminants of emerging concern (CECs) have been detected in MSW landfill leachate (see reviews by Slack et al. 2005; Ramakrishnan et al. 2015; Qi et al. 2018; Hamid et al. 2018). Many of these CECs are xenobiotic organic compounds, including per- and polyfluoroalkyl substances (PFAS), organophosphate esters (OPE), bisphenols, and various pharmaceuticals, and are typically present in trace concentrations in the environment. Currently, landfill operators are generally not required to monitor for these CECs. Scientific investigations have mostly

addressed CECs in large, modern, operational (active) or recently-closed landfills (e.g., Busch et al. 2010; Eggen et al. 2010; Regnery et al. 2011; Masoner et al. 2014; Lang et al. 2017). There are much fewer data on CECs in leachate of old, closed landfills, especially those closed ≥ 3 decades (termed here "historic"). Available data for historic landfills are often for a single landfill and/or limited numbers of CECs (Table A-1; Appendix A1), or are lumped in with that for modern landfills (e.g., Busch et al. 2010, Gallen et al. 2017). Leachate composition with respect to CECs may differ for historic landfills compared to modern ones due to less restrictive disposal practices and changing CEC abundance in wastes. For example, the PFAS chemicals perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) were introduced in the 1950s, but their use has been phased out or restricted in many countries over the past two decades (Buck et al. 2011). In addition, waste in historic landfills will have experienced greater time for degradation of CECs and any precursor compounds, and for removal processes such as vapour stripping of volatiles and leaching of soluble compounds (perhaps commonly exacerbated by thin or poorly maintained surface covers).

The objective of this study is to assess whether various organic CECs may be present in leachate-impacted groundwater from closed historic MSW landfills at concentrations that may pose an environmental risk. There is a special focus on PFAS (the so-called "forever chemicals") because of heightened global concern associated with their extreme environmental persistence and the current health concerns around these compounds (Sunderland et al. 2019), and given the rising frequency of detections above drinking water advisory concentrations (Hu et al. 2016). The other CECs targeted in this

study included OPE (24 congeners corresponding to flame retardants and plasticizers), artificial sweeteners (ASs), pharmaceuticals, bisphenols, sulfamic acid, and substituted phenols, for a total of 81 CEC analytes. These substances were prioritized based on detections in previous landfill studies (Table A-1; Appendix A1), perceived potential presence in landfill materials (Table A-2; Appendix A2) and the availability of analyses at Environment and Climate Change Canada (ECCC) laboratories. More than 100 additional more-commonly measured chemical parameters were also analyzed.

Multiple samples of leachate-impacted groundwater were taken at each of 20 historic MSW landfills from across Ontario, Canada, which had a range of operational ages from the 1920s-1990s (Table 3-1). The aim was to target highly leachate-impacted water using the sample methods available at each site (i.e., wells, seeps, surface water discharge areas, leachate containment systems, culvert; full details below), while also capturing some of the spatial and temporal (i.e., near-source vs. far-plume) variation in leachate composition expected within a site (Thomsen et al. 2012; Milosevic et al. 2012). The findings of this study will provide guidance to landfill owners and regulatory authorities on monitoring of CECs in closed historic landfills.

3.2 Methods

Between two and five samples of leachate-impacted groundwater were collected at each of 20 closed landfills (Table 3-1) from May-December 2018, totaling 48 samples. Due to confidentiality, exact locations are not provided and sites are therefore designated by code. Groundwater sample types included i) pre-existing monitoring wells (both

within and outside the landfill area), ii) leachate containment systems, iii) groundwater discharge zones along streams, lakeshores, or ponds, iv) flowing surface seeps, and v) one metal culvert passing under the landfill (site NW; likely corroded).

Most wells were sampled alongside the landfill operators' consultants during their annual sampling events, commonly using dedicated inertial pumps, although peristaltic pumps and bailers were used at some sites. Standard sampling procedure included purging three well volumes, although for wells with slow recovery or free product, only one well volume was purged. The leachate containment system was sampled from a maintenance hole that intersected the collection pipes on site. These samples, along with those of the seeps and culvert, were collected with a peristaltic pump. For discharge zones, drive point sampling (Roy and Bickerton 2010) targeted areas where the leachateimpacted groundwater plume discharged to a nearby surface water body (stream, lake, or pond), at depths of 20 to 70 cm beneath the surface water sediment interface. New or dedicated polyethylene tubing was used for all sampling. The Supporting Information provides complete details of sample collection, handling, preservation and storage (Appendix A3).

All chemical analyses were performed by one of four ECCC laboratories. Artificial sweeteners (acesulfame, saccharin, cyclamate, and sucralose) were run in a suite with perchlorate, sulfamic acid and various pesticides (not of interest in this study) by Ion Chromatography coupled to a tandem mass spectrometer with an electrospray ionization source in negative mode (IC/ESI/MS/MS). Complete instrument details can be found in Van Stempvoort et al. (2020) along with the compound specific parameters for

acesulfame, sucralose and perchlorate. Minimum detection limits (mdl) for these were 2, 20, and 1 ng/L, respectively. The multiple reaction monitoring details and compound specific parameters for sulfamic acid, cyclamate and saccharin are reported in Van Stempvoort et al. (2019). The mdl for these three compounds were 25, 3, and 2 ng/L, respectively. Practical quantification limits were at 3 times the mdl.

The PFAS analysis comprised 17 compounds (Table A-4; Appendix A4) and involved extraction from aqueous matrices using weak-anion exchange (WAX) solid phase extraction (SPE) (MacInnis et al. 2019). Final extracts were analysed by ultra high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS, Waters Acquity UHPLC and Waters Acquity TQS MS/MS). All mass spectrometry parameters including cone voltage and collision energies for precursor to product ion transitions were optimized using authentic standards and are available in previous publications (MacInnis et al. 2019). Similarly, the OPE analysis comprised 24 compounds (Table A-5; Appendix A4) and also involved extraction using SPE and UHPLC-MS/MS instrumental analysis (Waters Acquity UHPLC and Xevo TQS mass spectrometer), as reported by Sun et al. (2020). The minimum detection limits for both sets of compounds varied based on extraction volumes used for each sample, but were < 1.4 and < 14 ng/L for PFAS and OPE compounds, respectively (with information per compound provided in Appendix A5).

Analyses of chemical suites for 1) bisphenols and others, 2) substituted phenols, and 3) pharmaceuticals, were performed by electrospray ionization liquid chromatography tandem mass spectrometry (ESI-LC/MS/MS), high resolution gas

chromatography / low resolution mass spectrometry, and ESI-LC/MS/MS, respectively, in ECCC National Labs using standard methods. The mdl for bisphenol compounds ranged from 5.2-12 ng/L. For the substituted phenols the mdl were much higher, ranging from 100-5000 ng/L. Finally, the pharmaceuticals had a range of mdl from 0.16-35 ng/L. Appendix A5 provides further details of the six sets of CEC analyses introduced above, as well as their quality control measures and results, in addition to information on the analyses of ammonium, soluble reactive phosphorus, alkalinity, metals and major cations, anions, volatile organic compounds, and dissolved organic/inorganic carbon. Table 3-1. Details of the 20 municipal landfill sites investigated and the 48 leachateimpacted groundwater samples collected from them. Order of samples (roughly by median age of landfill) here matches the order in Figures 1-3, S1-2 (Appendices A6 and A8).

Landfill Code	Active Period	Landfill Area (ha)	Current Land-Use	Sample Type	Sample #'s
SKP	1920s	0.6	Recreation	Streambed	1,2
SMP	1928-1951	1.6	Recreation	Streambed	1,2
G4	1935-1958	11	Recreation	Well	1,2
BBC	1947-1956	12	Commercial/ Woodland	Streambed	1,2,3,4
OR	1943-1967	10.8	Recreation	Well	1,2
				Lakeshore	3,4
DC-A	1960-1961	0.9	Open Field	Streambed	1,2
DC-B	1961-1962	1.1	Recreation	Streambed	1,2
DC-C	1962-1963	3.2	Open Field	Streambed	1,2
G6	1958-1963	6.1	Recreation	Well	1,2
G9	1960-1962	6.1	Recreation	Well	1,2
ZW	1950s-1971	14	Recreation	Well	1,2
OV	1950s-1970s	2.7	Recreation	Streambed	1,2
				Well	3,4,5
CF	1940s-1982	3	Open Field	Well	1
				Seep	2,3
KBP	1952-1974	44	Recreation	LCS ^ξ	1,2
BBP	1957-1972	6.5	Recreation	Well	1,2
OG	1972-1976	0.3	Open Field	Well	1
				Seep	2
HB	1970-1986	10.12	Open Field	Well	1,2
				Pond edge	3
NW	1968-1993	1.5	Open Field	Well	1
				Culvert	2
SCU	1972-1990	7.2	Waste Transfer Station	Well	1,2
MR	1981-1993	4.1	Waste Transfer Station	Well	1
			Woodland	Seep	2

^ELCS refers to leachate containment system

3.3 Results and Discussion

Concentrations for the four most dominant groups of CECs (ASs, PFAS, OPE, and bisphenols) in this study of 20 historic landfill sites, with relatively high concentrations and detection frequencies, are shown in Figure 3-1. Complete results for all the analytes are provided in the Supporting Information (Appendix A10). For any of these 48 leachate-impacted groundwater samples, reasons for a low concentration may include that the contaminant i) was not originally present, ii) was removed from the landfill via volatilization or transport in leachate, iii) underwent biological or chemical transformation within the landfill or plume, or iv) was substantially diluted by groundwater. For this data set, it is important to realize that all of the samples, regardless of type (i.e., wells, seeps, leachate containment system (LCS), culvert, discharge areas; Table 3-1) or proximity to the landfill, likely represent leachate diluted to an unknown degree by mixing with surrounding groundwater. This means that the maximum concentration for leachate within the waste of a given landfill is likely higher than reported here, though leachate composition itself may be quite variable throughout the landfill. This means that strict comparisons of concentrations between any two samples may not be meaningful, although relative chemical composition would not be affected. However, not all variation in the concentration data is attributable to dilution. If a sample has an elevated concentration of any of the CECs (assuming these have no natural or common conflicting sources) then this would suggest that very low concentrations found for other CECs do not simply reflect dilution. The only sites with no samples having any CEC group at concentrations greater than the first quartile of its data set (Figure 3-1) are

the four oldest (SKP, SMP, G4, BBC; closed ~ 60-90 years) and OV (closed >40 years). All of these, with the exception of BBC, also have relatively low concentrations of ammonium (Figure A-1, with further interpretation, Appendix A6). Ammonium is a common tracer of modern and historic MSW landfill leachate, being typically detected at elevated concentrations and known to persist even in closed landfills for many decades to centuries (Christensen et al. 2001). Thus, a substantial impact from dilution on samples from those oldest sites cannot be dismissed, while the impact appears more moderate for the remaining samples, meaning relative patterns across the majority of sites may still be assessed with care. Considering the points raised above, a broader scale view is recommended for assessing this data set, with a focus on i) the CEC maximum concentrations across the 48 samples, as these set the lower threshold for what concentrations might occur at other historic landfills and provide a means of comparison to modern landfill leachate, and ii) the frequencies of relatively high or low CEC concentrations and their potential association with time elapsed since the landfill was operational (i.e., age of landfill).

3.3.1 Artificial Sweeteners (ASs)

Artificial sweeteners are generally considered safe to humans and wildlife at typical environmental concentrations (Lange et al. 2012; Luo et al. 2019), although Luo et al. (2019) suggest that sub-lethal and synergistic effects on organisms have not been adequately assessed. Their sources to MSW landfills include food waste, oral personal care products, pharmaceuticals, and biosolids from WWTPs. Saccharin was the dominant

AS across the 20 historic landfills (Figure 3-1A), with detection in 94% of the samples and a maximum concentration of 50.7 μ g/L. Two landfills operating in the 1960s, DC-A and G6, had saccharin > 20 μ g/L in one streambed and one well sample, respectively, while many others that have been closed for 30-60 years also had highly elevated saccharin concentrations (> 10 μ g/L). Meanwhile, cyclamate was detected in 48% of samples, with a maximum concentration of 16.6 μ g/L. These values are generally similar to those reported by Roy et al. (2014) for both active and closed landfills (15 total) across Canada. Together, they illustrate the common presence and long-term persistence of saccharin, and to a lesser degree cyclamate, in historic MSW landfills. This is fitting with the general reports of reduced biodegradation of saccharin, but less so for cyclamate, under low dissolved oxygen (DO) conditions (see review by Pang et al. 2020); noting that DO < 1 mg/L for the majority of these leachate-affected groundwater samples.

The ASs acesulfame and sucralose were largely absent in the historic landfills (Figure 3-1A), as was found by Roy et al. (2014) for the seven older (i.e., pre-1990) landfills in their study (one landfill was in both studies). This was expected given that acesulfame and sucralose were introduced to the Canadian market in the late 1980s. Thus, for those landfills closed before 1990, the detection of saccharin alone or with only cyclamate indicates a sample impacted by leachate, whereas the additional presence of acesulfame and/or sucralose would indicate a conflicting source, likely from modern wastewater. This is important because wastewater may contain many of the CECs assessed in this study. The AS data here (Figure 3-1A) suggest that the majority of the samples are predominantly influenced by old landfill leachate, with a few possible

exceptions. One landfill, MR, had notable concentrations of acesulfame in both samples (Figure 3-1A), but given its operation until 1993 and its remote location away from any town or housing development, these likely reflect acesulfame sourced from the landfill rather than nearby wastewater sources. The lack of saccharin (and cyclamate) in the one MR sample, a seep into a nearly dried up creek, may reflect degradation of these compounds (both are known to degrade substantially, > 90%, in aerobic wastewater treatment (Lange et al. 2012) and soils (Buerge et al. 2011)) in the more aerobic "puddle" receiving the groundwater discharge. Dissolved oxygen of this sample was approximately 4 mg/L, whereas the majority of the remaining samples were measured at < 1 mg/L. A few other samples (OV-2-5, OR-3, G4-1-2), had relatively low but detectable concentrations of acesulfame ($<0.3 \mu g/L$) and sucralose ($<0.7 \mu g/L$) despite being closed before 1990 (Table 3-1). These samples are likely influenced by modern wastewater sources, such as septic systems or leaky sewers or portable toilets, or by irrigation water containing these ASs. For example, a portable toilet was observed near the G4-2 well and all three sites are now repurposed sports fields with scheduled watering. The identified OV and G4 samples had relatively low saccharin concentrations compared to 9.2 µg/L for OR-3, so CEC results for these samples may not reflect the landfill leachate.



Figure 3-1. Stacked bar plots of concentrations of the most dominant CECs by group: A) ASs, B) PFAS, C) OPE, and D) bisphenols, for the 48 historic landfill leachate-impacted groundwater samples (ordered by approximate age, according to Table 3-1). Note the y-axis break in scale in A and B. Separate, larger graphs with colour-pattern markings are provided in Appendix A7.

3.3.2 Per- and Poly-Fluoroalkyl Substances (PFAS)

PFAS can occur in many products found within a MSW landfill, including cleaning products, dental floss, cosmetics, non-stick cookware, carpet, upholstery, and water- and stain- proof fabrics and paper, etc., as well as in WWTP biosolids (Hamid et al. 2018). While there are thousands of PFAS chemicals, perfluoroalkyl acids (PFAA), which includes both perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA), have been the main focus of most work on PFAS in landfill leachate (Hamid et al. 2018). These so-called "forever chemicals" are purportedly extremely difficult to degrade, although a recent study reporting in-lab PFOS and PFOA biodegradation by anaerobic oxidation of ammonium under iron-reducing conditions (Huang and Jaffé 2019), suggests it might be possible in landfill settings. The PFAS in landfills may also be flushed out with leachate or the lighter compounds volatilized over time. All but one (FOSA, perfluorooctane sulfonamide, a PFSA pre-cursor) of the 17 PFAS compounds analyzed in this study are PFAA, with fluorinated carbon chains between 4 and 12; i.e., C4 to C12. Many of these PFAA are the most commonly used and reported (e.g., PFOS, PFOA). Of the 17 PFAS measured, only 10 were detected at a concentration $> 0.2 \mu g/L$ and are included in Figure 3-1B. The maximum individual PFAS concentration was for PFECHS (perfluoroethylcyclohexanesulfonate), at 9.5 µg/L, while PFOS and PFOA reached 2.7 and 0.85 µg/L, respectively. The three landfills with markedly higher concentrations of PFAS, specifically PFSA, than the other sampling areas (i.e., DC-A, DC-B, DC-C; maximum Σ_{17} PFAS of 2.4 – 12.7 µg/L; Figure 3-1B) were all within the same city, with disposal limited to the early 1960s. It is possible that

waste from a local industry that used PFSA and/or their precursor compounds made it into these landfills. These specific PFAS congeners comprised of PFOS,

perfluorobutanesulfonate (PFBS), and perfluorohexanesulfonate (PFHxS), are associated with aqueous film forming foam (AFFF) used to extinguish fuel-based fires, which are typically elevated near airports and military bases (Anderson et al. 2016 and references therein). However, the other major contributor here, PFECHS, apparently has, based on limited information, a narrow range of application limited to aircraft hydraulic fluid (De Silva et al. 2011). Thus, the region pertaining to landfills DC-A, DC-B, and DC-C may suggest the relevance of a particular niche usage. There were another five sites with Σ_{17} PFAS > 1.0 µg/L – BBP, HB, NW, SCU and MR, and these had landfills operating through the 1970s-1990s predominantly (Table 3-1). Based on the congener pattern here, these sites appear to have received greater inputs of PFCA and/or their precursors, such as fluorotelomer compounds (Allred et al. 2014; Lang et al. 2017), than PFSA.

In contrast, the four sites with Σ_{17} PFAS concentrations < 0.1 µg/L were associated with landfills that closed prior to 1960, which was before the start of widespread use of PFAS in industry and consumer products in Canada. These might also be highly diluted samples as discussed with the ASs above. The low-level PFAS concentrations in those samples may simply reflect inputs of recharge water, given that PFAS are ubiquitously detected in precipitation and surface waters (Gewurtz et al. 2019), the latter of which may be used to irrigate recreational lands.

Of note, Björnsdotter et al. (2019) recently found high concentrations of ultrashort-chain PFAA (C1 to C3) in the environment, with trifluoroacetic acid seemingly

associated with landfills and at higher concentrations than PFOA and PFOS. Thus, actual total PFAS concentrations may be substantially higher than assessed here as Σ_{17} PFAS. Still, the results of this survey suggest that historic landfills from the 1960s onward may continue to be long-term sources of elevated PFAS concentrations to surrounding groundwater, despite experiencing 30-60 years of leaching, volatilization, and potential degradation.

Of the past landfill studies investigating PFAS, only Hepburn et al. (2019a) have focused exclusively on historic landfills, targeting groundwater around seven landfills operating from the 1930s-1990s within an industrial area of Melbourne, Australia. Their reported maximum individual PFAS concentrations are typically 5-10 times lower than was found for the 20 Ontario sites (Table 3-2), while their ammonium maximum (106 mg/L) is only two times lower (Figure A-1, Appendix A6). Concentrations for many PFAS found in this study were more similar for those historic landfills included in the broader studies of Huset et al. (2011) and Gallen et al. (2016), with some noted variation (perfluorobutanoic acid (PFBA) lower; perfluorononanoic acid (PFNA), PFHxS, PFOS all higher; Table 3-2). This highlights the importance of this study in sampling a larger range of historic landfills to better determine the maximum PFAS concentrations that may be possible. The maximum PFAS concentrations from this study were of a similar order of magnitude as those found in active and recently closed (< 3 decades) landfill sites (Table 3-2), as summarized in a recent review by Hamid et al. (2018), aside from much higher concentrations for many PFAS in landfills in China (Yan et al. 2015). Recall that maximum concentrations for the historic landfills might be underestimated somewhat
due to dilution with groundwater; however, mixing of leachate from different parts or cells of modern landfills may also reduce the average concentrations below their maximums. Higher concentrations in the leachate-impacted groundwater samples from the historic landfills of this study compared to the literature for modern landfills were found for compounds PFNA, perfluoroundecanoic acid (PFUnDA) (by an order of magnitude), and PFHxS (Table 3-2), which will be discussed further below. Of note, PFECHS had not been analyzed in any of these past studies, yet it had a high maximum concentration (Table 3-2) and was detected in all samples in this study (though only five landfills at > 0.01 μ g/L). Thus, it may be an important compound that has been missed in measures of PFAS emissions from historic, and possibly, modern landfills.

Comparisons of total PFAS concentrations between studies is complicated by the different numbers and/or types of individual PFAS compounds measured. However, most of the past studies include 8 or more compounds of the most common PFAA, which generally coincides with those with the higher concentrations found here (Table 3-2), but for PFECHS. Lang et al. (2017) stated that total PFAS of 2-30 μ g/L is common in leachate from new (< 25 years) active landfills, while in their review, Hamid et al. (2018) posit total PFAA may reach a few μ g/L in landfills 2-4 decades old. Nearly half of the post-1960 historic Ontario landfill sites had comparable total PFAS concentrations (Table 3-2). This comparison further highlights the long persistence of PFAS within landfills and the potential importance of historic landfills as long-term PFAS sources.

The most notable sites contaminated by PFAS are those with past use of AFFF for fire-fighting (e.g., airports, military bases, fire-training areas). Maximum groundwater

concentrations of PFOS, PFOA, and other C4-C8 PFAS have typically been 10s-100s $\mu g/L$ (e.g., Moody et al. 2003, Anderson et al. 2016, Banzhaf et al. 2017) but for PFOS reaching 2910 $\mu g/L$ at a fire-fighting training area in Sweden (Wennberg and Fridlund 2015; reported in Banzhaf et al. 2017) and 4300 $\mu g/L$ at a U.S. military base (AFFF-impacted but not firefighting training area; Anderson et al. 2016). These are notably higher than concentrations in samples from the 20 historic Ontario landfills, with maximum concentrations for the more prominent individual PFAS in the range of 1-10 $\mu g/L$ (Table 3-2), with other PFAS an order of magnitude or more less than that (Figure 3-1B). Thus, AFFF-sites will tend to pose a more severe risk of PFAS contamination to groundwater supplies and nearby surface waters than do historic landfills. However, the latter are undoubtedly more ubiquitous.

Landfill leachate from MSW sources tend to be dominated by short-chained (C4-C7) PFCA, rather than PFSA or longer-chained PFCA (Hamid et al. 2018), likely a result of their higher aqueous solubilities (Yan et al. 2015). However, due to the extensive use of PFOA and its perfluorooctyl-based precursor substances, PFOA is frequently detected at elevated concentrations as well (Hamid et al. 2018). This is consistent with the elevated C4-C8 PFCA in historic Ontario landfill samples (purple-dark blues; Figure 3-2). However, several sites (OG, ZW and DC-A, -B, -C) and some samples within a site (G6, OR, KBP) had higher percentage PFSA than PFCA. This contrasting composition may reflect inputs associated with local industries, given the more lax waste screening during the 1960s-1970s when these landfills were open. These results also highlight the substantial variation in PFAS composition that can occur within and between historic landfills. Hamid et al. (2018) also noted in their literature review that the PFSA in landfill leachates tend to be dominated by the shorter-chained PFBS and PFHxS, even for vintages pre-1993. However, this was not as widely observed here, with PFOS being one of the most ubiquitous PFAS, which may reflect its more common use 40-70 years ago. Finally, older sites tended to have a higher proportion of longer-chained compounds, particularly perfluorodecanoic acid (PFDA) and PFUnDA, than younger sites. Considering the lower PFAS concentrations at these sites (Figure 3-1B), this likely reflects the major source being atmospheric deposition of PFAS as opposed to landfillderived PFAS. It may also be that the shorter-chain PFAS have been preferentially leached out of the landfill due to their higher solubilities (see review of Hamid et al. 2018).

Given the typical dominance of PFOA relative to PFSA in MSW landfill leachate, Hepburn et al. (2019b) proposed using the ratio of PFOA/ΣPFAS concentrations as a diagnostic tool to differentiate MSW landfill leachate (ratio of 0.25-0.45) from groundwater impacted by mixed waste (municipal with some of construction, demolition and/or general industrial waste; 0.08-0.24), AFFF (0.03-0.16), manufacturing (0.42-0.65), and recycled wastewater (0.09-0.10). In applying the PFOA/ΣPFAS ratio to the historic Ontario landfills of this study (Figure 3-3), three of the fourteen congeners comprising ΣPFAS (perfluoropentanesulfonate, perfluoroheptanesulfonate, precursor 6:2 fluorotelomer sulfonate) were not analyzed; therefore, the ratio may be overestimated. Only 11 of the 39 post-1960 landfill samples (from 8 of 16 landfills) fall within the suggested MSW landfill leachate range, while 20 samples (from 13 landfills) fall within

the lower mixed waste range with many overlapping the AFFF-affected site range. A further five samples had a ratio < 0.08, while two samples (OV site) had ratios of 0.47 and 0.61, which fall in the manufacturing range. Only the sample with the 0.47 ratio might reasonably fall within the MSW range with the three missing PFAS congener concentrations added. This very broad range in the PFOA/ Σ PFAS ratio likely reflects the less stringent disposal practices of past decades, resulting in a mix of waste types, including household and industrial materials. Thus, it appears that this ratio cannot readily distinguish leachate of historic MSW landfills from other sources.



Figure 3-2. Stacked bar plots of relative composition (%, mass basis) of the 17 PFAS compounds measured in the 48 samples of leachate-impacted groundwater collected from 20 historic landfills in Ontario (ordered according to Table 3-1).



Figure 3-3. The ratio of concentrations of PFOA to the sum of 11 PFAS compounds (to match Hepburn et al. (2019b)) measured for the 48 samples of leachate-impacted groundwater from the 20 historic landfills in Ontario (ordered according to Table 3-1; SKP, SMP, G4, BBC are pre-1960). The range of ratios associated with MSW landfill leachate (0.25-0.45) and mixed waste (0.08-0.24) proposed by Hepburn et al. are shown in hatched grey and flat grey, respectively.

Table 3-2: Maximum PFAS compound concentrations (μ g/L) in leachate or leachateaffected groundwater from studies including historic landfills (closed \geq 3 decades), and the range of maximum concentrations from studies largely focused on modern (active and closed < 3 decades) landfills in the review by Hamid et al. (2018), but for Bossi et al. (2007). Data for modern landfills typically represent samples from leachate collection systems. Full names of PFAS provided in Table A-4 (Appendix A4).

		Modern				
	This study	Huset et al. 2011	Gallen et al. 2016	Hepburn et al. 2019a	Studies in Hamid et al. 2018 review	
Landfill Operations	(1920s- 1990s)	(1982-1993)	(1964-1995)	(1930s-1990s)	(most 1980s-current)	
Country	Canada	USA	Australia	Australia	Global	
Landfills ^ξ	20	1	6	7		
Samples ^x	48	2	7	8		
PFBA	0.29	0.43	1.6	0.049	0.030 - 9.3	
PFPeA	0.21	0.73		0.015	0.33 - 6.5	
PFHxA	0.67	0.36	0.26	0.046	0.31 - 25	
PFHpA	0.27	0.17	0.094	0.022	0.10 - 5.8	
PFOA	0.85	0.49	0.17	0.074	0.51 - 210	
PFNA	1.0	0.020	0.0096	<dl <sup="">ψ</dl>	0.028 - 0.45	
PFDA	0.006	0.011	<dl <sup="">ψ</dl>	<dl <sup="">ψ</dl>	0.019 - 1.1	
PFUnA	0.016	0.0095	<dl td="" ψ<=""><td>0.0053</td><td>0.003 - 0.12</td></dl>	0.0053	0.003 - 0.12	
PFDoDA	0.001	0.0007	<dl <sup="">ψ</dl>		0.003 - 0.030	
PFTriDA	0.007	0.018	<dl td="" ψ<=""><td></td><td>0.001 - 0.018</td></dl>		0.001 - 0.018	
PFTeDA	0.0002	0.002	<dl <sup="">ψ</dl>		0.001 - 0.069	
PFBS	0.71	0.39	0.25	0.016	0.110 - 42	
PFHxS	1.3	0.20	0.072	0.035	0.019 - 16	
PFOS	2.8	0.091	130	0.071	0.044 - 6.0	
PFDS	0.002	0.0008	<dl <sup="">ψ</dl>		0.003 - 0.063	
PFECHS	9.5					
FOSA	0.013	0.0014			0.007 - 0.22	
Total PFAS	12.7					

 ξ number of landfills investigated; χ number of samples from all landfills investigated; $\Psi < dl - less$ than detection limit

3.3.3 Organophosphate Esters (OPE)

Organophosphate esters have been used for decades for a wide variety of purposes, including as flame retardants, plasticizers, and anti-wear and anti-foaming agents, in many products that end up in landfills, such as plastics, rubber, lubricants, electronics, polyurethane foams, textiles, etc. (Wei et al. 2015; Qi et al. 2019). Investigations into OPE in MSW landfill leachate have generally been limited to 3-10 compounds and typically one, but up to six (Qi et al. 2019) landfills. Only six previous studies have included historic landfills, examining one each (Tables 3-3 and A-1). Furthermore, none of these previous landfill leachate surveys have included 14 of the 24 OPE compounds tested here (Table 3-3). Consequently, this study of 20 historic landfills is apparently the most comprehensive assessment of OPE in landfill leachate to date.

The maximum total OPE (Σ_{24} OPE) concentration for leachate-impacted samples of this study (Figure 3-1C) was 81.4 µg/L at site BBP, with three other samples (sites SCU and NW) at concentrations > 30 µg/L. Eight landfills, including two closed in the 1960s, had a sample with Σ_{24} OPE > 10 µg/L, while all 16 landfills that closed in the 1960s onward had a sample with Σ_{24} OPE > 1.0 µg/L. The four oldest landfills (SKP, SMP, G4, BBC; Table 3-1) had Σ_{24} OPE concentrations < 0.25 µg/L, which could reflect diluted leachate of these samples, as noted above. However, it may also result from low initial masses in the refuse, noting that while trialkyl and chlorinated trialkyl phosphates were widely used since the 1940s, their application increased greatly between 1960 and 1980 (Muir 1984). Losses due to degradation or leaching over the >60 years could also be factors. These total OPE results suggest that OPE are common contaminants in historic landfills, at least for those closed in the 1960s and later. Their general persistence within the landfills over this time may indicate reduced susceptibility to degradation under anaerobic conditions, as suggested by results for laboratory microcosms with leachate (Kawagoshi et al. 2002) and amended sewage sludge (Pang et al. 2018).

Three compounds were prevalent at relatively high concentrations across these 20 historic landfills (Figure 3-1C) – TBOEP (tris(2-butoxyethyl) phosphate), TnBP (tributylphosphate), and TEP (triethylphosphate); combined these three compounds typically comprised > 70% of the Σ_{24} OPE concentration (Figure A-2, Appendix A8). Most samples had notable concentrations of two or three of these compounds, but a few are dominated by TEP alone, including samples from wells and discharging groundwater (Figure A-2, Appendix A8 – see sites HB, OV, OR, G6). Most of these samples had low total OPE concentrations (Figure 3-1C; but for G6), so perhaps TEP from other sources (precipitation, irrigation water) is playing a role. In contrast, three of the compounds tested – TBPDPP (tert-butylphenyl diphenyl phosphate), TDBPP (tris(2,3-dibromo propyl) phosphate), and DOPP (dioctylphenyl phosphonate) – were not detected in any of the samples, while seven other OPE were detected in less than 20% of the samples. In many past studies, largely incorporating modern (active or closed in last 3 decades) landfills, TCPP (tris(2-chloroisopropyl) phosphate) or TCEP (tris(2chloroethyl)phosphate), two of the three chlorinated OPE, with TDCPP (tris(1,3dichloro-2-propyl)phosphate), was found to be the most dominant OPE (Deng et al. 2018; Cristale et al. 2019; Qi et al. 2019). In this study, TCPP was dominant in the two samples from the MR site (Figures 3-1C and A-2 (Appendix A8)), which closed in 1993,

comprising 73% and 79% of the total OPE concentrations. Otherwise, the three chlorinated OPE combined made up only a small fraction (mean of 8%) of the Σ_{24} OPE for samples from post-1960 landfills (Figure A-2, Appendix A8). TnBP had higher maximum concentrations than TCPP and TCEP (Table 3-3) in several other historic landfill studies (Öman and Hynning 1993; Paxéus 2000; Andrews et al. 2012), with more similar but lower maximum concentrations in other studies (Buszka et al. 2009; Regnery et al. 2011). This trend toward higher chlorinated OPE relative compositions in younger landfills may be a result, at least in part, of their increased use as flame retardants in replacement of polybrominated diphenyl ethers (Blum et al. 2019).

Despite the general dominance of a few of these 24 OPE, substantial differences in OPE composition were apparent for several of these historic landfills (Figures 3-1C and A-2 (Appendix A8)), and even between samples at a single site. For example, both samples from KBP landfill showed dominance by IDDPP (isodecyl diphenyl phosphate) and TPrP (tripropyl phosphate). Also, TXP (tris-xylenyl phosphate) had a high concentration (11.7 μ g/L) in one of the BBP samples, while it was < 0.002 μ g/L for all other samples. Interestingly, TXP showed a single high Pearson correlation (0.78), with acrylonitrile, suggesting a common source. Finally, one G9 sample with low Σ_{24} OPE concentration was dominated by TPPO (triphenylphosphine oxide) while the other was dominated by TnBP. All of these compositional differences may be due to a specific industry or waste type deposited at these sites that was not common for the rest of Ontario during the 1920s -1990s. For more in-depth investigations of OPE leachate composition relationships, a correlation matrix is provided in Figure A-3 (Appendix A8). Past studies of OPE in landfill leachate have typically measured a set of 3-10 OPE compounds. The maximum concentrations of these from past studies, including the five other historic landfills (pre-1990; 6 studies) and a synthesis of mostly modern (post-1990) MSW landfills by Qi et al. (2019) are provided in Table 3-3. Given the divergent set of analytes used in each study, a direct comparison of total OPE is not feasible. Individual OPE maximum concentrations varied over several orders of magnitude across the historic landfills studied, but were predominantly higher in this study of 20 Ontario landfills. This highlights the benefit of sampling from a large number of landfills for generalizing the high-end risk that might pertain to other historic landfills. All of the maximum concentrations from this study fell within the range of maximums of past studies (Table 3-3) that included, almost exclusively, modern landfills, though most OPE, including the chlorinated OPE, were much less than the high end of that range. However, the maximum concentration of TBOEP is two times higher in this study than the maximum previously measured.

Table 3-3. The maximum concentrations (μ g/L) of 21 of the 24 OPE compounds assessed in this study (TBPDPP, TDBPP and DOPP were all non-detect here and not measured in any other study) for landfill leachate or leachate-affected groundwater samples of this study and other studies on historic landfills (Table A-1; Appendix A1), and the range in maximum concentrations from 13 studies reported in Table 2 of Qi et al. (2019), with predominantly samples from modern landfills. Data for modern landfills typically represent samples from leachate collection systems. Full names and CAS #s for the OPE are provided in Table A-5 (Appendix A4).

		Modern						
	This	Oman &	Paxeus	Barnes	Buszka	Regnery	Andrews	Qi et al.
	study	Hynning	2000	et al.	et al.	et al.	et al.	2019
		1993		2004	2009	2011	2012	
Landfills ^ξ	20	1	1	1	1	1	1	
Samples ^x	48	3	1	4	5	11	4	
TEP	18.7		3					0.92 - 1320
TBPO	0.043							
TPrP	1.6							
TnBP	27.1	7	153		0.64	0.21	2.3	0.6 - 153
TiBP	2.1					0.7		0.56 - 350
TPPO	0.1							
TEEDP	0.034							
TCEP	2.9	n.d. ^v	2		0.74	0.32		0.91 - 5430
TCPP	7.9		4	0.74		0.34	0.8	3.9 - 50
TDCPP	1.7		0.4	<dl <sup="">ψ</dl>	$< dl^{\psi}$	0.045	0.2	0.2 - 34.7
TPHP	1		5	<dl <sup="">ψ</dl>			0.25	0.002 - 5
EHDPP	5.5							
TOTP	13.7							
IDDPP	3.3							
TBOEP	43.5		7			0.2	2.5	0.52 - 21
TEHP	0.15							
DPIPP	0.068							
TXP	11.7							
DTBPPP	0.03							
T2IPP	0.0004							
TTBPP	0.91							

 ξ number of landfills investigated; χ number of samples from all landfills investigated; Ψ n.d. – non-detect, $\langle dl - less$ than the detection limit

3.3.4 Bisphenols

The bisphenols analyzed included eight monomers (A, AF, AP, B, F, P, S, Z). These are used in plastics, paints, epoxy resins, flame retardants, and brake fluid (e.g., Careghini et al. 2015; Chen et al. 2016). Bisphenol A (BPA) is a common landfill leachate constituent, which is not surprising given its widespread use and the fact that it does not biodegrade in anaerobic MSW landfill leachate (Limam et al. 2013). Previous studies, predominantly of modern landfills, have revealed a concentration range spanning many orders of magnitude, reaching 1000s µg/L (Paxéus 2000; Masoner et al. 2014; review for China - Oi et al. 2018; Table A-6 (Appendix A8)). In this study, BPA was detected in two-thirds of the samples and at 17 of the 20 historic landfills (Figure 3-1D), with a maximum concentration of 29 µg/L. Given that BPA was commercialized in 1957 (Qiu et al. 2019), it is fitting that concentrations were below detection for the four landfills closed prior to 1960 (SKP, SMP, G4, BBC). The one exception was a low but detectable concentration for G4-1; however, this sample was flagged from the AS assessment above as likely being cross-contaminated by wastewater. Otherwise there is no obvious trend in BPA abundance or concentration with closure age of these historic landfills. Many of the post-1960 samples with non-detections were collected from seeps or groundwater discharging to surface waters. This may reflect retarded transport along groundwater flow paths, as BPA has moderate sorption to aquifer materials (Ying et al. 2003), or biodegradation where the leachate plume experienced mixing with more aerobic waters (BPA half-life: 3 – 38 days under aerobic conditions; Careghini et al. 2015). These findings indicate that BPA remains a common contaminant in leachate from

historic landfills dating back to the 1960s, potentially at similar concentrations to modern landfills.

Due to the health concerns and restrictions for BPA, which is a known endocrine disruptor, use of BPA analogs, including bisphenol S and bisphenol B, have become more common in recent decades, although these compounds have been in production for other uses for much longer (Chen et al. 2016). Many of these share some similar health concerns as BPA (Chen et al. 2016; Qiu et al. 2019). Of the seven of these compounds tested in this study (Appendix A5), the only one detected frequently was bisphenol S (BPS) (Figure 3-1D), which has also been used as a dye for over a century. Apparently this is the first study to measure BPS concentrations in leachate from landfills of any age. BPS was detected in 56% of samples, with a maximum concentration of 4.8 µg/L and with seven samples from six different landfill sites at $> 1.0 \mu g/L$. Similar to BPA, BPS was detected less frequently (only 39%) in samples from seeps and discharging groundwater, perhaps for similar reasons, though it is reported to have a higher persistence in aquatic environments (Chen et al. 2016). Bisphenol B was only detected at the BBP landfill site (Figure 3-1D), at a maximum concentration of 0.9 µg/L. This landfill has a unique leachate composition, with relatively greater concentrations of OPE (Figure 3-1C) and some dissolved metals (data spreadsheet, Appendix A10), which may reflect inputs from a specialized local industry or manufacturer. Together, these findings suggest BPS may be a common contaminant in historic landfills, and likely in modern ones too, while the remaining six compounds tested are likely only rare contaminants.

3.3.5 Other Contaminants of Emerging Concern (CECs)

Of the ten substituted phenols analyzed in this study, only four (2,4dimethylphenol, 2-chlorophenol, p-chloro-m-cresol, pentachlorophenol) were detected, with maximum concentrations of 12, 1.6, 1.1 and 1 μ g/L, respectively. Each was detected in <20% of the 48 samples, likely due in part to the higher detection limits (0.1 - 5 μ g/L) in comparison to the other CECs of this study. There was no apparent trend between detection and landfill age or sample type. Pentachlorophenol and phenol have both been found at 10-100s μ g/L in modern landfills (Masoner et al. 2014; Table A-6 (Appendix A8)).

The eight pharmaceuticals analyzed here were generally found at relatively low concentrations in these historic landfills (Table A-6, Appendix A8) compared to those reported for 19 modern landfills in a United States Geological Survey (USGS) study of CECs (including 119 pharmaceuticals; Masoner et al. 2014). Most notable was cotinine, a metabolite of nicotine, which was detected in 98% of these historic landfill samples with concentrations reaching 6.6 μ g/L. It was also nearly ubiquitous in the USGS study, with a maximum concentration of 51 μ g/L. Thus, cotinine seems a very prevalent and persistent pharmaceutical contaminant for old and modern landfills. Carbamazepine (introduced in the 1960s), which was another frequently detected pharmaceutical in the USGS study (maximum concentration 2.6 μ g/L), was detected in a third of samples here, with a maximum concentration an order of magnitude less (0.17 μ g/L). Caffeine, codeine, paraxanthine and acetaminophen were detected in very few historic landfill samples, while theophylline and aspartame were not detected in any samples.

Perchlorate is a chemical best known for its use as a rocket propellant and in various explosives (including fireworks and air bags) and ammunitions, amongst other uses (Urbansky 2002). Concentrations were very low in the historic landfill leachate samples, reaching a maximum of 0.13 μ g/L, likely as a result of degradation under anaerobic conditions (Robertson et al. 2013).

Finally, sulfamic acid is a high-production volume chemical with a large list of uses in multiple industries (Freeling et al. 2020). Though there are few studies on the presence of this highly water-soluble compound (sulfamate in its anionic form) in the environment, it has been found at concentrations of typically $0.1s-10s \mu g/L$ in precipitation, groundwater, surface waters, and drinking waters, and $10s-1000s \mu g/L$ in WWTP effluent (Castronovo et al. 2017; van Stempvoort et al. 2019; Freeling et al. 2020). Here, the maximum concentration reached $42 \mu g/L$ in one of the younger historic landfills (MR), while 18 samples surpassed $1 \mu g/L$, indicating that historic landfills can be a source of elevated sulfamic acid to environmental waters.

3.3.6 CEC Tracers of Historic Landfill Leachate

Considering Pearson correlations (log-transformed concentration data; raw data in Supporting Information, Appendix A10) between the various contaminants in these historic landfill samples, ammonium showed significant (p<0.05) and good correlation (Pearson correlation coefficient >0.60) with many of the CECs, particularly the AS saccharin (0.66), total PFAS (0.74), total OPE (0.73), BPA (0.67), as well as common landfill leachate indicators, inorganic carbon (0.75) and boron (0.65). Of the

pharmaceutical set, only cotinine showed any commonality with those above (0.73 with saccharin). Total BTEX (benzene, toluene, ethyl-benzene, xylenes) concentrations were also well-correlated (0.72 with ammonium), whereas the chlorinated ethenes (solvents) were not well-correlated to any of these compounds. Diethyl ether, another volatile organic solvent, was well-correlated to saccharin (0.77) and total OPE (0.74). Metals that were correlated to this group and themselves included chromium, tin, cesium, niobium, rubidium, titanium, vanadium, and cobalt. In contrast, chloride and copper, commonly considered as landfill leachate tracers, were not well-correlated with these compounds. These findings suggest that the CECs noted above, preferably applied in some combination, can be additional useful tracers for historic MSW landfills of a similar waste composition and background to these in Ontario.

3.4 Conclusions and Implications

Many of the CECs assessed here were frequently found at elevated concentrations $(0.1s - 10s \text{ of } \mu g/L)$ in leachate-affected groundwater of these 20 historic landfill sites, particularly the AS saccharin; the PFAS: PFBA, PFPeA, PFHxA (perfluorohexanoic acid), PFOA and PFOS; the OPE: TBOEP, TnBP, and TEP; BPA; and cotinine. There was no clear decline in these CECs concentrations with age across landfills closed from 30 up to 60 years, at least as far back as when the compounds were first introduced or became broadly used, which highlights their long persistence at historic landfill sites. These data indicate that historic landfills may remain long-term sources of these CECs to the environment for the foreseeable future. Several other CECs (e.g., PFECHS, PFBS,

PFNA, TCPP) were found at similarly elevated concentrations but less frequently. Indeed, this data set also provides evidence of the strong variation in CEC concentrations and composition that can occur between and even within historic landfills, as has been noted before for basic geochemical components (e.g., chloride, ammonium, organic matter) by Kjeldsen et al. (1998), and for heavy metals and xenobiotic organic compounds by Slack et al. (2005). All told, this data set informs managers and regulators of historic landfill sites and of WWTPs receiving historic landfill leachate, of the types of CECs they may need to monitor and that measurements at multiple locations will likely be necessary.

The maximum observed concentrations for many of these CECs in these leachateimpacted groundwater samples were within the ranges reported for modern (i.e., more recently closed or currently active) landfill leachate. Both historic and modern landfills can supply leachate-impacted water to WWTP and have the potential to leak, thus impacting the surrounding groundwater. However, historic MSW landfills, while typically ignored as sources of CECs such as PFAS, may pose the greater risk to human and environmental health. Historic landfills are more likely to lack the engineered infrastructure typical of modern landfills, such as clay or geotextile liners, leachate containment systems, and reactive barriers, which prevent leachate from entering the groundwater system. Furthermore, historic landfills are often located near surface water bodies, having typically been situated on valley bottoms or floodplains that were too wet for other development, and that had thick soils useful for cover material and low grades allowing for easy equipment access (Lisk 1991). In a study of the proximity of 1153 U.S.

sanitary landfills to wetlands and deeper surface waters, Lambou et al. (1990) determined that almost all of the them were close to a wetland (72% within ¼ mile; 98% within 1 mile), while about half were fairly close to a deep water habitat (48% within 1 mile, though only 17% within ¼ mile). In addition, while older landfills are often smaller, there are many more of them because each community essentially had their own landfill or 'dump' site. For example, as of September 2017, the province of Ontario, Canada, had 3200 closed (mostly historic) landfills on record, compared to 693 operational or inactive (but modern) landfills (Ontario Ministry of the Environment, Conservation and Parks 2019), and there are likely more historic landfills that are undocumented. The total number of active and closed landfills in the U.S. is over 100,000 (Suflita et al. 1992), with the vast majority likely historical.

Groundwater containing PFAS and many of these other CECs emanating from historic landfills may contaminate drinking or irrigation water wells. Substantial dilution is expected for municipal wells, but may be much less for private domestic wells located near the landfill. CEC concentrations in groundwater reaching surface waters may be reduced by dispersion and various uptake (e.g., soil vapour, phreatophytes) and biodegradation processes (if susceptible and the biogeochemical conditions are right). However, many of the samples here were from seeps and discharging groundwater entering streams, ponds, and wetlands, and these still had high concentrations (e.g., all samples of DC-A, -B, -C, and HB-03 for PFAS; Figure 3-1B), suggesting the concentrations measured in this study are generally applicable to groundwater plumes. The part of the aquatic ecosystem most at risk is likely the benthic zone, especially for

those organisms buried or burrowing in the sediment (i.e., endobenthic), as these will tend to experience contaminated groundwater less diluted by the overlying surface waters (Roy and Bickerton 2010). A full assessment of the risk posed by CECs sourced from historic landfills is beyond the scope of this work. It is complicated by the fact that many of these CECs lack guidelines. There are also issues of accounting for effects of mixtures of CECs and other toxic compounds (e.g., metals, ammonium, petroleum compounds), as were obviously present in these samples (Figure 3-1; additional compounds in data spreadsheet, Appendix A10), and the appropriateness of aquatic life guidelines for the groundwater matrix and endobenthic organisms (Roy et al. 2019). Regardless, a brief comparison of water quality standards for drinking water or the protection of aquatic life that are available for the CECs in this study, is given in the Supporting Information (Appendix A9). Many of the CECs do exceed the water quality guidelines in several samples, including PFOA and PFOS for drinking water, and BPA, pentachlorophenol, and 2,4-dimethylphenol for aquatic life (including some samples of discharging groundwater), which is an indication of the seriousness of this contaminant threat posed by historic landfills, if not a true assessment of the risk posed.

Chapter 4: Evaluation of contaminants from historic landfills impacting an urban stream

4.1 Introduction

Understanding the processes of groundwater-surface water (GW-SW) interaction are important in answering questions about water quality, contaminant transport, and ecological exposure. Groundwater has been shown numerous times in previous work to have the potential to be a major source of various contaminants to surface water, such as nutrients, chlorinated solvents, sewage wastewater, acid mine drainage, and landfill leachate (Cherry 1987; Howard and Livingstone 2000). Groundwater contaminants discharging to surface waters are a concern due to their potential detrimental impacts on endobenthic organisms living in the shallow sediment (Roy et al. 2019). Also, continuous mass loading of contaminants can impact organisms that live within or depend on the surface water. For flowing water bodies, such as streams, mass loading of contaminants to the stream can be transported downstream and impact downgradient receptors, including human drinking or recreational water. The focus for the rest of this chapter will be on contaminated groundwater interaction, and the associated risk, with stream ecosystems.

Groundwater fluxes to streams are complex and have been shown to change drastically on rather small spatial and temporal scales. Conant (2004) developed a conceptual model for a stream which had complex spatial variations in discharge, recharge, and hyporheic flow at the sub-reach scale. Groundwater fluxes also vary temporally, on a diurnal scale (Gerecht et al. 2011; Ren et al. 2019), seasonal scale

(Conant 2004; Bieroza and Heathwaite, 2015; Malzone et al. 2016; Ren et al. 2019; Lemaire et al. 2020) and during precipitation events (Karan et al. 2014; Malzone et al. 2016). In order to locate contaminated groundwater discharge zones within a stream, and furthermore to then evaluate risk from the influence of such water, conceptual models must include detailed spatial and temporal analyses of groundwater flux along the streambed (Conant et al. 2019).

Urban streams tend to have added complexity due to multiple sources and pathways of contaminant input (Howard and Livingstone 2000; Roy and Bickerton 2012). In these environments, analysis of only the surface water quality frequently does not provide the full picture and a detailed analysis of shallow streambed groundwater is required to distinguish contributions from multiple contaminant sources. Previous work has suggested methods to identify and distinguish contaminant sources, such as the use of unique tracers like artificial sweeteners (Van Stempvoort et al. 2011; Roy et al. 2014), contaminant mass discharges (Sonne et al. 2017), and mass ratios like chloride to bromide mass ratios (Mullaney et al. 2009; Roy 2019) or modified ratios with emerging contaminants (Hepburn et al. 2019b). The effectiveness of these methods is also dependent on hydrogeological conditions that influence transformation and sorption of contaminants. Hyporheic flow, which occurs in streams due to changes in streambed topography and morphology, can cause local changes in the biogeochemical conditions of the transition zone, resulting in spatial and temporal differences in the degradation of compounds at the sub-reach scale (Freitas et al. 2015; Magliozzi et al. 2018). Temporal changes in hyporheic exchange occur on both daily and seasonal scales as well as during

precipitation events (Malzone et al. 2016; Ren et al. 2019). Bank storage, where a rapid rise in stream level causes a gradient into the stream banks, can also cause mixing of waters that can alter biogeochemical conditions in the transition zone (Conant et al. 2019). Overbank flooding, where stream water spills over the bank during large increases in stream stage, recharges groundwater with surface water and can effectively change the conditions of the riparian groundwater (Ledford et al. 2016).

Historic landfills are often located near surface water bodies and urban centres (Coakley 1989; Lambou et al. 1990) due to the thick sediments available for cover and ease of access (Lisk 1991). Landfills have been a well-known source of environmental pollution for decades; however, new attention has recently been given to historical landfill sites that closed before modern regulations, as they pose a risk to the surrounding environment due to the many unknowns surrounding their location, design, and waste composition (Environmental Commissioner of Ontario 2010). With most historical landfills lacking engineered liners and leachate collection systems, there is a high chance of leachate-impacted groundwater migrating off-site and intercepting a surface water body. Table 4-1 summarizes previous studies that have investigated landfill leachate influence on surface waters. Most of these studies test for common leachate constituents such as salts, volatile organic compounds (VOCs), nutrients, and metals. Regular monitoring of landfill leachate by operational authorities typically tests for these same constituents on an annual to bi-annual basis. Sampling typically includes leachate and downgradient wells, as well as surface water grab samples. Surface water sampling locations often include a sample upstream of the landfill, near the landfill and further

downstream. There is some question as to whether this typical testing and monitoring properly captures the threat posed by leachate-impacted groundwater to the environment.

Most jurisdictions do not currently require the testing of contaminants of emerging concern (CECs) at municipal landfills. Recent work has detected CECs in active and historic landfills (Chapter 3) at concentrations of concern to the environment. Per- and polyfluoroalkyl substances (PFAS) are particularly concerning due to their extreme persistence and adverse environmental and human health effects (Sunderland et al. 2019). There is currently a paucity of research on the impact of CECs, especially PFAS, from leachate-impacted groundwater discharging to surface water bodies. In addition, past work has not targeted the benthic zone, especially endobenthic shallow sediments (Roy et al. 2019) with studies on CEC plume discharge having taken a strongly hydrogeologic viewpoint and not rigorously considered the potential ecological threat posed.

The motivation behind this project is to better understand the threat to the ecosystem and any downgradient receptors from leachate-impacted groundwater from a historic landfill discharging to a stream. Additionally, this work will provide guidance to regulatory authorities on the monitoring of landfills and other contaminated sites that have plumes interacting with surface water. The objectives of this study are to: (i) assess the potential risk of leachate-impacted groundwater discharging to a stream (CECs and common contaminants), and (ii) investigate the hydrogeological controls on groundwatersourced contaminants discharging to an urban stream, particularly the temporal and spatial variability. An additional key focus is placed on determining the concentrations of

PFAS compounds in leachate impacted groundwater from a historic landfill discharging to a stream, noting that few reports exist of PFAS-contaminated groundwater from any source impacting surface waters. The study approach consisted of a full year field study on a section of an urban stream receiving contaminated groundwater from a group of nearby historic landfills. At this site, detailed investigations of the hydrogeological controls and the contaminant conditions were performed. A complimentary investigation on the ecotoxicological effects of landfill-impacted groundwater discharging to this stream is in progress.

4.2 Methodology

4.2.1 Study Location

The stream under study is Dyment's Creek, an urban stream located in Barrie, Ontario. This stream flows through residential, park/ recreational, commercial, and industrial areas before discharging to Lake Simcoe's Kempenfelt Bay. The stream has been impacted by urbanization through changes to stormwater management, sedimentation, widening, incised channels, and narrowed riparian corridors (Golder Associates, 2019).

There are three historical landfills adjacent to one another along 0.5 km of Dyment's Creek (Figure 4-1). The landfills were operational from 1960-1963, predating the formation of Ontario's Ministry of the Environment, Conservation and Parks in 1970, resulting in a lack of documented information about the waste type and site management. There are no leachate collection systems in place at these sites, and previous work has

shown that leachate-impacted groundwater interacts with the stream (Roy and Bickerton 2012; Fitzgerald et al. 2015). There are no known landfills further upstream.

Based on this information and on initial screening assessments described in the subsequent sections, two stream stretches were chosen for detailed GW-SW interaction assessments: a 20 m long section at the B site (Stretch B), and a 40 m long section at the C site (Stretch C) (Figure 4-1). The general layout of monitoring instrumentation emplaced at both sites is given in Figure 4-2 and photographs of the sites are included in Appendix B2 (Figures B-11 and B-12). Broader impacts on the stream quality were assessed across a larger reach extending from a location upstream of Stretch C to another downstream of Stretch B (Figure 4.1). Water sampling and stream flow measurements were made at both locations, with additional occasional sampling at a middle stream location (Figure 4-1). The upstream and downstream locations were chosen to i) maximize the length of stream while staying in close proximity with the landfills, ii) avoid a small unidentified drain from landfill C located further upstream, iii) ensure safe stream access, and iv) allow for stream stage and discharge measurements.

4.2.2 Hydrology Measurements

4.2.2.1 Stream Stage and Discharge

Stream stage and discharge measurements were performed within a 10 m section at each of the upstream and downstream locations (Figure 4-1). Photographs of the site locations are included in Appendix B2 (Figures B-9 and B-10). Permanent stilling wells, made of slotted PVC pipe, were installed at deeper positions within the stream in both locations. Levelogger Edge (Solinst) pressure transducers were placed in the stilling wells to monitor water pressure (converted to surface water level as explained below), temperature, and electrical conductivity (EC) continuously every 15 min from July 2019 to July 2020. A Barologger Edge (Solinst), and from August 2019 onwards a Baro-Diver (Van Essen), monitored on-site barometric pressure, which was used to correct water pressure measurements for changes in barometric pressure to determine water levels (stage). Stream discharge was determined with the midsection method (Buchanan and Somers 1969) based on approximately 10-20 vertically-averaged velocities recorded across the stream section, which were measured manually with a flow meter (FP101 Global Water Flow Probe) biweekly to monthly over the year. An attempt was made to derive a rating curve from the discharge and related stage measurements, which could be used to derive continuous discharge; however, the uncertainty in this relationship was too large and the rating curves are excluded.

4.2.2.2 Water Table Wells

Two fully-screened (1" diameter slotted-PVC) water table wells were installed at each of the B and C sites, one on each bank (0.3-5 m from the stream edge) at about the middle of the stretches (Figure 4-2). Wells were placed in holes that were hand augered to ~1.5-2 m depth, which was deep enough to capture the lowest water table height, with surrounding material (largely sand) allowed to collapse around the well. Micro-Diver (Van Essen) pressure transducers were hung on fishing line tied to a fixed location on the well casing so that they were submerged just above the bottom of the well. A Baro-Diver

(Van Essen) barometric pressure transducer was installed in one of the wells, above the ground surface to avoid saturation, to correct for barometric pressure changes.

4.2.2.3 Potentiomanometer

A potentiomanometer was used to measure vertical hydraulic gradient between groundwater and surface water as described by Winter et al. (1988) and shown in Figure 4-3. This method was applied in June 2019 following initial sampling with a mini-profiler (as described further in section 4.2.4.1) at depths of 0.2-1.0 m below the streambed.

4.2.3 Temperature Methods for Groundwater-Surface Water Interaction

4.2.3.1 Temperature Mapping

Temperature mapping consists of manual temperature measurements within the streambed to determine 2D temperature distribution within a stretch of stream. Temperature mapping is ideally performed in summer and winter when the contrast between surface water and groundwater temperatures are the highest. Temperature mapping was performed as part of the detailed assessments at Stretch B and C. Temperature measurements were taken in the sediment 10 cm beneath the streambed using a thermometer (accuracy $\pm 0.2^{\circ}$ C), in a crude grid pattern. Measurements were made in transects spaced every 1 m along the stream, with approximately 10 measurements taken across the stream at spacing intervals ranging from 10-50 cm. Spacing was generally denser near the shores due to larger temperature changes with distance when compared to the middle of the stream. Measurements of the surface water temperature were recorded periodically to compare to the sediment temperature mapping values. Mapping for the B stretch included two 20 m sections in July 2019, but only one 20 m section in January 2020. Mapping for the C stretch covered a single 45 m section for both July and January. July values were used as part of the initial assessment to locate areas of potential groundwater contamination discharge.

Plots of the temperature maps were created using Surfer (v.18 Golden Software). Delaunay triangulation with linear interpolation method was used to grid the raw data $(0.04 \times 0.1 \text{ m grid})$ to produce contoured maps of temperature over space.

4.2.3.2 Temperature Profiles

Temperature profiles below the streambed were measured over time using Maxim Integrated iButton temperature loggers (resolution ± 0.5 °C). The iButtons were placed at 0, 0.1, 0.2, 0.4, and 0.9 m depths inside hollow steel rods with pointed tips that were hammered into the streambed, as described by Fitzgerald et al. (2015). Temperature was measured every 15 min from August 2019 to July 2020. Wooden dowel was used between the iButtons to achieve required depths and to isolate them from one another within the rod. A threaded cap allowed for iButtons to be retrieved from the steel rods and downloaded without removing the rods from the sediment. Four temperature profile rods were installed at both the B and C stretches (Figure 4-2).

4.2.3.3 Groundwater Flux Calculations

The streambed temperature profile data was analyzed with two 1D steady-state flow temperature models, FLUX-LM (FLUX in Layered Media; Kurylyk et al. 2017) and VFLUX2 (Vertical Fluid [Heat] Transport Solver 2; Gordon et al. 2012; Irvine et al. 2015). Both require estimates of sediment and thermal parameters summarized in Table 4-2. Sediment parameters, such as porosity, thermal conductivity and the heat capacity were used from Fitzgerald et al. (2015), who studied the same site and had a similar sediment based on visual/hand inspection.

The key assumptions of FLUX-LM are that the system is at steady-state and has only 1D vertical groundwater and heat fluxes. Also, this solution assumes isotropic fluid and media properties, with optional inclusion of simplistic layered heterogeneities, and a steady state thermal regime (Kurylyk et al. 2017). The steady state thermal regime requires no change in temperature with time, and therefore no diurnal signal should be measured at any of the measurement depths. However, this was not always the case. Thus, daily temperature averages for each depth were used as the input for FLUX-LM for periods where a diurnal signal was observed (Kurylyk et al. 2019). Also, due to uncertainty in whether the top iButton was at the interface between sediment and surface water that could arise with streambed scour, it was sometimes necessary to omit the top iButton depth during analysis.

The key assumptions for VFLUX2 are that the system has only 1D vertical groundwater and heat fluxes, homogeneous and isotropic fluid and media properties, and discernible sinusoidal temperature variations (propagated from the surface into the

sediment and differing from the ultimate constant deep groundwater temperature). Therefore, only the topmost iButtons (0, 0.1, and 0.2 m) were used for this method since the temperature fluctuation extinction depth was often reached around 0.2 m beneath the streambed. The amplitude of the diurnal signal is smaller in the winter and larger in the warmer summer months. As a result, VFLUX2 could only be applied here to the summer and spring data. Due to the coarse resolution of the iButtons, a 6-hour moving average was used to smooth out the raw data prior to analysis with VFLUX2.

4.2.4 Groundwater Quality Measurements

4.2.4.1 Initial Drive-Point Sampling

Drive-point sampling was used to sample groundwater at two discrete depths from underneath the streambed, following the mini-profiler procedure outlined by Roy and Bickerton (2010), as an initial assessment to determine the locations of groundwater contamination input along two 100 m stream sections. A 15 cm long stainless-steel sampling point, with screened holes along 5 cm of its length, was attached to a hollow steel rod (5/8" diameter). Polyethylene tubing (1/4" diameter) was attached to the sampling point and run up through the steel rod to a peristaltic pump (Figure 4-3). Samples were taken as close to the shore as possible, every 5 m along the shore. A hammer drill was used to pound the steel rod into the ground to the desired first depth of approximately 20 cm. Stream water was pumped down through the point during hammering to prevent sediment from entering and clogging the sampling ports. The direction of the peristaltic pump was then reversed to pump groundwater through the sampling point to a graduated cylinder in which YSI multi-parameter probes were used to measure pH, electrical conductivity/ specific conductance (EC), dissolved oxygen (DO) and temperature (T). Once parameters stabilized, samples of groundwater were collected for ammonium and artificial sweetener analyses (described below). After sampling occurred at this depth, the mini-profiler was subsequently driven deeper and the sampling procedure repeated. The targeted depth for the second sample was 50 cm, but this varied for each location along the stream depending on the ease of groundwater extraction (e.g., if very slow groundwater flow was encountered at 50 cm then the drive-point would be driven deeper to sample from more ideal flow conditions). Finally, a hydraulic potentiomanometer measurement was made after sampling at each of the depths, as described in section 4.2.2.3.

4.2.4.2 Mini-Piezometers

The mini-piezometers used in this study consisted of 2.5 cm drive-point stainless steel screened tips (Gas Vapor Tip, AMS) connected to 1/4" polyethylene tubing and were installed at a depth of 15 cm beneath the streambed. The tip was attached to a hollow steel rod and pushed by hand into the sediment. Once in place the rod was removed leaving the tip and tubing within the streambed. Mini-piezometers were developed and sampled using a peristaltic pump, after which the tubing was clamped and attached to a stake driven into the streambed nearby, to avoid the piezometers continually discharging to the stream, filling with surface water or sediment, or being pulled out by passing debris.

For each site, mini-piezometers were installed along five transects (approximately every 5 m along the stream for the B stretch and every 10 m for the C stretch) at three positions across the stream (one close to each shore and one in the middle area of the stream) (Figure 4-2). Initial sampling for ammonium analysis occurred immediately following installation on July 23rd -24th, 2019. Three additional sampling campaigns were carried out in August and November, 2019, and March, 2020, which tested for the "full-suite" of water chemistry: ammonium (NH4⁺-N), artificial sweeteners (AS), anions, soluble reactive phosphate (SRP), VOCs, alkalinity, dissolved metals and cations. Additionally, two groups of CECs, PFAS and bisphenols (BP), were analyzed in samples from the southmost mini-piezometer in the transects at the B stretch, and the northmost mini-piezometers from the C stretch (i.e., five from each stretch).

4.2.5 Surface Water Quality Measurements

4.2.5.1 Year-Round Surface Water Monitoring

Surface water grab samples were taken biweekly to monthly over the course of one year at the upstream and downstream locations of the study site (Figure 4-1). Samples that did not require filtering were collected by submerging the bottle in the stream before opening and filling to prevent exposure to the atmosphere (especially important for PFAS). For those that required filtration, a plastic syringe was filled with surface water and attached to a 0.2-µm filter to fill the sample bottles. Samples were collected for NH₄⁺-N and AS analysis every sampling period. Additionally, in July,

August, November and March, the stream was also sampled at a middle location and for a selection of anions, SRP, VOCs, alkalinity, dissolved metals, cations, PFAS, and BP.

4.2.5.2 Precipitation Event Sampling

Surface water samples were collected at the upstream and downstream locations before, during and after a precipitation event on October 15th -18th, 2019 to assess temporal changes in contaminant inputs to the stream. Additional dates were planned for the spring of 2020, but this work was halted due to the Covid-19 pandemic. Samples were collected following the same procedure as in section 4.2.5.2. Samples were taken every 3-4 hours during the rain event, and then for two days afterwards at intervals increasing from 4 to 12 hours between samples (10 total sample times). Samples were collected for NH₄⁺-N, AS, anions, and PFAS. Daily values for rainfall amount were downloaded from a nearby Environment Canada weather station (Climate ID 6110556).

4.2.5.3 Epibenthic Zone Measurements

On July 16th, 2019, YSI multi-parameter probes were placed along the stream sediment-surface water interface to measure pH, EC, DO and T of the epibenthic zone; given probe dimensions this represents water at 1-3 cm above the sediment. Measurements were taken in transects every 5 m along and at 3-4 locations across the stream (near each shore and in the middle of the stream). Surface water measurements were also taken, with the probes being held within the flowing water column of the pelagic zone and not in contact with the streambed sediment.

4.2.6. Sample Handling and Analyses

For all sample collection, proper procedure for in-field filtration, preservation and transport were followed as outlined in Appendix A, Table A-3. Nitrile gloves were worn to prevent contamination (e.g., salts) from human skin. Care was taken to avoid materials containing PFAS during fieldwork (e.g., new waterproof gear, Teflon tape) though a recent study suggests contamination of water samples from field materials is not likely when simple and reasonable precautions are taken (Rodowa et al. 2020). Samples requiring filtration were filtered with either a 0.2-µm or 0.45-µm polyethersulfone membrane filter and preserved in the field. All samples were stored on ice or in a fridge prior to and during transport to Canada Centre for Inland Waters (Burlington, ON). In-lab storage details prior to analyses are also provided in Table A-3 of Appendix A. The details of chemical analyses for all contaminant analyses are provided in section A5 of Appendix A. Complete analyses for 60 groundwater and 10 surface water samples are still to be processed due to Covid-19 laboratory restrictions holding up analysis.

4.3 Results

4.3.1 Groundwater-Surface Water Interaction

4.3.1.1 Stream Stage

Stream stage versus time (both upstream and downstream locations; Figure 4-1) shows that this stream has a typical flashy signature (Figure 4-4B), in that there are drastic short-term responses to precipitation events measured in the stream stage. Urban streams are often flashy due to effects of urbanization such as decreased permeability and

stormwater management discharging to the stream. Overall, the stream stage is lower in summer, rising gradually over the month of November and peaking in December. The stage is relatively constant from December to March, and then gradually decreases over March and April. Manual flow meter measurements of stream discharge are plotted with continuous stream stage over the study year in Figure 4-5 and show a similar trend of increased baseflow in the cooler months. This trend is likely due to the influence of vegetation along the riparian zone having higher levels of evapotranspiration (ET) rates in the warmer months. In the fall, the downstream stage appears to begin to rise sooner than the upstream stage, which may be linked to increased groundwater inputs as ET rates begin to decrease. The upstream stage appears to have larger spikes in stage with precipitation than downstream for several days between December 3rd, 2019 and February 28th, 2020. This matches the dates with some of the largest snow events and is likely due to the proximity of a parking lot that plows their snow directly into the stream at the upstream location (photograph shown in Figure B-10). The notable short-term decline in stream stages in February may be a result of plowed snow damming up the stream. Other short-term sharp declines, often with associated spikes in stage, may reflect damming due to fallen trees catching debris which was occasionally observed at several locations along the study reach.

The downstream discharge is generally greater than the upstream discharge values (Figure 4-5B). This suggests that the stream is receiving groundwater along this stretch. The upstream discharge is larger for a couple of dates in the winter (January 15th and March 5th, 2020) and once in the fall (September 3rd, 2020) although for these dates the

error bars, indicating 5% uncertainty calculated with the USGS method by Sauer and Meyer (1992), overlap for the upstream and downstream measurements (Figure 4-5B). Dates influenced by precipitation events, as indicated by arrows along the x-axis on Figure 4-5, have some of the largest discharges measured. There is a general trend of increasing discharge into the winter, from December to February, which matches the increase in stage in Figure 4-5A. There is no apparent seasonal trend in the difference between the discharge at the downstream and upstream locations. Large differences are seen during rain events (e.g., September 24th, 2019) which may in part be due to the stream level changing during the time between conducting measurements at the upstream and downstream locations (5 hours between measurements on September 24th, 2019; discussed further in section 4.3.2.5). A large difference in stream discharge is also observed on January 30th, 2020 and, although no precipitation events occurred in the preceding days, this could be due to the damming of water from snow plowing, ice buildup, or fallen trees as discussed above.

4.3.1.2 Temperature Spatial Maps and Hydraulic Gradient

Initial investigation of the two stream reaches included measurements of the hydraulic gradient with a potentiomanometer between surface water and groundwater along the shores closest to the landfill at each site. These show the driving direction of flux, either discharge to the surface water or recharge to groundwater, and can help identify areas that are more likely impacted by groundwater discharge. Landfill impact on the stream was also initially assessed with visual observations, such as the presence of
groundwater seeps in the low-lying areas adjacent to sharp changes in topography near Dyment's Creek. These groundwater seeps were characterized by orange iron flocculate deposits and bacterial biofilms that are commonly observed in the strong reducing environments surrounding landfills (Parisio et al. 2006).

Groundwater typically remains close to the average air temperature, whereas surface water is more greatly influenced by seasonal and daily temperature fluctuations. Therefore, in the summer, groundwater is cooler than surface water and areas of cooler streambed temperature represent a stronger groundwater temperature signal, indicating groundwater discharge. In the winter, the opposite is true, so warmer areas represent groundwater discharge. Temperature maps, based on gridded measurements, show the spatial distribution in temperature beneath the streambed and can provide an indication of how groundwater-surface water fluxes change spatially along a stream.

At both the B and C sites, there is a general pattern of stronger groundwater temperature signatures near the shores, which quickly fade moving towards the middle of the stream (Figures 4-6 and 4-7). This suggests that groundwater discharge is strongest along the shores, which is consistent with the theory of converging groundwater flow lines resulting in greater groundwater flux at the edge of surface water (in the case of homogeneous conditions; Winter et al. 1998). At both sites, the southern shore appears to have a stronger groundwater influence compared to the northern shore, which is evident from the cooler temperatures observed in the summer, and warmer temperatures in the winter, at the southern shore in Figures 4-6 and 4-7. At the C site this is apparent around the 40 m position along the stream where there is a localized area of strong groundwater

influence that also spreads towards the middle of the stream. At both sites, the shore topography rises more steeply to the south which may be associated with a stronger hydraulic gradient toward the stream. In the middle portions of the stream temperatures are closer to those observed in the surface water, and therefore lower hydraulic gradients for groundwater discharge are expected. At these locations, there is the potential that hyporheic flow may be dominating the shallow temperature regime.

At the B site, in both the summer and winter, there is a stronger groundwater temperature signal upstream than downstream, from approximately 10-20 m along the stream length in Figure 4-6. This matches the potentiomanometer data that was measured along the southern shore approximately one month prior to the temperature mapping (Figure 4-8). From approximately 10 m to 20 m along the B stream stretch, there is a notable upward hydraulic gradient. At the 0 m position, the gradient is in the downward (recharge) direction, likely due to a change in topographic relief along the stream from a road culvert located just downstream (Figure 4-1) causing downwelling associated with hyporheic flow. This is also measured upstream of the B site, where the hydraulic gradient switches from a strong upward gradient to a downward gradient just upstream of an area of fallen sticks damming the surface water. In these locations, stream groundwater gradients are altered due to changes in streambed topography, causing downward flow into the sediments. Sections on Figure 4-8 with no hydraulic gradient data are due to gas bubbles in the potentiomanometer groundwater tubing preventing an accurate head difference reading at those locations. At the C site, there may be local areas

of hyporheic flow associated with small streambed islands that are present at low stream levels and appear as white areas on the temperature maps in Figure 4-7.

4.3.1.3 Temperature Profile – FLUX-LM Calculations

Temperature profiles were measured in the streambed using iButtons in temperature rods at four locations at each stretch (Figure 4-2) continuously from August, 2019 until the start of July, 2020. In the summer, temperature decreases with depth into the subsurface, since, as mentioned above, groundwater temperatures are cooler than surface water temperatures in the summer. The profile reverses in the winter and there is an increase in temperature with depth, as illustrated in Figure 4-9. Reversals between these two seasons occur in the spring (around April, Figure B-1B) and fall (around October, Figure B-1A), where the direction of the profile changes and for a brief period of time temperature becomes constant with depth. FLUX-LM cannot accurately determine flux when such conditions exist. Also, FLUX-LM assumes a steady state temperature regime with no diurnal temperature changes. Therefore, winter is the most ideal season for discharge calculations using the temperature-depth methods because there is often a measurable change in temperature with depth, as well as minimal diurnal variations (Kurylyk et al. 2017). In the summer when diurnal signals are stronger, using the daily average temperature in FLUX-LM for each depth can improve results by reducing the impact from diurnal signals (Kurylyk et al. 2019).

Figure 4-9 shows the temperature-depth profiles (0 - 0.9 m below streambedsurface) for each of the temperature rods averaged over a 24-hour period on December

19th, 2019. This day was chosen because it had a very low diurnal signal measured in the iButtons, with limited variation in temperature at each depth over the course of the day. Since diurnal signals are attenuated with depth, the top iButton is most likely to be impacted by diurnal effects that make it unusable in temperature-depth analyses. The top depth is also more likely to be affected by streambed scour, deposition, changes in soil texture, and hyporheic flow. The top iButton (0 m) in Figure 4-9 shows a tendency not to match well with the shape of the rest of the profiles (e.g., BSW, CNW) despite December 19th 2019 being a very steady day. The degree of curvature in the profiles is proportionate to the degree of groundwater flux (a linear profile represents no groundwater movement) and the direction of curvature represents flux direction (convex upwards is discharge, concave upward is recharge). Figure 4-9 shows that all profiles with clear curvature have a convex upward curve, which represents discharge conditions. Some of the straighter curves are more difficult to discern curvature and may have very low fluxes that are difficult to distinguish between recharge and discharge with this method. The profiles from the C site mostly have a higher degree of curvature than the B site profiles, likely representing larger magnitude fluxes at this site on that day. The one exception is the CNE temperature profile that is notably straighter. It appears that the temperature profiles that are measured on the same shore (i.e., either the north or south) are more similar to one another than to the profiles from the opposite shore at the same site.

FLUX-LM was run for multiple steady periods throughout the year and the results are plotted on Figure 4-10. For each date, an ~24 hour average of temperature was used to reduce the diurnal signal impact. This model was first run with all five sampling depths

and then again with only the bottom four depths (excluding the top 0 m depth). If the percent decrease in root mean square error (RMSE) was greater than 20% when excluding the top measurement depth, then the result from running FLUX-LM with only the bottom four depths was used. If the RMSE improved by less than 20%, or did not improve, then the result from all five sampling depths was kept. This ensured that as many data points as possible were used, unless the first depth did not fit with the rest of the data due to one of the reasons mentioned in the previous paragraph. However, for profile CNE, it is suspected that streambed scour after installation resulted in the top iButton depth being above the streambed. There was very little difference in temperature between the first and second iButtons which skewed the temperature-depth profile. Therefore, only the bottom four iButtons were used for all dates with this rod. Furthermore, data with greater uncertainty are indicated in Figure 4-10 as open symbols. These are determined by the following criteria: (i) the RMSE is larger than 0.1, and/or (ii) if the range of temperature measured in the top iButton (either 0 m or 0.1 m depending on the number of depths used) is larger than 80% of the difference between the bottom and top iButton (thus representing a relatively large diurnal fluctuation). FLUX-LM is more accurate in steady systems where there is little to no diurnal signal. By averaging the values for each depth over a 24-hour period, the difference between the maximum and minimum temperature at a given depth indicates the amount of diurnal signal, and when this signal is close to or greater than the spread of temperature with depth, erroneous flux values are more likely to occur. Therefore, there is greater confidence associated with solid dots on Figure 4-10.

Finally, it was determined through a crude visual assessment that the flux must have a magnitude of at least 10 m/yr to accurately determine the direction of flux with FLUX-LM, given the resolution of the iButtons (0.5°C) in this study. A flux with a magnitude smaller than 10 m/yr could change from recharge to discharge by making only small adjustments, within the iButton resolution, to the temperature at one of the depths. This area is shaded pink on Figure 4-10 to represent the zone of low flux and indiscernible flux direction.

FLUX-LM results for the B site in Figure 4-10A show more flux data points within the indiscernible flux direction range for all four of the temperature rods, indicating the predominance of low fluxes, whether recharge or discharge. A few flux results indicate recharge in early August 2019. Meanwhile stronger discharge fluxes are indicated in October-November for all four rod locations. In the spring there appears to be another period of increased discharge; however, there is less confidence associated with these fluxes (open symbols). Through the winter, BNW shows consistently discernible groundwater discharge into the stream, while the other locations show mostly small fluxes with only the odd point showing discernible discharge. The average flux for the entire year was notably higher for BNW, about double the magnitude of the other B site temperature rods (Table 4-3). Comparing these values to the temperature maps in Figure 4-6, BNW is expected to have a larger flux since the locations of the other temperature rods are in areas with temperatures more similar to surface water, whereas the location of BNW has notable temperature differences in Figure 4-6. Rod BSW, which is closer to the higher discharging shore, was installed too far away from the shore and

did not capture the large discharge area along the southern shore that is apparent in Figure 4-6.

FLUX-LM results in Figure 4-10B show that the C site temperature rod locations have discharging groundwater conditions that prevail during steady periods across the entire year. The one exception is CNE, which has periods of slight recharge and results that are typically within the zone of indiscernible flux direction. This result is comparable to the temperature map (Figure 4-7) where the area near the location of the CNE rod shows temperatures similar to surface water temperature. For all four locations, the discharge magnitude appears to be similar in the summer and the winter. There are a few points of higher discharge in the fall (November) and the spring (April-May), but many of these points are open symbols so there is less certainty. The lack of certainty in these points is unsurprising since these times are near the transition period for the temperature profiles (Figure B-1). This shows that, from a hydrogeological perspective, discharge of leachate contaminants during base flow periods may be similar in the summer and winter, but it might be higher during the spring and autumn. The average flux for the entire year was generally higher at the C site than the B site, with the one exception being CNE. This finding fits with the interpretation of the temperature profile curvatures (Figure 4-9). The maximum fluxes (recharge conditions for all rods except CSE and CSE) were greater for the B site temperature rods, again with the one exception being CNE (Table 4-3). However, the minimum fluxes (representing high discharge) were similar between both sites, with CSW being the only rod notably higher (Table 4-3). This suggests that there may be greater variation in groundwater flux throughout the year at the B site.

4.3.1.4 Temperature Profile – VLUX2 Calculations

The VFLUX2 model assesses flux using continuous temperature measurements over time considering the difference in diurnal temperature signal between two depths within the sediment. Figure 4-11 shows an example of temperature measurements with depth from iButtons from the BNW temperature rod plotted over time. The sinusoidal shape of the lines is due to the diurnal temperature signal, propagating from the surface. The VFLUX2 model has two solution options, Hatch et al. (2006) and Keery et al. (2007), that determine flux from the attenuation of the diurnal signal amplitude with depth. It is clearly shown in Figure 4-11 that with depth, the amplitude of the temperature signal is attenuated. By 0.4 m the temperature signal is completely attenuated, and the changes to temperature are on a seasonal scale. This means that temperature-time methods to determine flux cannot use the diurnal signals from 0.4 m or lower at this site. VFLUX2 also has solutions, by the same authors as for the amplitude solutions, that use the phase shift of the sinusoidal signal to determine flux. There is a slight phase shift seen in this data; the temperature peak is experienced slightly later in time as you move down through the profile. This phase shift is minimal in this data and therefore the phase methods offered in VFLUX2, as well as combined amplitude and phase methods, were not used (see Irvine et al. 2015 and their included references for issues and uncertainties associated with phase shift and amplitude methods).

The Hatch et al. (2006) amplitude method was chosen with a thermal dispersivity of zero (note that when $\alpha^*=0$, the Hatch et al. (2006) and Keery et al. (2007) amplitude methods have very similar solutions). The amplitude of the diurnal signal should be

larger than the resolution of the sampling device, and results from any periods where the diurnal signal is smaller may be uncertain (Gordon et al. 2011). Due to the coarse resolution of the iButtons of 0.5°C, VFLUX2 assessed that the top 0 m iButton was the only depth with consistently large enough diurnal signal in the summer and spring. During the fall and winter months, none of the depths had strong enough diurnal signal to be used in this model. Therefore, although all three pairs of iButtons were analyzed, only the top pair are considered accurate during the periods of August 15th, 2019 to September 30th, 2019, and April 1st, 2020 to June 15th, 2020. In the case of the CNW rod, it is believed that streambed scour occurred and that the top iButton was located out of the sediment, and therefore the 0.1 m and 0.2 m iButtons were used.

The graphs for VFLUX2 results over time (Figure 4-12 and B-2) are quite sporadic, bouncing around from recharge to discharge conditions in the case of most of the locations. VFLUX2 flux results tend to decrease (i.e., move towards discharge conditions) at all locations as you use deeper modelling depths (i.e., deeper pairs of iButtons). This may indicate potential issues with the top iButton such as streambed scour, as well as the influence of hyporheic conditions that would most likely be stronger nearer to the streambed-surface water interface. There does not seem to be a consistent response in the VFLUX2 values from precipitation events as signified by sharp increases in stream stage (Figure 4-12). For some precipitation events, the increase in stage matches an increase in flux; however, for many events there was no matching increase, and even slight decreases, in flux during events. Precipitation events may disrupt the sinusoidal shape of the diurnal temperature signal, resulting in a poor match of the

diurnal signal by VFLUX2. An in-depth analysis of these short-term trends is beyond the scope of this work.

Mean flux values from these VFLUX2 results were calculated for late summer of 2019 and the spring of 2020 (Table 4-4). The modelling depths in Table 4-4 represent the midpoint between the two iButtons used in the analysis (i.e., 5 cm modelling depth uses the temperature recorded at the 0 cm and 10 cm iButtons, 10 cm uses 0 cm and 20 cm, and 15 cm uses 10 cm and 20 cm). The results from the shallowest pair of iButtons was used, except for the rod with known scour, CNW, and two other rods where it was uncertain if the shallowest depth was better than the middle depth. Contrary to the FLUX-LM results, the B site is predominantly showing large recharge conditions, except for the BNW location in late summer 2019. This may be in part due to the hyporheic conditions at the B site causing downward flow, especially in the top 10 cm of sediment. FLUX-LM uses a deeper profile (90 cm), and sometimes excludes the top iButton and therefore would be less influenced by the shallow hyporheic effects. This interpretation is supported by the VFLUX2 flux results that tend to decrease (i.e., move towards discharge conditions) at all locations as you use deeper modelling depths. Results in Table 4-4 match overall what is observed in the temperature map in Figure 4-6, in that the BNW rod is in an area of stronger groundwater discharge influence than the other locations.

The C site is showing overall discharge conditions (Table 4-4). The values for CNW, CSW (10 cm) and CSE are all relatively similar to one another in both the FLUX-LM and VFLUX2 models. The CNE location has lower discharge compared to the other rods in FLUX-LM, but shows higher discharge than the other rods in VFLUX2. Based on

the temperature map for the C site (Figure 4-7), CNE is not expected to have a large amount of groundwater discharge compared to the other rods, as is shown in the FLUX-LM results.

Overall, VFLUX2 was more problematic than FLUX-LM when applying it to real shallow streambed temperature data. Although FLUX-LM is limited by the requirement of no diurnal signal, this can be compensated for rather easily by using average daily or weekly temperatures (Kurylyk et al. 2019). Therefore FLUX-LM can be used for both summer and winter data, and with caution during the fall and spring transition periods. However, the diurnal signal was too weak to use VFLUX2 in the winter, and data during the transition period here in the fall showed poor results, limiting its applicability to primarily the summer. There was no advantage of having continuous time flux data due to the uncertainties, so no conclusive relationship between flux and temporal events, such as changes over a day or during a precipitation event, could be developed. For a full analysis of these processes, use of a complete water flow and heat transport numerical model may yield better results. With a better sampling device resolution, finer diurnal signal amplitudes could be measured which would improve the VFLUX2 results (Soto-López et al. 2011), however this equipment is more costly. For the same resolution, FLUX-LM appears to be more robust.

4.3.1.5 Well Water Levels and Stream Stage

Figure 4-4C shows the water level in the near-shore wells (locations in Figure 4-2) over the study period of approximately one year. For all four wells, the level tends to be lowest in the late summer and begin to rise around the end of October. This matches to the approximate time that trees lose their leaves in Barrie. The water level in the wells remains higher throughout the winter, with some lows around February/March. All show a sharp increase around March 10th, 2020, which reflects a precipitation event mixed with peak snowmelt. There is a gradual decrease in water level from the end of March through to July. This coincides with the time that the riparian vegetation would begin using more water for ET. These seasonal trends match what is observed in the stream levels up and downstream in Figure 4-4B.

A fairly regular diurnal pattern can be seen in all of the wells and the stream from the start of the data collection in August through to the start of November, and then again from the start of March through to July (Figure 4-13). However, occasionally a diurnal signal can be observed in the water levels during the winter months, which is likely linked to snowmelt (discussed fully below; Figure 4-13B and C, Figure 4-14, Table 4-5). In the summer, CS has the largest diurnal signal. At the B site, the diurnal signal at BN is larger than at BS (Figure 4-13A). However, in the spring as the diurnal signal first starts to appear, all wells seem to have more comparable diurnal amplitudes (Figure 4-13D and Table 4-5). The diurnal amplitude upstream is higher than what is seen downstream.

For a majority of the year, the diurnal pattern oscillates with peak water level at anywhere from 24:00-07:00 and lowest levels in the afternoon from 13:00-19:00 (Table 4-5). This diurnal pattern has an asymmetric shape, with a sharp fall in water level in the afternoon followed by a more gradual increase. This diurnal signal is likely due to evapotranspiration. The riparian zone has deciduous tree vegetation cover that stretches

between 10-30 m away from the stream. Trees will begin to transpire during the day causing a drop in water level, with peak evapotranspiration in the afternoon. During the night, ET drops off and the water level slowly rises. The diurnal signal is strongest (larger amplitude) for several of the wells in August 2019, whereas it is strongest in the stream in the spring (2020). This suggests that ET more strongly impacts the entire stream when water levels are higher in the spring, and affects groundwater at these monitoring locations more during baseflow summer conditions. Differences in the amount and type of vegetation, and in the soil material surrounding each of the wells (Figure 4-1) may cause the differences in diurnal signal amplitude between locations in the late summer (Figure 4-13A). Upstream from the study site, not shown in Figure 4-1, there is a larger riparian area, including wetlands, that may contribute to greater ET in the spring and may potentially dry up and not support ET in the late summer.

Briefly in the spring (February 23rd – March 5th, 2020) the pattern changes from peaking in the night to peaking in the afternoon (Figure 4-13C). This pattern is likely due to the freeze/thaw cycle as temperatures increase above freezing during the day, causing snowmelt, and then decrease below freezing again during the night. This freeze-thaw pattern is also seen periodically throughout the winter, due to days of above-freezing temperatures causing snowmelt in the winter months (Figure 4-13B and Figure 4-14). Figure 4-14A shows the depth of snow on the ground and the air temperatures measured at a nearby Environment Canada weather station. When the air temperature peaks around 5°C on December 22nd and December 23rd, 2019, the stream stage and well water levels shown in Figure 4-13B go from being relatively steady to showing distinct diurnal

afternoon peaks. This pattern has a sharp increase in water level in the afternoon followed by a gradual decrease through the night, as has been reported in streams previously by (Gribovszki et al. 2010). Figure 4-13C shows the end of this snowmelt period in the spring, where the afternoon water level peak switches back to a night peak on March 5th, 2020, representing a switch from snowmelt to evapotranspiration diurnal signals.

Several other causes of diurnal patterns that have been reported in the literature have been considered and dismissed here. Diurnal patterns in water demand and extraction from municipal well fields has been shown to cause diurnal changes to groundwater and surface water levels (Gribovszki et al. 2010). In Barrie, municipal wells are in a deeper confined aquifer and not expected to interact on a diurnal scale with the shallow unconfined groundwater and surface water of Dyment's Creek. If such an interaction was occurring, the diurnal signal would be expected all year rather than solely in the warmer months. In addition, diurnal variations in stream level have been shown to be accentuated in non-vented loggers when the barometric logger is located far from the stream such that it is at a temperature different from the stream logger's (Cuevas et al. 2010). In this study, a barometric logger was placed in a tree about 3 m away from the stream at a height of 1 m from the ground, and another was hung at ground surface height within a 1 m deep groundwater well located <1 m from the stream. The temperature recorded at both loggers was similar to the temperature of the stream water, but with larger diurnal fluctuations (Figure B-3). The amplitude of temperature fluctuations in the stream were around 1.4°C compared to 5.0°C and 8.5°C for the well and tree loggers, respectively. The temperature amplitudes in Cuevas et al. (2010) that were shown to

accentuate diurnal effects differed by 11°C, greater than what is seen here. Stream stage was corrected using the pressures from both transducers and the difference in resulting diurnal stream stage amplitude was negligible. Based on the recommendations of Cuevas et al. (2010), data from July 30th, 2019 onwards were corrected using the barometric pressure from the logger placed in the well, although the tree logger does not appear to increase the measured diurnal signal. For the purposes of this study the diurnal signal is not considered to be accentuated by pressure transducer effects.

The wells respond nearly simultaneously with one another and the stream to precipitation events (Figure 4-4 and Figure 4-13A). There is a sharp increase, or rising arm, in the water level at the start of the rain event and a shallower decrease, or falling arm, as the system returns to pre-rain conditions. Such fast and sizeable response during wet and dry periods of the year suggests the well levels reflect bank storage during rain events, where the rise in stream level causes a gradient towards the groundwater, temporarily raising the water table near the shore. There will also be a rising water table from percolation through soil, however for these wells located near shore, bank storage likely dominates over the precipitation percolation signal. All wells except CS have a similar increase in water level during a rain event. Well CS tends to have a smaller rise in water level from rain events, which may be due to its greater distance from the stream than the other three wells (Figure 4-2). At well CS, there is a mucky floodplain on the inside of the meander causing the well to be located 5 meters from the stream channel. The snowmelt signals, observed periodically throughout the winter and in the spring, are almost negligible at this CS well (Figure 12). At CN the snowmelt signal is the strongest

of the wells, which may be in part due to the dumping of snow into the stream from a nearby parking lot as mentioned above in the stream section (section 4.3.1.1).

The hydraulic gradient between groundwater at the bank at the wells, and the adjacent stream water was not measured. However, relative changes in well and stream levels can provide qualitative information about how the gradient is changing over time (e.g., Figure 4-15). The stream stage was first subtracted from the well level for each time step, and then the value from the previous time step is subtracted from the current time step value. A positive resulting value represents an increase in the parameter over time (effectively an increase in the difference between well head and stream head) and negative values represent a decrease over time. An increase over time could be due to (i) a rise in well level, (ii) a drop in stream level, (iii) both rising over time but a larger rise in the well, or (iv) a decrease in both over time but a larger drop in the stream level. Viseversa is true for a negative value/ decrease over time. Therefore, positive values represent a change in hydraulic gradient conditions towards discharge; the system may either be experiencing an increase in discharge from one time step to the next, or if initially recharging, the system may be experiencing lower recharge over time.

Figure 4-15 shows the temporal changes in the gradient during an afternoon rain event on August 21st, 2020 and a midday rain event on August 22nd, 2020. A 1-hour moving average was applied to smooth the data. Prior to the rain event, values hovered around zero, representing minimal changes in the difference in head between the waters over time. During the rain event there is a distinct shift from around zero to negative values, followed by a sharp peak to positive values. This supports the bank storage effect

mentioned above. Early in the rain event, the stream level rises more than the well levels (also observed in Figure 4-4 and Figure 4-13A) causing a gradient towards recharge to the groundwater. The increase in well level, and eventual drop in stream level causes a sharp reversal to positive values over the course of a couple hours, although not as large in magnitude as the initial drop. There is then a gradual decrease in values back to zero, which shows the gradual decrease in water table height as the bank storage water is released and the system returns to regular conditions. The temporal change in gradient due to snowmelt is a similar response as the precipitation events but muted in magnitude (not shown), indicating an initial rise in the stream level greater than the rise in the wells.

The effect of the diurnal signal on the temporal changes in gradient shown from August 23rd to 26th, 2019 on Figure 4-15 indicates that in the summer months the values are negative in the afternoon, sharply change to positive in the evening and then gradually return to zero overnight and through the morning. This implies a greater flux of groundwater to the stream in the night. In April, however, the values tend to be positive midday and negative in the evening (not shown). This suggests that in the late summer ET more strongly impacts the wells, and in the spring ET impacts the stream more, matching with the interpretations from Table 4-5.

4.3.1.6 Conceptual Model

The findings from these hydrology measures show that Dyment's Creek is dominantly a gaining stream along this study reach, with increases in stream discharge from up to downstream indicative of overall groundwater inputs (matches observations of previous studies Roy and Bickerton 2012; Fitzgerald et al. 2015). The stream is flashy and responds simultaneously with the near-shore water table wells to precipitation, suggesting bank storage is a dominant process in the near-stream subsurface (transition zone). This occurs because the stream rises faster than the water table, causing a temporary and localized reversal in hydraulic gradients that drive stream water infiltration into the ground adjacent to the stream. Based on visual observations during precipitation events, it is possible that overbank flooding also occurred, especially on the north bank of stretch B and the south bank of stretch C, causing additional mixing of surface water and groundwater in the riparian zone. Fast declines in stream level lead to stronger groundwater discharge to the stream, including potentially as seeps along the banks, which were often observed in the low-lying areas adjacent to sharp changes in topography near Dyment's Creek.

Diurnal fluctuations, due to evapotranspiration from late March – November and snow melt in early March and throughout the winter, are observed in both the stream levels and the water table wells, with evidence of this driving similar patterns in groundwater flux to the stream. In the summer when ET is strong, fluxes to the stream are lowest in the afternoon, with maximum groundwater discharge expected overnight. Overall, stream and well levels are higher in the winter and lower in the summer months, likely reflecting the effect of ET leading to drier conditions in summer. However, the groundwater fluxes across the streambed remain similar between the summer and winter, with perhaps greater magnitude fluxes observed in the spring and fall. This reflects the balance between ET versus precipitation and snowmelt across the different seasons.

Despite overall being a gaining stream, a majority of groundwater discharge is spatially restricted to near the shores due to the predominance of hyporheic flow in the middle of the stream, especially notable at the B site. Areas of focused downwelling associated with hyporheic flow occur upstream of culverts (road crossings), stick dams (maybe snow/ice dams too), and sediment islands, with associated upwelling areas expected downstream of these features. However, these focused hyporheic upwelling and downwelling areas are predominantly avoided for sampling in the rest of the study.

4.3.2 Landfill Leachate Contaminants

4.3.2.1 Contaminant Sources Affecting Streambed Groundwater

Shallow groundwater samples were collected from 30 mini-piezometers installed 15 cm below the streambed in 5 transects of 3 mini-piezometers at each of the B and C stretches (Figure 4-2). Only 10 of the mini-piezometers, those located closest to the landfill at each site, were sampled for PFAS and BP. Sample collection occurred three times throughout the study year (August 20th, 2019, November 26th, 2019, and March 5th-6th, 2020). An early round of sampling was performed for just ammonium immediately after mini-piezometer installation on July 23rd-24th, 2019. A complete data set (ammonium, AS, anions, cations, SRP, VOC, metals, PFAS, BP) was received for August, while PFAS data for November and March are still awaiting analyses, and in March only VOC and SRP data have been received. Therefore, March groundwater concentration data will not be discussed further here.

Artificial sweeteners were detected in all groundwater samples (Figures 4-16 and 4-17). Two distinct contaminant sources appear from this data: (i) the landfill leachateimpacted groundwater characterized by elevated saccharin (> 50 ng/L), with occasionally cyclamate present, and (ii) another contaminant source, likely modern wastewater escaping from leaky sewers in the area, characterized by elevated acesulfame (>100 ng/L) and sucralose (> 100 ng/L). Additionally, shallow groundwater samples here could be influenced by surface water, background groundwater, or a mix of any of these sources, all characterized by low concentrations of both saccharin and acesulfame (<50 ng/L and <100 ng/L, respectively). Saccharin and cyclamate have been commercialized for decades and were used quite heavily in the 1960s, whereas acesulfame and sucralose became commercially available in the early 1990s. Roy et al. (2014) showed how AS can be used to distinguish leachate from older (pre-1990s) landfills from modern wastewater sources based on the absence of acesulfame and sucralose. The landfills studied here were operational and closed within the early 1960s, therefore only saccharin and cyclamate are expected in the leachate from these landfills. Any acesulfame or sucralose must be from a modern source of contamination, and as shown in Van Stempvoort et al. (2011) that source is likely wastewater. Saccharin and cyclamate are also present in modern wastewater; however, in oxic conditions these compounds are more likely to biodegrade than acesulfame or sucralose (Lange et al. 2012). A Pearson correlation was calculated for the log normalized groundwater concentrations from the August and November sampling campaigns (n=60) as shown in Figure B-4. Sucralose was only detected in a third of samples and had a very strong correlation to account (0.81).

Cyclamate was only detected in 13% of samples yet had a strong correlation with saccharin (0.62). There were moderate negative correlations between all other AS analytes.

Plotting acesulfame against saccharin, the two sources of AS contamination are clearly distinguished (Figure 4-18). Based on the criteria outlined in Table 4-6, to be discussed further below, samples that are strongly believed to be wastewater influenced are plotted as yellow squares, while the leachate-impacted groundwater samples are plotted as red crosses. For samples with high concentrations of saccharin, acesulfame is always less than 100 ng/L, and for samples with greater than 100 ng/L acesulfame, there is less than 50 ng/L saccharin. Surface water samples collected during the sampling campaigns (n=6) are plotted as green triangles and represent the typical maximum acesulfame and saccharin concentrations that could be in the mini-piezometer groundwater samples because of hyporheic flow or short-term stream recharge, such as during precipitation events. Groundwater samples that were believed to be primarily surface water influenced are plotted as blue diamonds, and consistently plot beneath the surface water samples. This further suggests that accould are values detected in groundwater at or below around 100 ng/L are likely due to mixing with surface water through processes such as bank storage or hyporheic flow. Note that samples that were believed to be a mix between these three groundwater influences, based on the criteria in Table 4-6, are excluded from Figure 4-18 for clarity as they obscure the demonstration of source influences discussed above. The two samples collected at B20S, however, are included as orange circles on Figure 4-18. The B20S location shows strong wastewater

influence in August, plotting near the top of the y-axis, whereas in November there is strong leachate influence with the point plotting near the middle of the x-axis on Figure 4-18. This suggests a shift in groundwater flow paths at this location, rather than a mixing of the sources, which is discussed fully below.

The concentrations of chloride (Cl) and bromide (Br) were used in an attempt to further distinguish contaminant sources. Chloride concentrations can be elevated in landfill leachate, as well as wastewater, but are also typically high in urban groundwater in temperate climates due to road salt inputs (Roy 2019). Chloride concentrations are not notably greater closer to the landfill in this stream; however, bromide concentrations are higher closer to the landfill. Chloride to bromide mass ratios (Cl/Br) can be used to help distinguish various contaminant source influences for each sample. Mullaney et al. (2009) determined that Cl/Br ratios >5000 typically represent road salt, values between \sim 500–1000 represent sewage, landfill leachate was typically between 150–200, and dilute groundwater ratios were generally <200. Roy (2019) used a biplot of Cl/Br to Cl to evaluate different chloride sources, including landfills, and found general dominance of road salt for urban streams with substantial overlap between sources, potentially complicating source identification. Figure 4-19 shows log-log plots of Cl/Br versus Cl for groundwater and surface water samples from August and November 2019. The data falls along a general mixing line showing high road salt influence on the top right of the figure which may be obscuring the influences of leachate and wastewater. There are no background dilute groundwater samples included in these plots but, based on previous work by Roy (2019), moving down along this mixing line likely represents mixing with

background groundwater which would plot on the lower left hand side of these graphs. The surface water samples tend to plot near the higher end of the mixing line near many of the shallow groundwater samples with Cl/Br ratios near 4000 indicating that the stream surface water is likely very influenced by road salt. The samples that fall below the mixing line, in August B15S, C20N and C30N and in November B15S, and B20S, may represent strong landfill leachate influence because these same locations also had high saccharin detections. The Cl/Br ratios for these samples are larger than what is reported in Mullaney et al. (2009) for landfill leachate, however this is likely due to mixing with road salt contaminated waters raising the Cl content and thus the Cl/Br ratio. Interestingly, many of the samples flagged as wastewater influenced plot near the lower Cl end of the mixing line, including COM, COS, and in August B20S, and may represent the wastewater composition with less influence from surface applied road salt. Overall, there is a road salt influence on the chloride levels in the stream and shallow groundwater that is overpowering what is seen from the landfill in a majority of samples. Given the close proximity of the stream to numerous roadways and parking lots, a high chloride concentration in this stream is unsurprising. For these urban stream samples, Cl/Br mass ratios were supportive when added to other information in distinguishing samples strongly affected by landfill leachate from samples impacted by other contamination sources. The few samples with the highest leachate influence were separated from the mixing line on Figure 4-19, but did not fall within the range for leachate reported in the literature. This does, however, support that the samples with high saccharin are likely not from the same source as those with high acesulfame.

Ammonium concentrations are often high in landfill leachate and are therefore used as a leachate indicator compound (Christensen et al. 2001; Buss et al. 2003), but could be elevated due to other sources, such as degrading organic matter within stream sediments, fertilizers, or wastewater. Ammonium has been shown to impact streams near landfills; however, due to heterogeneous composition within municipal waste and attenuation in the environment through cation exchange and nitrification, it can be difficult to assess leachate impact through analysis of ammonium as the only constituent (Buss et al. 2003; Lorah et al. 2009; Yusof et al. 2009; Milosevic et al. 2012; Thomsen et al. 2012). Ammonium results for the shallow groundwater samples from July, August and November are plotted in Figure 4-20. The shore closest to the landfill (south for B site, north for C site) typically has higher ammonium concentrations, which matches the results for saccharin in the AS analyses (Figure 4-16, 4-17), except for at CON and C10N, which have wastewater and background groundwater influences, respectively. At C20S in August there is a very large concentration of ammonium detected that is not observed in the saccharin results. At B20S, high ammonium concentrations occur with high saccharin in November, but are low in August when wastewater influence is apparent in the AS results. Overall, there is a very strong correlation between ammonium and saccharin and a strong correlation with cyclamate in groundwater (Figure B-4). Thus, the ammonium detected in these samples is likely indicating landfill leachate contamination. These findings do suggest that high ammonium concentrations are representative of leachate, but not of wastewater (Table 4.6). Ammonium can be transformed to nitrate in oxic conditions, which may occur along the wastewater flow pathway. Additionally,

ammonium concentrations were low (<0.6 mg/L) in stream samples likely due to transformation. Given the ammonium data shown here for August and November, and considering the additional July ammonium sampling period, it is clear that at the B20S location, the July and November concentrations (>180 mg-N/L) indicate leachate influence while the August concentration (1.3 mg-N/L) does not. This supports the likelihood that a shift in groundwater flow paths in August resulted in wastewater influenced groundwater discharging to the stream near B20S.

Several other common leachate constituents were correlated to either saccharin and/or ammonium and are included in the Pearson correlation in Figure B-4. A few volatile organic compounds, such as benzene, chlorobenzene and naphthalene had moderate to strong correlations with these leachate tracers (Figure B-4 and B-5A), and weak negative correlations with wastewater tracers (Figure B-4 and B-5B). These compounds are often found in landfill leachate and would not be expected in wastewater. Some samples with elevated levels of leachate tracers had lower than expected concentrations of these VOCs, which may be due to the volatization of the VOC (e.g., points in Figure B-5A where some samples with elevated ammonium had low concentrations of benzene). Chloroethane has a moderate correlation with acesulfame and sucralose, and a negative correlation with saccharin and cyclamate, suggesting a possible connection to the wastewater source (Figure B-5C and 5D). Chloroethane has been detected in raw and treated wastewater samples, and its presence may be linked to the chlorination of drinking water (Otson 1987). Some samples with elevated acesulfame had lower than expected levels of chloroethane, again potentially due to the volatization of

chloroethane in these samples. Sulfamic acid and a number of metals including chromium, nickel, cesium, cobalt, niobium and boron had moderate to very strong correlations with saccharin, and negative correlations with acesulfame, suggesting input from the historic landfill and not wastewater (Figure B-4).

From all these lines of evidence, a classification was developed for the main contaminant sources influencing each shallow groundwater sample location at the B and C stream stretches (Figure 4-21). Table 4-6 shows the criteria used to distinguish the following sources at these study sites: landfill leachate (LL), wastewater (WW), surface water influence (SWI, as in hyporheic flow path), and background (BK, for samples with no dominant influence). Not all criteria indicated in Table 4-6 has to be met within a given classification, as some minor mixing and potential for attenuation mechanisms affecting each location is expected. Samples meeting multiple criteria from two of the sources were shown as a mix between the two by separating them with a slash in Figure 4-21. Artificial sweeteners and ammonium were the main criteria used to distinguish sources, in addition to consideration of some common leachate constituents, such as certain inorganics and VOCs. A basic assessment of redox conditions, using McMahon and Chapelle (2009), resulted in most samples showing variable conditions; leachate influenced samples, though, had a tendency to fall within the range of methanogenesis and surface water influenced samples tended to have more oxidizing conditions. Hydrogeological flow assessments from section 4.3.1 were considered as further evidence of the potential contaminant source influences. Figure 4-21 shows the final

classification for each sampling location, illustrating the overall spatial influence of different contaminant sources at the B and C stretches.

4.3.2.2 Shallow Groundwater Contaminant Patterns

The spatial distribution of the contaminant sources at stretch B is further illustrated in Figure 4-16. Saccharin was the most dominant of the AS found in the groundwater mini-piezometer transects at the B stretch, reaching a concentration of 46200 ng/L (Figure 4-16), indicating strong landfill influence at this stretch. The highest concentration of saccharin per position along the stream typically occurred on the southern shore and was as much as three orders of magnitude higher than the concentrations measured at the middle or northern shore positions (see transect 15 m). Locations with high saccharin often had high concentrations of cyclamate, although cyclamate was detected less frequently, as was the case for AS plumes in Roy et al. (2014). Based on the temperature map (Figure 4-6) showing higher discharge near the shores, the elevated concentrations observed along the southern shore were expected due to the proximity of the landfill (Figure 4-1). The north shore mini-piezometers, while also receiving groundwater inputs, did not show the presence of saccharin, presumably due to the landfill location being predominantly to the south. The low levels of AS detected at the northern shore mini-piezometers suggest a surface water influence on background groundwater, which fits the conceptual model of frequent bank storage and potential for overbank flooding at the north shore during high flows. These processes would also explain the detection of low levels of acesulfame in samples from the south shore with

large amounts of saccharin, since acesulfame is not expected within the leachate due to the age of the landfill predating the onset of acesulfame usage. Concentrations of saccharin and acesulfame were low in the mini-piezometers in the middle of the stream, often around 100 ng/L or less (Figure 4-16), which is typical of surface water concentrations observed in this stream. This is not surprising as hyporheic exchange in the middle of the stream was suggested in the temperature map at the B stretch (Figure 4-6). Slightly higher concentrations of acesulfame (but still within the range of surface water influence) are observed along the B2 m transect, where downward hydraulic gradients were measured with the potentiomanometer.

In August, the B20S sampling point had high concentrations of acesulfame and sucralose, paired with negligible saccharin, suggesting a wastewater source of contamination, but this location had a change to landfill dominance in November (Figure 4-16). This was also observed in the ammonium results (Figure 4-20). In November, there were small amounts of acesulfame and sucralose with negligible saccharin detected at B10N suggesting an influence from wastewater contaminated groundwater (Figure 4-16). The nature of this change at stretch B is quite uncertain; however, with no sanitary sewers located near the south side of the B site (based on City of Barrie sanitary sewer diagrams), the wastewater influenced groundwater is potentially a deeper groundwater path coming from the residential area to the north which discharges at the southern bank. The water table at the southern shore rises more than the water table at the northern shore between August and November (Figure 4-4C), and the temperature rod nearest B20S shows recharge in August compared to discharge in November (rod BSW on Figure 4-

10A). This suggests a potential change in the flow system, with greater groundwater flow entering the stream from the north in August to more southern groundwater flow path inputs to the stream in November. This has been shown before by Karan et al. (2013), which demonstrated how groundwater discharge to a stream's north shore had flow paths coming from both the north and south. Also, the stick dam just upstream at this location may be adding further complexities to the flow paths in the area, as was observed in the potentiomanometer hydraulic gradient measurements (Figure 4-8).

Figure 4-17 shows the AS concentrations for the groundwater mini-piezometer transects at stretch C. The artificial sweetener results show that the spatial distribution of groundwater from the landfill and wastewater sources appears to be driven by the stream meanders. Groundwater discharge tends to be focused along the outside edge of stream meanders (see model simulations in Cardenas 2009) with discharge often extending towards the middle of the stream as well. At stretch C, the upstream meander starts around the 40 m transect, goes through the 30 m transect and ends around the 20 m transect, with the outside edge of this meander towards the northern shore (landfill side). The concentrations of saccharin in these northern shore mini-piezometers are two to three orders of magnitude higher than the other locations in this stretch. At the 30 and 40 m transects, elevated saccharin is also observed in the middle mini-piezometer locations. The downstream meander then starts around the 20 m transect, bending with the outside edge towards the south for the 10 m and 0 m transects. Many of the mini-piezometers from this half of the stream (0N, 0M, 0S, 10M, 10S, 20M, and 20S) have elevated concentrations of acesulfame and sucralose (180-880 ng/L and 70-2000 ng/L,

respectively) with negligible saccharin (< 50 ng/L). This suggests that a wastewater source is affecting groundwater that is flowing from the south. Sewer lines from the south-southwest may be the source of this wastewater plume. Location C30S also has elevated concentrations of acesulfame and sucralose, indicating influence from the wastewater plume at this location on the southern bank. Two samples, C10N and C40S, were flagged as likely background groundwater or surface water influenced, due to relatively low levels of AS and inconclusive concentrations for most of other indicators outlined in Table 4-6.

Considering the classification of different contaminant sources above (Figure 4-21), a conceptual model was developed for the shallow groundwater contaminant sources and pathways at the two study stretches. Both sites have evidence of receiving groundwater from both sides of the stream (i.e., from north and south). At the B site, there is strong leachate influence along the southern shore, with temporary wastewater influence at B20S in August and B10N in November. These wastewater influences may represent deeper groundwater flow paths from north of the stream. Surface water influences are stronger near the middle of the stream and towards downstream (2 m transect) due to the mixing of surface water in the shallow sediment in areas of hyporheic flow. Mini-piezometers along the northern shore were also influenced by surface water, where bank storage and overbank flooding were suggested to occur in the hydrogeological assessment. Generally, there is a stronger leachate influence observed at all locations in November.

At the C site, changes in contaminant source influences are due to GW-SW interaction processes caused by the stream meanders. The landfill leachate influence is strongest near the northern and middle mini-piezometers of the upstream meander that bends towards the landfill on the north shore. Wastewater influence is observed in the mini-piezometer locations near the downstream meander that bends towards the south, with the southern and middle locations generally showing stronger wastewater influence (except for the C0 m transect which shows wastewater inputs at all three locations). Surface water influences are observed in two of the samples along the southern shore, which potentially could be due to increased likelihood of overbank flooding on this bank. Location C10N had a weak signal from all sources, and may represent background groundwater for this area, although surface water and unpolluted background water are not easily distinguished. As was observed for B20S, flow paths to this stream stretch may shift over time, causing temporal variability in the relative groundwater inputs from the areas to the north and south of the stream. This means that the spatial variability in sample sources (Figure 4-21) is not constant; longer study analysis would strengthen the evidence of the dominant long-term leachate discharge zones at Dyment's Creek.

4.3.2.3 CECs in Shallow Groundwater

Both PFAS and BP compounds were detected in leachate-impacted (high saccharin) groundwater samples collected at Dyment's Creek in the 2018 leachate survey (Chapter 3) with DC-B and DC-C representing the B and C sites in this chapter, respectively. For this part of the study, samples for the CECs PFAS and BP targeted the

five mini-piezometers from each site that were closest to the banks by landfills (north for C site, south for B site). CECs were detected in all samples analyzed to date from these 10 groundwater sampling locations. However, many of these CEC compounds can be found in landfill leachate and in wastewater (Chen et al. 2016; Hu et al. 2016), which exemplifies the need to distinguish these sources to determine the landfill's impact with respect to CECs on the stream. Most of these shallow groundwater sampling locations were strongly, partially, or periodically influenced by the landfill, with some influence from the wastewater source or surface water (Figure 4-21) based on the AS and common constituent classification (Table 4-6) analysis above. For the following CEC analyses, the August B20S sample is included as solely wastewater influenced and the November B20S sample is considered leachate influenced, due to each sample strongly meeting the criteria set for each source on those sampling days (e.g., Figure 4-18).

From the BP analysis suite, for which data were received for both August and November, only bisphenol A (BPA) and bisphenol S (BPS) were found. The pattern of BP concentrations strongly matches the landfill-influenced locations suggesting little contribution from wastewater, potentially due to the tendency for BPA to biodegrade in oxic environments (Careghini et al. 2015). The concentrations of BPA and BPS ranged from below detection limits to 7400 ng/L and 840 ng/L, respectively (Table 4-7 and Figure 4-22). These two compounds were detected in the four samples from Dyment's Creek in Chapter 3 at ranges of 540-6100 ng/L and 69-540 ng/L, respectively. Thus, these historic landfills are a source of high BPA, and some BPS, to the endobenthic zone.

The relationship between the concentrations of PFAS from wastewater and leachate contaminant sources is more complex than for the BP compounds. Elevated concentrations of total PFAS (Σ_{27} PFAS; only samples from August campaign to date) were found in samples associated with landfill leachate as well as samples associated with wastewater (Figure 4-23A). Distinguishing PFAS inputs from leachate and wastewater is further complicated by knowing that the impacted areas at these stream stretches may change over time, as was shown for B20S above. PFAS compounds have a higher tendency to sorb to aquifer material than AS, especially for long chain PFAS. PFAS concentrations have been shown in the literature to lag behind inputs due to long aquifer residence times (Sunderland et al. 2019; Briggs et al. 2020). With all this in mind, it may be better to consider the PFAS composition alongside concentrations when trying to distinguish landfill leachate from wastewater influence. Modern wastewater has been shown by Weber et al. (2017) to have a higher percentage of perfluoroalkyl carboxylic acids (PFCAs; ~60%) than perfluoroalkyl sulfonic acids (PFSAs; ~30%) with the dominant compound being perfluorooctanoic acid (PFOA). The survey of CECs in leachate from historic landfills in Chapter 3 shows that older landfill leachates frequently have higher percentages of PFSAs. Also, detections of the compound PFECHS (perfloroethylcyclohexanesulfonate), not typically found in wastewater, can be an indicator of landfill leachate at this site (Chapter 3). The main use of PFECHS is as an erosion inhibitor in aircraft hydraulic fluids, but it is possible that it was used in consumer products such as resistors (De Silva et al. 2011) or printer ink (MPART HHWG, 2020), or PFECHS may have precursors that are present in municipal landfill leachate.

The composition of the PFAS compounds in the six leachate influenced samples (as determined above using AS and common constituent analyses) in this study were used to confirm the influence of landfill leachate at these locations. For these samples, the average percentage of PFSAs is 91% (Figure 4-23B), clearly distinct from the typical wastewater composition mentioned above. Also, the dominant compound in these samples, especially for stretch B, is PFECHS, which on average composes 72% of the total PFAS concentration at the B site (Figure 4-23B). The most dominant compound at stretch C is perfluorooctanesulfonate (PFOS), composing on average 64% of the total PFAS detected at the leachate influenced samples locations are indeed from the landfills, with some potential differences in composition between the two landfills.

The wastewater influenced samples do not appear to have clear indications of PFAS from modern sewage. Despite having a contrasting artificial sweetener composition, sample C0N has a similar PFAS composition as the leachate influenced samples at the C site, as can be seen in Figure 4-23B. One difference is that samples C20N, C30N and C40N have a greater percentage of short chain perfluoroalkyl acids (PFAA) than at C0N. If the flow system changed, causing the leachate plume to move away from the area around C0N and a greater influence from a wastewater plume to enter, there will still be PFAS that originated from the landfill plume sorbed to the sediment, even if that is not apparent in the AS analysis (due to lower sorption tendencies). Short chain PFAA will more readily move with the other compounds, such as saccharin, that do not strongly sorb while longer chain PFAS will lag behind

(Sunderland et al. 2019). Sample CON could possibly include PFAS from wastewater; however, it does not have a similar percentage of PFCAs (~60%) and dominance of PFOA, seen in modern wastewater by Weber et al. (2017). In their study, where the wastewater plume mixes with a fire training area plume, the lower wastewater concentrations were overwhelmed by the large PFAS concentrations of the fire training area plume. Concentrations of PFAS compounds in septic systems, reported in Table 3 of Subedi et al. (2015), were often lower than what is seen in this study for leachate impacted groundwater. For example, the median concentration of PFOA, the dominant wastewater PFAS compound, was shown to be 14.6 ng/L in septic systems (Subedi et al. 2015), but is detected here in leachate influenced samples at a median concentration of 130 ng/L. Thus, at this location, if there are PFAS inputs from the wastewater, they are potentially masked by the legacy inputs observed from the landfill.

Sample B20S also does not show clear wastewater influence. This location has a higher PFCA percentage of 17% compared to the rest of the B site, which has an average of 5% PFCA (Figure 4-23B). However, this PFCA percentage is still less than reported for wastewater (Weber et al. 2017). Many of the PFSA concentrations at B20S are larger than what was reported for septic systems by Subedi et al. (2015), while a few of the PFCAs are at lower concentrations at B20S than reported for the septic samples (e.g., perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA)). Sample B20S has notable concentrations of PFECHS and short chain PFAA, suggesting that, at one point, there was a landfill influence at this site, and that the short chain PFAA from the leachate plume have not yet desorbed. Ammonium data

indicates that this location was leachate influenced in July, suggesting that perhaps this shift in contaminant source influence towards the wastewater plume occurred not long before sampling in August. HFPO-DA (commercial name GenX) is detected at this location as well, however this compound was invented to replace PFOA in 2009 and therefore would not be expected to be in a landfill of this age. A smaller concentration of HFPO-DA is also detected at B15S and may represent a mixing of the leachate and wastewater contaminant plumes there as well. Concentrations of HFPO-DA observed here range from 1.9-5.1 ng/L, similar to those observed by Brandsma et al. (2019) in drinking water downgradient of a fluoropolymer manufacturing plant in the Netherlands. These patterns may become clearer once more of the collected samples are analyzed.

Overall, it appears that the leaky sewer is not a main source of PFAS at any of the shallow groundwater sampling locations, and thus, likely does not contribute much PFAS to the stream. Another piece of evidence for wastewater not contributing much PFAS to Dyment's Creek is that the change in PFAS mass discharge across the study reach was predominantly due to increases in PFSAs, especially PFECHS and PFOS. There was hardly any increase in PFCA mass between the up and downstream locations, which would be expected if wastewater was influencing the surface water. These data will be fully discussed below in section 4.3.2.6.

The background influenced groundwater sample, C10N, had a very low total PFAS concentrations of 28 ng/L (Figure 4-23A), which is about a quarter to half of what is seen in the surface water samples (section 4.3.2.6). The PFAS composition at C10N differs from that of the other groundwater samples (Figure 4-23B) and perhaps is
influenced by trace PFAS concentrations in precipitation, or occasional mixing with surface water or wastewater. Sample B2S, which has influences from both surface water and landfill leachate, differs in composition from the leachate samples at the B site with a higher PFCA percentage of 15% and a low total PFAS concentration of 261 ng/L. However, at B2S PFOS and PFECHS compose 79% of the total PFAS concentration, supporting the classification of a mix of landfill leachate and surface water influence at this location.

The range of total PFAS (Σ_{27} PFAS) for leachate-impacted groundwater was 530-31000 ng/L, with an average of 10300 ng/L and a median of 4500 (n=6, Table 4-7, Figure 4-23A). Of the 27 PFAS compounds analyzed, 5 were at levels lower than detection limits in all samples (PFHxDA, PFDoDS, ADONA, 9-CI-PF3ONS and 11-CI-PFOUdS; see Table B-2 for full compound names). The higher C number PFCAs PFDoDA-PFTeDA (C12-14; see Table B-4 for full compound names) were detected at very low levels (<0.032 ng/L) in the surface water and were not detected in groundwater (although it should be noted that minimum detection limits for groundwater samples were all >0.034 ng/L). In the samples, these compounds contributed to less than 0.01% of the total PFAS concentration and are not included in further analyses. Although elevated PFOS concentrations are detected at both sites, PFECHS is by far more dominant at the B site (Figure 4-23B), similar to what was observed in Chapter 3. The range in total PFAS (Σ_{17} PFAS) for the Dyment's Creek samples from the leachate survey in Chapter 3 was 3000-13000 ng/L, with an average 6900 ng/L (n=4). The total PFAS values from Chapter 3 exclude 10 PFAS compounds that were tested for here. The sum of these additional 10

compounds, predominately (60-100%) perfluoropentanesulfonate (PFPeS) and perfluoroheptanesulfonate (PFHpS), measured in the six leachate influenced groundwater samples for this chapter ranged from 26 – 1300 ng/L (average 550 ng/L), indicating that the maximum total PFAS values detected at the B site and C site in Chapter 3 (13000 ng/L and 4500 ng/L, respectively) could be notably higher if tested for all 27 PFAS compounds. However, it is not expected that having included those 10 compounds would increase the maximum from Chapter 3 to the maximum concentrations detected in August, 2019 of 31000 ng/L.

At stretch B, transects 5S and 15S have notably higher total PFAS concentrations, two orders of magnitude higher than what is seen at B2S and B10S (Figure 4-23A). A similar spatial trend is seen at the C site, where the C30N sample is about twice as high as C40N, and about an order of magnitude less than the maximums at the B site. These data show the drastic spatial variability at these sites. With a separation of only 5 m, there is nearly two orders of magnitude difference in the shallow groundwater concentration at B5S, B10S, and B15S. If stretch B had been sampled every 10 m, in a similar manner as stretch C, these high concentration locations at 5S and 15S may not have been captured. It is also possible that even higher concentrations have been missed in between the current spacing. This shows the benefit of creating a detailed conceptual model of groundwater-surface water interaction, in order to identify discharge, recharge or hyporheic flow zones, and therefore potential high ecotoxicology risk zones.

Pearson correlations and biplots between the emerging contaminants and tracers show that accould and saccharin have similar but low correlation values to many of

the PFAS compounds. This may be because of variation in leachate composition spatially. This may also be due in part to the shifting of the contaminant plumes. As the plume shifts, contaminants with lower tendencies to sorb will move conservatively with the groundwater whereas others may be retarded. Changes to redox conditions in the shallow groundwater, potentially caused by periods of hyporheic flow, bank storage, or overbank flooding which occur at this site, could result in degradation of other leachate constituents that are typically persistent in anoxic groundwater conditions. Attenuation of PFAS and other persistent compounds may be less impacted from these varying biogeochemical conditions as other leachate constituents. With a limited data set, it is difficult to conclusively determine correlations between parameters as any potential outliers have a large effect on the result.

4.3.2.4 Endobenthic Zone Exposure to Contaminants

To the best of our knowledge, this study is among the first and most detailed reported for PFAS compounds in a landfill leachate plume interacting with a surface water body. Briggs et al. (2020) analyzed PFAS in groundwater 0.2-1.0 m beneath a creek for the six compounds that are under investigation by the United States Environmental Protection Agency for the development of drinking water standards (perfluorobutanesulfonate (PFBS), perfluoroheptanoic acid (PFHpA), PFOA, PFNA, perfluorohexanesulfonate (PFHxS), and PFOS) and found a total PFAS maximum of 1610 ng/L with a median of 52.2 ng/L. The values in this current study are greater than what was seen by Briggs et al. (2020), with a maximum for those six compounds of 4605

ng/L and a median of 492 ng/L. This indicates that even without including the dominant compound at Dyment's Creek, PFECHS, the values seen in the shallow groundwater are comparable with those of other sites.

The full suite of analytes measured in the groundwater samples will be used in ecotoxicology testing as part of the larger project focus. As expected here, and previously shown by Roy and Bickerton (2012) and Fitzgerald et al. (2015), there were a number of common landfill leachate constituents detected in the shallow groundwater beneath the stream that represent direct exposure to endobenthic organisms. Some of these compounds exceeded drinking water or aquatic life standards (Table B-1). Chloride is above the water quality guideline for aquatic life in 93% of groundwater samples. Benzene and chlorobenzene were above their respective guidelines in groundwater samples located near the shore on the landfill side. A high value in one of these compounds typically meant the other was present as well. Trichloroethene, toluene, 1,4dichlorobenzene, 1,2-dichlorobenzene, and fluoride also exceeded water quality guidelines in at least one sample. There is some question as to the applicability of these aquatic life guidelines for groundwater matrix and endobenthic organisms, as well the effect that mixing of multiple contaminants will have on toxicity levels (Roy et al. 2019).

Chapter 3 demonstrated that despite their age, historic landfills can have CEC concentrations that exceed water quality guidelines. Table 4-7 compares the maximum concentrations seen in the leachate influenced groundwater samples from this chapter, all samples from the leachate survey (Chapter 3, n=48), ranges from the Hamid et al. (2018) review of PFAS in landfill leachate, and the current water quality guideline if available.

Many of these guidelines are preliminary and require continued research to substantiate. As stated above, guidelines do not factor in the mixing of multiple contaminants that could have additive toxicity effects (Ahrens and Bundschuh 2014; Roy et al. 2019). Much of the PFAS toxicology work is in its early stages, and as a result many current guidelines do not consider that multiple PFAS compounds are often found together in the environment along with other chemical stressors that, especially in the case of historic landfills, could cause chronic exposure to organisms over multiple generations (Ahrens and Bundschuh 2014). Of note from Table 4-7 is the PFECHS maximum of 30000 ng/L, higher than what was seen at any of the 48 samples taken from the 20 historic landfills studied in Chapter 3. The compound with the next highest concentration was PFOS, an order of magnitude smaller than PFECHS and similar to what was seen in Chapter 3. Higher detections of PFECHS may be due to greater solubility or larger emissions (De Silva et al. 2011). As mentioned above, the main use of PFECHS is in aircraft hydraulic fluids, but it is possible that it was used in consumer products or may have precursors that are present in landfill leachate (De Silva et al. 2011). The toxicity levels of PFECHS to aquatic organisms are still unknown, although preliminary work has suggested endocrinedisruption at water concentration levels higher than detected here (Houde et al. 2016).

4.3.2.5 Epibenthic Zone Exposure

Given the spatial distribution of the leachate-impacted shallow groundwater concentrations noted above, the greatest impact to the stream benthic zone was expected to be along the bank closest to the landfill (south for B site, north for C site). From the

temperature maps, this matched high groundwater flux areas at the B site near B15S and at the C site near C30N and C40N. High contaminant concentrations associated with high groundwater flux are expected to maintain higher concentrations at and just above the streambed surface, thereby causing contaminant exposure to the epibenthic zone. Within areas of hyporheic flow, towards the middle of the stream and the eastern end of the B stretch, downwelling and horizontal flow leads to lower concentrations in the shallow sediment and restricts upward flow of contaminated groundwater. Thus, strong hyporheic exchange can limit spatial exposure to the epibenthic zone organisms.

Based on the hydrogeological data, groundwater flux to the stream in the summer would likely be highest during the night/early morning, when the water table is the highest after recovering from ET and the temporal change in gradient is towards discharge conditions (Figure 4-15). In the winter, diurnal effects are small and there is not a time of day more prone to discharge conditions. Although in the winter, the stream discharge is higher than in the summer (Figure 4-4), yet the groundwater flux is comparable (Figure 4-10) and therefore dilution of contaminants with faster stream flow may occur in the winter. Spring and fall may have higher groundwater fluxes and represent periods of potentially greater risk to epibenthic organisms.

During precipitation events, there is a temporal change in gradient towards the banks followed by a reversal towards discharge conditions that is stronger than what is observed for diurnal changes. Therefore, with potential for stream water infiltration into the surrounding sediments, the initial pulse of discharge, or release of bank storage water back to the stream, may be surface water influenced with notable dilution of groundwater

contaminant concentrations. Along with the potential of overbank flooding for very high flows, there is more likely a mixing of contaminated groundwater with surface waters as a result of precipitation events. But higher groundwater inflows may last past flushing of surface water and give later periods of higher contaminant flux.

An attempt to measure spatial patterns in contaminant flux across the sediment interface, as a proxy for epibenthic risk, was made using YSI multiparameter probes placed just above the sediment-surface water interface. Epibenthic zone parameter levels (T, pH, EC, Cl) were compared to the overlying surface water values on July 16th, 2019 (Table B-3 and B-4). Note that an approximately 7 mm rain event occurred on the preceding day and stream flow was elevated above base flow; however, this was still completed during the summer low stream flow period. As a result, though, the bank storage effect seen in the conceptual model may result in surface water that had initially entered banks now re-entering the stream, hiding any groundwater signal. Overall, at a majority of locations along the transects there were negligible differences between the parameters measured within the flowing water column (above the streambed) compared to those measured against the streambed.

Values for EC, a common indicator of dissolved contaminants, ranged from 1020-1290 μ S/cm near the sediment bed (note the next largest EC value was 1180 μ S/cm; Table B-3, B-4). Values for EC measured when the probe was suspended in the surface water ranged from 1130-1160 μ S/cm. The highest EC value (1290 μ S/cm) was measured at the northern shore of stretch C along the 40 m transect. Based on the temperature maps in Figure 4-7, this is potentially a higher groundwater discharge area, but also an area

with lower stream flow rates. Figure 4-7 clearly shows how a sediment island divides flow at this location, with a majority of water moving through the southern larger channel. This northern, more stagnant area may allow for greater concentrations of contaminants with less dilution from flowing water. The shallow groundwater samples most influenced by leachate typically had an EC 400-600 μ S/cm greater than surface water, while the average for all shallow groundwater samples was 200 μ S/cm greater than surface water.

At the northern shore of the 40 m transect at stretch C, the pH was 6.94 compared to 7.63 when the probe was suspended in the surface water, much closer to the average leachate-impacted groundwater pH of 6.8. This location, as well as multiple locations along the south shore at stretch B had slightly elevated chloride concentrations based on the field meter; however, the shallow groundwater analysis showed that chloride concentrations at this site are greatly influenced by road salt inputs. At the B site, the location along the 20 m transect shows the most contaminant influence, with a chloride concentration 240 mg/L greater than the surface water and a pH of 7.08. This location was shown in the groundwater analysis to have mixed leachate and wastewater contaminant plume influences throughout the study year. This location is also just downstream of a stick dam and has a greater (2x average) water depth and perceptibly less stream flow velocity.

Overall, these data show that there is generally not a notable difference in parameters between the streambed and flowing water column on this day. Further work should be carried out to complete this analysis during base flow conditions, to ensure that

bank storage was not the main reason for negligible differences. Also, even during baseflow conditions, the stream flux is roughly four orders of magnitude greater than the groundwater vertical flux, resulting in rapid dilution of groundwater as it enters the flowing stream. As is, this suggests that the concentrated contaminant exposure will be limited to the shallow sediment and potentially the interface between sediment and surface water, and that by a distance just above the sediment, concentrations are considerably diluted. However, an exception to this is areas where the stream flow rate is low, such as near C40N and B20S. When stream flow is low, there is less dilution of discharging groundwater. Impacts may also be more apparent in sheltered areas along stream edge or for seepage along the banks. Exposure to contaminants will also increase in areas of higher contaminated groundwater flux and as shown by Conant (2004), streams can have rather localized areas where the groundwater discharge is much higher than surrounding areas due to heterogeneity. High groundwater discharge locations are the ideal nesting habitat for several fish, some of which spawn in the autumn months, resulting in potential exposure to higher contaminant concentrations if groundwater is contaminated (Briggs et al. 2020).

4.3.2.6 Surface Water Exposure and Mass Loading

Discharge of leachate-impacted groundwater adds contaminant mass to the stream, potentially increasing the contaminant concentrations in the surface water. Knowing the concentrations of contaminants in the surface water is important for assessing pelagic and epibenthic organism exposure. Mass inputs are important in determining downstream mass loading of contaminants to other receptors such as lakes. By sampling upstream and downstream of the landfill, an increase in contaminant concentrations indicates input from the landfill (if no other contaminant source in that reach). The added contaminant mass may not be apparent when only considering concentration differences due to inputs from upstream contaminant concentrations and the potential for dilution from inputs of clean water. Therefore, comparing upstream to downstream mass discharge (concentration multiplied by stream flow) provides a better indication of contaminant input over the stream stretch. However, in considering concentrations or mass discharge, some contaminants may be attenuated or removed during stream transport due to biodegradation, volatilization, biological uptake, or sorption to sediment, and via recharge or hyporheic flow, which adds some uncertainty to the assessment.

Surface water was sampled at the upstream and downstream locations (Figure 4-1) 21 times between June 2019 and July 2020, and at the middle location three times, on August 20th and November 26th, 2019 and March 5th, 2020. Three sets of samples have not yet been received from the laboratory and another three sets of the surface water samples, two from June 2019 and one from August 2019, were not included for mass discharge analysis due to missing stream discharge measurements. The upstream and downstream sampling locations only encompass about 60% of the stream that is adjacent to the three landfills (Figure 4-1) and therefore there is likely a greater input of contaminants from these three landfills than what is captured here.

Ideally, the same stream water would be measured as it passes by the upstream and downstream sampling locations, however this was not practical given requirement for manual sampling and limited staff resources. Therefore, stable conditions, both for stream flow and groundwater inputs, are required to make acceptable comparisons between the two locations. The differences in mass discharge between the up and downstream locations for saccharin and ammonium were plotted against the number of hours between sampling at the two locations to ensure that there was no effect on the mass discharge from the sampling timings (Figure B-6). The longer amount of time between sampling upstream and downstream while on the rising or falling arm of an event could result in greater differences in mass discharge between the upstream and downstream sites, but generally during steady conditions timings were not an issue (Figure B-6). Also, sampling in the days after a precipitation event, during the falling arm of the stream stage peak, may result in dilution of landfill leachate-impacted groundwater from bank storage water releasing back to the stream. For these reasons, four samples were not included due to precipitation events either occurring during sampling, or in the preceding days causing sampling to occur on the falling arm of the stream stage. For these samples, the change in stage between sampling times was measured to be greater than 1.7 cm at the downstream location, while all other sampling periods had a change in stage of 0.7 cm or less.

There is an increase in surface water concentrations of saccharin and ammonium, both parameters highly indicative of landfill leachate inputs, from the upstream to downstream sampling locations for all of the samples received to date (July 2019 to January 2020; Figure 4-24). Note that the concentrations observed in the upstream

sample may be due to the fact that there is more landfill area further upstream of this sampling location. This trend holds true for mass discharge as well, where the downstream mass discharge is greater than what is measured upstream (Figure B-7) as shown by the positive difference in mass discharge in Figure 4-25. The average percent increase in saccharin and ammonium mass discharge from upstream to downstream is 278% and 264%, respectively. Thus, there is a clear sign of an impact from groundwater discharging from the landfill on the stream water quality.

Stream acesulfame concentrations stay relatively constant from upstream to downstream and switch back and forth as to which is greater (Figure 4-24B). However, the difference in mass discharge of acesulfame shows that downstream is typically greater than upstream throughout the year, aside from one point in January 2020 that is negative and may be due to uncertainty associated with the stream discharge values (Figure 4-25). This means that there is an overall increase in the amount of acesulfame in the surface water as it passes through the study site, indicating input from groundwater influenced by a wastewater source. This wastewater could be contributing CECs to the overall mass load of contaminants in Dyment's Creek.

Ammonium exhibited a trend of increasing mass discharge towards the winter months, while any such trend for saccharin is slight at best, although a full annual data set would be required to substantiate this observation (Figure B-7A and 4-24B). This trend is unlikely from a strong increase in leachate-groundwater inputs, and rather may be due to less attenuation of ammonium in the stream (plant uptake, nitrification) in the winter months due to colder temperatures (Buss et al. 2003), as was seen at a pond receiving

landfill leachate in a companion study (Hua, unpublished) within the broader landfill project. Unfortunately, there is no nitrate data in winter to see if it follows a similar trend as ammonium (Figure 4-25). The negative difference in mass discharge for nitrate at the start of July 2019 indicates a higher mass discharge upstream than downstream and may be due to influences from a wetland further upstream from the landfill study site, losses of nitrate along the stream stretch, or uncertainty in stream discharge measurements.

Saccharin and acesulfame mass discharges do not seem to have a strong seasonal trend of increasing differences in mass discharge into the winter months. There are large concentrations of saccharin and acesulfame on July 29th and August 9th, 2019 that were not seen for ammonium (Figure 4-24). The reason for the resultant high mass discharges (Figure B-7) is unclear. Both dates had small rain events within 24 hours of sampling, but the change in stage between sampling upstream and downstream was not large enough to remove these samples. For the upstream location, there could have been inputs of wastewater infiltrating from the storm sewer system, combined with sewer overflow, increasing the AS concentrations. Increases in the downstream concentrations, especially seen for saccharin, may be due to the rising stream level capturing seepage of contaminated groundwater that discharged along the banks and low-lying wet areas adjacent to the stream (observed on several occasions). In these places, ammonium may have oxidized or volatilized leaving AS to potentially accumulate. This indicates that with some precipitation events there may be an increase in the concentrations of saccharin and acesulfame, and thus potentially other CECs that are non-volatile, observed in the stream at some point post-rain.

Three surface water samples (upstream, midstream, and downstream) were collected for bisphenols and PFAS from the August 20th and November 26th, 2019 sampling campaigns, as well as two samples (upstream and downstream only) from July 3rd, 2019. No bisphenol analytes, not even BPA and BPS, were detected in any surface water samples. This could be due to dilution in the surface water lowering the concentrations past detection limits. Also, since BPA will biodegrade under aerobic conditions with a half-life of 3 - 38 days (Careghini et al. 2015) and has moderate sorption to aquifer materials (Ying et al. 2003), it is possible that the non-detects are due to these attenuation processes. In the groundwater samples, BPA and BPS had strong correlations to PFOS (Figure B-8). The trendlines from the biplots in Figure B-8 were used to predict what the bisphenol concentrations should be in the stream based on the stream PFOS concentrations in order to determine if the non-detects were due to detection limits or degradation. Results show that in all surface water samples, except one upstream sample, the predicted BPA concentrations were greater than detection limits, suggesting that degradation or sorption may be at play. For BPS, all concentrations except one downstream concentration were below detection limits. BPS is considered to be more persistent in the environment (Chen et al. 2016), therefore the non-detects here may be due to detection limits. All predicted bisphenol concentrations were less than the aquatic life guideline for BPA of 3.5µg/L by at least two orders of magnitude.

In the five stream samples analyzed for PFAS (two dates, no data yet for November 26th), the range in total PFAS (Σ_{27} PFAS) was 50-130 ng/L (average 80 ng/L). The total PFAS concentration increased from upstream to downstream (Figure 4-26).

This increase is almost entirely due to an increase in PFSA concentrations, especially PFOS and PFECHS, with most PFCA concentrations remaining nearly constant across this study reach. This results in the composition of total PFAS within the surface water changing substantially downstream. The percent composition of PFCA ranges from 68-73% upstream to 38-53% downstream. This suggests that increasing concentrations are largely a result of the input of leachate-influenced groundwater to the stream along the landfill length. The increase in concentration from upstream to downstream is larger in July than in August, and as a result the composition shift towards PFSA is greater.

The annual contribution of PFAS from the landfill between the upstream and downstream monitoring locations was determined to be at least 32 g/yr (Table 4-8). This was determined using the annual average baseflow stream discharge of 0.025 m³/s multiplied by the average difference in PFSA concentration between the upstream and downstream locations from July 3rd and August 20th, 2019. PFSA concentration was used instead of total PFAS because there is greater confidence in the input of PFSA from solely landfill leachate than PFCA or other PFAS groups (when using total PFAS concentrations, the annual contribution only increases to 35 g/yr). The PFAS contributions to the stream from the landfill are likely an underestimate due to the locations of the upstream and downstream surface water sampling sites. There is 515 m of landfill adjacent to the stream, however only 60% of this length is covered in this study (Figure 4-1). Therefore, when taking the difference from the upstream and downstream concentrations in order to determine PFAS input from the landfill, there is likely leachate-impacted groundwater entering the stream upstream of this study's

upstream location, as well as downstream from this study's downstream location. Fitzgerald et al. (2015) examined a 28 m reach that was about 50 m downstream of this current study's downstream sampling point and found notable leachate-impacted groundwater discharge. To estimate what the contribution of PFAS could be if sampling locations encompassed the entire landfill, the mass flux was multiplied by 1.67, yielding an annual mass discharge of 53 g/yr (Table 4-8). This assumes that both the contribution of leachate-impacted groundwater and the discharge are the same further upstream and downstream, which may not be the case, yet still provides a general estimate of the actual Dyment's Creek mass loading to Lake Simcoe. The annual mass discharge may also be underestimated because it does not include potentially greater mass loads during events.

A very crude estimate, assuming that the concentrations of PFAS and stream discharge measured over this study year were constant over time, suggests that since the landfill closed in the early 1960s, the landfill may have contributed 1900 g of PFAS to the downgradient receptor Lake Simcoe's Kempenfelt Bay. This value again only factors in the study reach (60% of the stream adjacent to the landfill), and when considering the entire landfill reach, may be as high as 3200 g. This value may also be an underestimate because the PFAS concentration has likely slowly diminished over time, with the preferential flushing of short-chain PFAA. These landfills contribute to the contaminant mass load in Kempenfelt Bay, and with additional inputs from other landfills in the area and a wastewater treatment plant (WWTP), there may be a threat to pelagic and benthic organisms due to chronic PFAS exposure. Kempenfelt Bay is also a source of drinking water to about half of the residents of Barrie, although the intake is ~4 km away from

where Dyment's Creek reaches the bay (South Georgian Bay-Lake Simcoe Source Protection Committee, 2015).

Scott et al. (2009) reported stream fluxes for individual PFAS compounds for streams located all across Canada (their Table 4). The flux values seen here are comparable to the values from their study observed in Big Creek (Norfolk County, ON) during 2005, which has a stream discharge an order of magnitude higher than Dyment's Creek. The values of PFAS mass discharge from the landfills along Dyment's Creek observed here are orders of magnitude smaller than the PFAS daily flux for WWTP influent and effluent (Guerra et al. 2014).

Finally, these findings also demonstrate that the inputs of landfill leachate contaminants from groundwater to this stream could be measured with surface water sampling for CECs like saccharin and PFAS, but not for all CECs (e.g., BPA). Without sampling the shallow groundwater beneath the stream at this site, it is clear that along this stretch, there is a contaminant source adding PFAS to the stream and any attenuation of PFAS does not mask these inputs. Only sampling the upstream and midstream location would still show a notable increase in PFSA; however, the PFECHS concentration increases more from midstream to downstream (Figure 4-26), as expected due to the higher concentrations of PFECHS in the groundwater at the B site. Future work could investigate how far downstream surface water samples still indicate leachate influence. Although PFAS are persistent and not expected to biodegrade in surface water, further input of clean groundwater to the stream could potentially dilute surface waters so that PFAS concentrations are below detection limits; however, the PFOS and PFECHS

concentrations detected here in surface water are between two - four orders of magnitude higher than detection limits. Briggs et al. (2020) reported PFAS concentrations in surface water of 163-242 ng/L over a 1 km reach receiving contaminated groundwater discharge, and then a gradual decrease to 111 ng/L for another 5 km downstream, indicating persistently high levels not greatly attenuated through dilution.

4.5 Conclusions and Implications

This study demonstrates how historic landfills can impact nearby streams with high contaminant concentrations, including CECs such as PFAS. Organisms experience chronic exposure to elevated contaminant stressors at this site, with leachate indicator compounds such as ammonium and saccharin showing high concentrations in the shallow groundwater of the streambed (max. 200 mg-N/L and 46 µg/L, respectively) despite landfill closure occurring approximately 60 years ago. Leachate contaminant concentrations are frequently two orders of magnitude higher in the shallow groundwater than in the surface water, demonstrating a much higher contaminant exposure for the endobenthic organisms than the pelagic or epibenthic organisms. However, the shallow groundwater of the endobenthic zone is rarely monitored by authorities when evaluating impacts of contaminant plumes on the surrounding environment, for example during annual monitoring of municipal landfills, and therefore impact to the stream may be underestimated if only collecting surface water samples. Elevated contaminant concentrations were detected in the stream surface water as well, with exposure varying both temporally and spatially. Epibenthic and pelagic organism risk will be greater in

high discharge zones near the shore located closest to the landfill during the lowest baseflow periods. Mass loadings of contaminants to the stream may also accumulate downgradient, impacting the Lake Simcoe ecosystem.

PFAS were detected in all groundwater samples up to $31 \mu g/L$, with the average concentration from leachate impacted locations being three orders of magnitude higher than in surface water samples. The dominant PFAS compounds were the PFSAs PFOS and PFECHS, the latter having a maximum concentration an order of magnitude higher than the former. With minimal definitive information on the toxicology of PFAS compounds, it is difficult to concisely evaluate the risk PFAS pose to organisms in this stream; however, based on preliminary work on the likelihood of additive toxicological effects between different PFAS compounds and other chemical stressors such as common leachate constituents (Ahrens and Bundschuh 2014; Roy et al. 2019), the risk posed to endobenthic organisms as undilute leachate-impacted groundwater discharges to the stream could be substantial. Mass loadings of PFAS and common leachate constituents to downgradient receptors, in this case Lake Simcoe, could be of considerable importance when taking into account that the long-term inputs of these chemicals could be possible for at least a half century.

Hydrogeological assessment revealed that groundwater flux, and thereby also concentrations and mass loadings that could threaten the benthic zone, had notable variation both spatially and temporally. The majority of groundwater discharge was located along the shores, with leachate contaminant input occurring at the shore closest to the landfill and only accounting for 10-20% of the distance across the stream. This results

in substantially higher risk to benthic organisms near the shore since hyporheic flow near the middle of the stream may create regions that experience minimal contaminant exposure or regular relief from leachate. Bank storage and overbank flooding may provide organisms living in the near-shore contaminant discharge zones temporary relief from chemical stressors. The spatial variability in shallow groundwater concentrations at this site are noteworthy, with leachate tracers such as saccharin varying three orders of magnitude from one of the near-shore to the middle stream sampling locations (46 000 ng/L versus 25 ng/L), a distance of only 1.1 m. Along the shore there is also pronounced variation in groundwater contaminants, as illustrated by total PFAS concentrations at one location two orders of magnitude higher than either 5 m up or downstream from that location (31 000 ng/L versus 710 ng/L and 260 ng/L). This detailed spatial assessment of stream conditions revealed patchy differences in contaminant exposure along the stream, indicating that a broad assessment of risk may not accurately describe what is being experienced by organisms in this ecosystem. Future work with this project will reveal if there are differences in endobenthic organism populations throughout different locations in the stream, as more pollution-tolerant species may be present at contaminant discharge locations. It is important to undergo a detailed spatial evaluation of the hydrogeological controls on the system, specifically including analysis of groundwater discharge across the streambed, in order to produce an accurate conceptual model that will allow monitoring to target the high contaminant discharge zones.

This conceptual model should also include assessment of diurnal, seasonal and event-based changes to groundwater flux. For streams with riparian cover,

evapotranspiration induced diurnal variations in water levels in summer results in greater groundwater discharge overnight and in the early morning. Therefore, in the summer there will be greater contaminant input to the stream overnight as respiration continues but photosynthesis stops, resulting in low DO groundwater discharge at these times that may pose a greater risk to organisms than during the day. The diurnal signals subside into the winter months, where snowmelt inputs are the driving factor for any diurnal changes in groundwater flux, so there is not an expected higher exposure at night. The groundwater fluxes were shown to be similar between the summer and winter, with larger discharge values potentially occurring in autumn and spring. In autumn, when stream levels are just starting to rise and groundwater discharge is high, there may be high exposure in discharge zones that are often the preferential nesting habitat for several types of fish, some of which spawn in the autumn months. In the summer, baseflow conditions result in less dilution of discharging groundwater than in the winter, however in the winter it would be expected that there is less microbial and plant activity. The start of a trend of increasing mass loading to the stream from the landfill during the winter months can be observed at this site for the leachate tracers ammonium and possibly saccharin, indicating the need for further work to more accurately evaluate risk into the winter months. Precipitation events increase the likelihood of mixing of surface waters with riparian groundwater through bank storage and overbank flooding; however, more fine-scale temporal analysis of stream concentrations during events is also needed.

Assessing the temporal and spatial variability of contaminated groundwater discharge to streams is important for ecological health, but also for how contaminated

sites are monitored. It can be argued that completing a detailed conceptual model of GW-SW interaction is especially beneficial for urban stream sites where multiple contamination sources and pathways may be present. This study demonstrates the need for groundwater sampling along the stream for evaluation of endobenthic exposure, but also shows the usefulness of spatially and temporally targeted stream sampling. With growing interest to revive urban streams, through cleanup efforts aimed at restoring natural conditions alongside the addition of recreational infrastructure for residents, a full understanding of groundwater contaminant discharge could greatly impact how such projects move forward and the overall success of restoration. Oftentimes, an aspect of urban stream restoration includes the natural re-meandering of the stream, but as shown here, that can cause complex spatial interactions between contaminant plumes along the stream. From all the conclusions and implications mentioned here, operators in charge of monitoring closed municipal landfills, as well as other contaminated sites, which have plumes interacting with surface water may have to change how they monitor these sites. They may not be making the best measurements, in terms of where and when they sample, to adequately capture the risk posed to the environment.

4.6 Figures and Tables

Table 4-1: Summary of previous published studies investigating landfill leachate plumes impacting streams and which indicator parameters were included in assessing leachate impact.

Study	Location	NH4 ⁺	AS	Cl	Р	Metals	VOCs	Inorganics	Comment
Borden and Yanoschak	North Carolina			✓		√	√	√	71 municipal landfills, active
1990	USA			•		•	·	·	or closed after 1984
Yusol et al. 2009	Malaysia	✓		✓	✓	\checkmark		\checkmark	Three active and closed landfills monitored for a year
Maqbool et al. 2011	Abbottabad, Pakistan					✓			One open landfill, monitored over all seasons
Milosevic et al. 2012	Denmark	✓		✓		~	✓	\checkmark	One closed landfill, monitored over all seasons
Thomsen et al. 2012	Denmark	✓		√					One closed landfill (same as above), using mass balance
Gooddy et al. 2014	UK	✓		✓					One landfill sampled quarterly for 2 years near urban stream
Fitzgerald et al. 2015	Barrie, ON, Canada	\checkmark	✓	✓	✓		✓	~	Same site as this current study
Stefania et al. 2019	Northern Italy	✓	✓	✓	✓			\checkmark	One old unlined landfill downstream of a new landfill

Ammonium (NH4⁺), artificial sweeteners (AS), chloride (Cl), phosphorous (P), volatile organic compounds (VOCs)



Figure 4-1: Map of study area along Dyment's Creek (blue line, arrows indicate flow direction), with estimated extent of the three landfills (A, B, C; red dashed line) located to both the north and south. Stream surface water monitoring locations are depicted as stars (5 pointed star = upstream, 6 pointed star = midstream, 7 pointed star = downstream) and detailed GW-SW assessment areas as yellow portions of the stream (Stretch B and Stretch C).



Figure 4-2: General layout of the instrumentation beside and within the stream (blue, arrows indicate flow direction) at the detailed GW-SW interaction study stretches at the (A) B site and, (B) the C site.



Figure 4-3: Schematic of potentiomanometer and drive-point sampling setup. A vacuum set up in the potentiomanometer allows for measurement of hydraulic head difference between the groundwater and surface water.

Table 4-2: Parameters and thermal properties used in temperature modelling to determine
groundwater flux across the streambed using FLUX-LM (Kurylyk et al. 2017) and
VFLUX (Gordon et al. 2012; Irvine et al. 2015).

	Parameter	Description	Value	Unit
FLUX- LM	Total thickness (d)	Total length of temperature-depth profile from the top (or second) to the bottom iButton	0.9 (0.8)	m
	Bulk thermal conductivity (λ)	Ability of the medium, sediment and water, to transfer heat	1.8	W m ⁻¹ °C ⁻¹
	Heat capacity of water $(c_w \rho_w)$	Heat required to raise the temperature of water by 1 unit; specific heat of water multiplied by the density of water	4.18E+06	J m ⁻³ °C ⁻¹
VFLUX2	Sampling rate reduction (Rfactor)	Positive integer which the number of samples per day in divided by; if entered as zero model chooses the best reduction so that the samples are as close as possible to 12/day	0	None
	Windows	Spacings between iButtons used to calculate fluxes	1, 2	None
	Pf	The period of the fundamental signal used to filter the data	1	day
	Porosity (n)	Fraction of void space in the sediment	0.39	None
	Thermal dispersivity (α*)	Empirical property of porous media determining dispersion characteristics	0	m
	Bulk thermal conductivity (λ)	See above	0.043	cal·s ⁻¹ ·cm ⁻¹ ·C ⁻¹
	Sediment heat capacity $(c_s \rho_s)$	Heat required to raise the temperature of sediment by 1 unit; specific heat of sediment multiplied by the sediment density	0.65	cal·cm ⁻³ ·C ⁻¹
	Heat capacity of water $(c_w \rho_w)$	See above	1.0	cal·cm ⁻³ ·C ⁻¹



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Figure 4-4: (A) Total precipitation, (B) stream stage at upstream and downstream locations, (C) water table well levels at the B and C sites on both the north and south banks (BN, BS and CN, CS respectively). Note that the water levels in (B) and (C) are not relative to one another (i.e., each is the height of water above its respective transducer).



Figure 4-5: (A) Stream stage over the study year compared with (B) manual stream flow discharge measured with a flow meter 18 times over the study year. Error bars represent 5% error calculated with the USGS method by Sauer and Meyer (1992). Arrows along the x-axis indicate dates influenced by precipitation events.



Figure 4-6: Contoured temperature maps showing the temperature measured at discrete points, indicated by black dots, at a depth of 10cm beneath the streambed for the B site in (A) Summer (July 9th, 2019) and (B) Winter (January 30th, 2019). Delaunay triangulation with linear interpolation was used to interpolate the data between measurement points. Cooler temperatures in summer and warmer temperatures in winter represent areas of potential groundwater discharge. Note the temperature scales here match the range of those in Figure 4-7.



Figure 4-7: Contoured temperature maps showing the temperature measured at discrete points, indicated by black dots, at a depth of 10cm beneath the streambed for the C site in (A) Summer (July 9th, 2019) and (B) Winter (January 30th, 2019). Delaunay triangulation with linear interpolation was used to interpolate the data between measurement points. Cooler temperatures in summer and warmer temperatures in winter represent areas of potential groundwater discharge. Note the temperature scales here match the range of those in Figure 4-6.



Figure 4-8: Vertical hydraulic gradient between groundwater and stream water measured at approximate depths of 20 cm and 50 cm below the streambed along the north shore of the C site and the south shore of the B site. These were measured with a potentiomanometer on June 18th - 19th, 2019. An upward gradient (discharge) is shown as positive. Locations along the stream coincide with those shown in Figures 4-2, with measurements for the B site extending past the main sampling stretch (bracketed). Blank spaces represent locations where the gradient was not measurable.



Figure 4-9: Temperature-depth profiles at the (A) B site and (B) C sites for rods located upstream and downstream (W and E respectively) near the north and south banks (N and S respectively) averaged over December 19th, 2019, which falls within a period of stable sediment temperatures. iButtons are located at depths of 0, 0.1, 0.2, 0.4 and 0.9 m below the streambed surface and have a resolution of 0.5°C.



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Figure 4-10: Groundwater flux results from FLUX-LM for each temperature rod at the (A) B site and (B) the C site (locations in Figure 4-2). Negative fluxes indicate discharge. Pink boxes show area of indiscernible flux magnitude and direction. Hollow symbols represent points of less confidence due to high RMSE values or large diurnal signals causing a range in temperatures at the upper iButton to be greater than 80% of the range in temperatures from the upper to lower iButton.

Table 4-3: Average, maximum and minimum groundwater flux values calculated with FLUX-LM over the study year for each temperature rod (locations in Figure 4-2). Negative fluxes indicate discharge.

Profile	BNW	BNE	BSW	BSE	CNW	CNE	CSW	CSE
Number of calculations	18	20	19	18	20	19	20	23
Average Flux* (m/yr)	-16	-6.0	-8.5	-7.6	-31	-9.8	-28	-25
Maximum Flux (m/yr)	10	20	29	21	4	21	-12	-4
Minimum Flux (m/yr)	-40	-48	-33	-36	-58	-34	-80	-46

*Note averages include values with an absolute magnitude < 10 m/yr for which the flux direction may be indiscernible



Figure 4-11: Example sediment temperature-time data showing strong diurnal signal in upper iButtons for the BNW temperature rod at depths of 0, 0.1, and 0.2 m below the sediment surface. A seasonal temperature signal is observed at depths 0.4 and 0.9 m.



Figure 4-12: Groundwater flux calculated for the three modelling depths used in VFLUX2 compared to stream stage in the late summer (August 15th – September 30th, 2019).

Table 4-4: Average groundwater fluxes calculated with VFLUX2. Negative flux values indicate discharge. Brackets show a second modelled depth and flux, when it is uncertain which depth produced a better result.

Season	Profile	BNW	BNE	BSW	BSE	CNW	CNE	CSW	CSE
	Modelling	5	5	5	5	15	5	5	5
Late	depth (cm)								
Summer	Mean flux	-22	40	69	57	-39	-52	-21	-26
	(m/yr)								
Spring	Modelling	5	5	10 (5)	5	15	5	10	5
	depth (cm)							(5)	
	Mean flux	50	50	67	59	-16	-69	-19	-25
	(m/yr)			(91)				(7)	

Late Summer: 8/15/2019 – 9/30/2019 Spring: 4/1/2020 – 6/15/2020



Figure 4-13: Stream stage (upstream and downstream) and nearby well levels (north and south at each of B and C stretches; location in Figure 4-2) showing the presence or absence of diurnal signals in (A) August, (B) December, (C) March, and (D) April.
		Water table wells			Surface water		
		BN	BS	CN	CS	Upstream	Downstream
August	Diurnal	2.4 cm	1.6 cm	2.2 cm	6.2 cm	1.1 cm	1.0 cm
(ET)	amplitude						(only start
							of month)
	Time of	16:00-	16:00-	17:00-	16:00-	17:00-	17:00-19:00
	Min	18:00	17:00	19:00	17:00	19:00	
	Time of	05:00-	05:00-	05:00-	05:00-	24:00-	05:00-07:00
	Max	06:00	06:00	06:00	06:00	04:00	
Early	Diurnal	2.5 cm	2.1 cm	2.6 cm	1.2 cm	3.1 cm	2.7 cm
March	amplitude						
(Snowmelt)	Time of	12:00-	12:00-	12:00-	12:00-	12:00-	12.00 14.00
	min	14:00	14:00	13:00	14:00	14:00	12.00-14.00
	Time of	16:00-	16:00-	16:00-	16:00-	16:00-	16.00 10.00
	Max	19:00	19:00	19:00	19:00	19:00	10.00-19.00
April	Diurnal	2.7 cm	2.6 cm	3.4 cm	2.1 cm	4.0 cm	2.7 cm
(ET)	amplitude						
	Time of	14:00-	14:00-	14:00-	13:00-	15:00-	14:00-17:00
	min	16:00	16:00	17:00	16:00	17:00	
	Time of	05:00-	05:00-	05:00-	05:00-	05:00-	05:00-07:00
	Max	07:00	07:00	07:00	07:00	07:00	

Table 4-5: Timing and magnitude of diurnal fluxes caused by evapotranspiration in August (2019) and April (2020), and by snowmelt in early March (2020).

ET = Evapotranspiration

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Figure 4-14: (A) Depth of snow on ground and air temperature with, (B) stream stage and nearby water table wells (north and south at each of B and C stretches; locations on Figure 4-2) responses for a mid-winter snowmelt event, with major melt signals being observed on December 22^{nd} and 23^{rd} when air temperatures are above 0°C; ND = no data



Figure 4-15: (A) Stream stage compared with (B) temporal changes in the hydraulic gradient between surface water and nearby water table wells (north and south at each of B and C stretches; locations on Figure 4-2) during precipitation events (August 21st and 22nd, 2019) and a regular summer diurnal period (vertical gridlines every 12 hours).



Figure 4-16: Artificial sweetener concentrations in shallow groundwater collected in mini-piezometers at stretch B from the (A) August 20th, 2019 and (B) November 26th, 2019 sampling campaigns. Note the different y-axis scales. (C) Map of shallow groundwater sampling locations at stretch B, with the landfill located on the southern shore.



Figure 4-17: Artificial sweetener concentrations in shallow groundwater collected in mini-piezometers at stretch C from the (A) August 20th, 2019 and (B) November 26th, 2019 sampling campaigns. Note the different y-axis scales. (C) Map of shallow groundwater sampling locations at stretch C with the landfill located on the northwestern shore (simply referred to as the north shore in text).



Figure 4-18: Biplot of acesulfame against saccharin concentrations for water samples collected on August 20th and November 26th, 2019. Red crosses, yellow squares, and blue diamonds represent groundwater samples categorized as being influenced by landfill leachate, modern wastewater, or surface water respectively. Green triangles represent surface water samples collected during groundwater sampling. Orange circles represent groundwater samples from B20S, which show strong wastewater influence in August and strong leachate influence in November. Refer to Table 4-6 for source classification.



Figure 4-19: Log-log plot of chloride to bromide mass ratios (Cl/Br) against the chloride (Cl) concentration on (A) August 20th, 2019 and (B) November 26th, 2019 with arrows representing ranges for various chloride sources or end-members, as reported in Mullaney et al. (2009). Labels indicate groundwater and surface water sampling locations (see Figures 4-1, 4-16 and 4-17).



Figure 4-20: Ammonium concentrations in shallow groundwater samples from 15 cm below the streambed in study stretches C and B, collected on July 3rd, August 20th, and November 26th, 2019. Refer to Figures 4-16 and 4-17 for maps showing labeled locations of groundwater mini-piezometers.

Table 4-6: Indicator parameters considered for classifying the dominant influence(s) on each shallow groundwater sample location for the B and C study stretches – landfill (LL), wastewater (WW) or surface water influence (SWI, as in hyporheic flow path), and the criteria for this determination (values in brackets are crude guide, not strict limits). Listed as background (BK) if there is no strong or dominant influence of any of the three above. Note that not all criteria have to be met within a given classification, with some minor mixing affecting each location expected.

	Landfill Influence	Wastewater Influence	SW influence
Artificial	High saccharin (>50 ng/L)	Low saccharin (<50 ng/L)	Low saccharin (<50 ng/L)
Sweeteners	Low acesulfame	High acesulfame	Low acesulfame (<100ng/L)
	(<100ng/L)	(>100ng/L)	
Ammonium	High (>10 mg-N/L)	Moderate (1-7 mg-N/L)	Low (<0.6 mg-N/L)
Inorganics	High Br (>0.1 mg/L)	Low Br (<0.1 mg/L)	Low Br (<0.1 mg/L)
	Low Cl/Br ~400	Higher Cl/Br	Higher Cl/Br
	High iron (10 -56 mg/L)	Moderate iron (3 -30	Low iron (<2 mg/L)
	Low SO ₄ ²⁺ (<4 mg/L)	mg/L)	High SO ₄ ²⁺ (>10 mg/L)
	Moderate Mn ²⁺ (>0.2	Low SO ₄ ²⁺ (<4 mg/L)	Low Mn ²⁺ (<0.2 mg/L)
	mg/L)	Moderate Mn ²⁺ (>0.2	
		mg/L)	
SRP	Moderate (~200 µg/L)	Moderate to high (>200	Low (<100 µg/L)
		μg/L)	
VOCs	High BTEX (>30 µg/L)	Low BTEX (<1 µg/L)	Low BTEX (<1 µg/L)
		Presence of chloroethane	
Redox	Methanogenesis	Variable	More oxidizing conditions
Flow	Discharge on temperature	Discharge on temperature	Area of hyporheic exchange,
	map	map	bank storage, or overbank
			flooding

	N	M	S	
<i>B2</i>	SWI	SWI	LL/SWI	<i>↑Downstream</i>
B5	SWI	LL/SWI	LL	
B10	WW/SWI	SWI	LL	
B15	SWI	LL/SWI	LL	
B20	SWI	SWI	LL/WW	
<i>C0</i>	WW	WW	WW	
<i>C10</i>	BK	WW	WW	
<i>C20</i>	LL	WW	WW/SWI	
<i>C30</i>	LL	L	WW	
<i>C40</i>	LL	LL	SWI	$\downarrow Upstream$

Figure 4-21: Classification of shallow groundwater sampling locations as landfill leachate influenced (LL), wastewater influenced (WW), surface water influenced (SWI), or background groundwater (BK), or a mix of these source influences based on the criteria in Table 4-7.

Table 4-7: Maximum values (ng/L) for CECs in the shallow groundwater influenced by landfill leachate in this study and the Chapter 3 leachate survey, compared to ranges seen for landfill leachate in the review by Hamid et al. (2018) and water quality standards in Canada and the USA.

Acronym	This	Leachate	Studies in Hamid et al.	Water Quality Guidelines	
	study	Survey	2018 review		1
	max	Maximums	(mostly modern landfills 1980s-current)	Value	Туре
PFBA	53	290	30 - 9300	$30\ 000^{1}$	Drinking water
PFPeA	88	200	330 - 6500	200^{1}	Drinking water
PFHxA	150	670	310 – 25 000	200^{1}	Drinking water
PFHpA	110	270	100 - 5800	200^{1}	Drinking water
PFOA	420	850	510 - 210 000	200^{1}	Drinking water
				70^{2}	
PFNA	21	1000	28 - 450	20^{1}	Drinking water
PFDA	0.17	6	19 - 1100		
PFUnA	0.04	16	3 - 120		
PFDoDA	<mdl< td=""><td>1</td><td>3 - 30</td><td></td><td></td></mdl<>	1	3 - 30		
PFTriDA	<mdl< td=""><td>7</td><td>1 - 18</td><td></td><td></td></mdl<>	7	1 - 18		
PFTeDA	<mdl< td=""><td>0.2</td><td>1 - 69</td><td></td><td></td></mdl<>	0.2	1 - 69		
PFHxDA	<mdl< td=""><td></td><td></td><td></td><td></td></mdl<>				
PFBS	770	710	$110 - 42\ 000$	$15\ 000^{1}$	Drinking water
PFPeS	1000				
PFHxS	1400	1300	$19 - 16\ 000$	600^{1}	Drinking water
PFHpS	700				
PFOS	2600	2800	44 - 6000	600^{1}	Drinking water
				70^{3}	
				6800^{4}	Aquatic life
PFDS	0.54	1.8	3 - 63		
PFDoDS	<mdl< td=""><td></td><td></td><td></td><td></td></mdl<>				
PFECHS	30000	9500			
8C1-PFOS	7.1				
FBSA	42				
FOSA	2.0	13	7 - 220		
HFPO-DA	3.0				
ADONA	<mdl< td=""><td></td><td></td><td></td><td></td></mdl<>				
9-CI-PF3ONS	<mdl< td=""><td></td><td></td><td></td><td></td></mdl<>				
11-Cl-PFOUdS	<mdl< td=""><td></td><td></td><td></td><td></td></mdl<>				
BPA	7400	29 000		3500 ⁵	Aquatic life
BPS	840	4800			

¹Health Canada 2019; ²USEPA 2016a; ³ECCC 2018a; ⁴USEPA 2016b; ⁵ECCC 2018b;



Figure 4-22: BPA and BPS concentrations in shallow groundwater from the sampling campaigns on August 20th and November 26th, 2019.



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Figure 4-23: (A) Stacked concentrations (note break in y-axis) and (B) relative composition (%, mass basis) of the 19 PFAS compounds that were detected in 10 shallow groundwater samples collected August 20th, 2019 (named according to locations show on Figures 4-16 and 4-17). Location names (bottom axis), leachate influence (top axis) and legend shared between both plots.



Figure 4-24: Surface water concentrations at the upstream and downstream sampling locations (as indicated on Figure 4-1) for (A) ammonium and nitrate (NO_3^-) and (B) saccharin and acesulfame. Dashed lines are only to guide the eye, as variation between sampling times is expected. Lines were excluded for nitrate due to the low frequency of analysis for this compound. Vertical gridlines at one-month intervals.



Figure 4-25: (A) Manual stream discharge measurements with error bars representing 5% error calculated with the USGS method by Sauer and Meyer (1992). Difference in mass discharge between the upstream and downstream sampling locations (as indicated on Figure 4-1) for (B) NH_4^+ -N and nitrate (NO_3^-) and, (C) saccharin and acesulfame. Vertical gridlines at one-month intervals. Dashed lines to guide the eye only as variation between sampling times is expected.



Figure 4-26: Surface water PFAS (A) concentrations and (B) percent composition for samples collected on July 3rd and August 20th, 2019. The 16 PFAS compounds included here all composed >0.1% of the total PFAS concentration in at least one sample (excluded PFAS compounds were non-detects or composed <0.07% of the total PFAS concentration in all samples). Refer to Table B-2 for PFAS compound names. PFCA (left two columns in legend; reds-yellows); PFSA and precursors (right two columns in legend; green-purple).

	Average downstream concentration (ng/L)	Average upstream concentration (ng/L)	Average difference in concentration ¹ (ng/L)	Mass discharge across study site ³	Estimated total landfill mass discharge ⁴ (g/yr)
		10.00	1.10	(g/yr)	
PFBA	11.51	10.33	1.18	0.93	1.55
PFPeA	9.55	9.83	-0.28	-0.22	-0.37
PFHxA	8.93	8.80	0.13	0.10	0.17
PFHpA	3.88	3.68	0.21	0.16	0.27
PFOA	10.04	8.26	1.78	1.41	2.34
PFNA	0.52	0.54	-0.03	-0.02	-0.04
PFDA	0.30	0.35	-0.05	-0.04	-0.07
PFUnDA	0.03	0.05	-0.02	-0.01	-0.02
PFBS	4.07	3.59	0.48	0.38	0.63
PFPeS	1.14	0.56	0.58	0.46	0.77
PFHxS	5.36	2.79	2.57	2.03	3.38
PFHpS	1.16	0.30	0.86	0.68	1.13
PFOS	29.64	8.70	20.94	16.51	27.51
PFECHS	15.64	0.62	15.02	11.84	19.73
FOSA	0.12	0.03	0.09	0.07	0.11
FBSA	1.63	1.10	0.53	0.42	0.70
ΣPFAS	103.53	59.53	43.99	34.68	57.81
ΣΡΓΟΑ	44.77	41.85	2.92	2.30	3.84
ΣPFSA*	57.01	16.55	40.45	31.89	53.16

Table 4-8: Study site contribution and estimated total landfill contribution to the stream PFAS mass discharge.

¹ Average of the downstream concentration minus the upstream concentration for July 3rd and August 20th, 2019; ³Calculated using the concentration difference across the study site; ⁴Calculated using the mass discharge across the study site multiplied my 1.67 to account for the study site only coving 60% of the landfill adjacent to the stream; *ΣPFSA including PFECHS

Chapter 5: Conclusions and Implications

5.1 Summary of Conclusions

Municipal landfills are a well-recognized source of pollution to the environment; however, new attention has recently been given to historical landfill sites that closed before modern regulations (≥30 years since closure). Unlike modern municipal landfills, historic landfills often lack infrastructure to prevent leachate plume migration and have been shown numerous times in previous work to impact nearby surface waters (e.g, Borden and Yanoschak 1990; Yusol et al. 2009; Maqbool et al. 2011; Milosevic et al. 2012; Thomsen et al. 2012; Gooddy et al. 2014; Fitzgerald et al. 2015; Stefania et al. 2019). Historic landfills are often located near surface water bodies and urban centres due to the thick sediments available for cover and ease of access, resulting in shorter flow paths and less attenuation of contaminants discharging to the environment (Coakley 1989; Lambou et al. 1990; Lisk 1991). Discharge of leachate-impacted groundwater to surface water poses a risk to the benthic and pelagic organisms, as well as any down gradient receptors.

Evaluating the risk posed to the environment from historic landfills is complicated by the many unknowns surrounding their location and leachate composition (Environmental Commissioner of Ontario 2010), especially for contaminants of emerging concern (CECs). CECs, such as per- and polyfluoroalkyl substances (PFAS), have been detected and broadly reviewed in modern, active landfills; however, until this study no extensive investigation of a broad number of CECs in numerous historic landfills had been completed. The purpose of this two-part study was to evaluate historic landfills

within Ontario as a potential source of harmful contamination to surface waters. A leachate survey of 20 landfills was completed to address the objective of accessing the prevalence of CECs in leachate-impacted groundwater from historical, closed landfills that may pose an environmental risk. A detailed investigation of an urban stream receiving contaminated groundwater from a group of historic landfills was completed to evaluate the potential risk posed to a stream ecosystem from leachate-impacted groundwater discharge. The last objective of this investigation was to assess the spatial and temporal variability of leachate-impacted groundwater as it discharges to a stream, with consideration of the different ecosystem compartments (i.e., endobenthic, epibenthic, pelagic zones, plus downstream ecosystems).

The findings from the leachate survey (Chapter 3; Propp et al. in press) were that many of the CECs investigated were found at elevated concentrations $(0.1s - 10s \text{ of} \mu g/L)$ across several of the 20 historic landfills closed 30-60 years ago. This included the artificial sweetener (AS) saccharin, PFAS, organophosphate esters (OPE), and cotinine. Some compounds showed consistent elevated concentrations across most sites (e.g., perfluorohexanoic acid (PFHxA), perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA), tris(2-butoxyethyl) phosphate (TBOEP), bisphenol A (BPA)) whereas other compounds have elevated concentrations that are observed less frequently (e.g., perfluoroethylcyclohexanesulfonate (PFECHS), perfluorobutanesulfonate (PFBS), perfluorononanoic acid (PFNA), tris(2-chloroisopropyl) phosphate (TCPP)). These results illustrate the strong variation that occurs both between and within landfills, likely due to the heterogeneous nature of waste age, composition, and biogeochemical conditions (Kjeldsen et al. 1998; Slack et al. 2005). The concentrations observed here are in many cases comparable to those found at modern municipal landfill sites, despite these landfills being closed > 30 years. Note that the results for several of the OPE are the first data for any landfill leachate, historic or modern, yet reported. Both modern and historic landfills pose a risk to the environment; however, historic landfills are often subject to less stringent regulation, are more likely to leak due to a lack of or degrading infrastructure such as liners or leachate collection systems, and are generally located closer to surface water bodies (Coakley 1989; Lambou et al. 1990; Lisk 1991). Thus, historic landfills may pose a greater risk to the environment than modern landfills when considering that the concentrations observed here are similar to modern sites yet the likelihood of leachate plume migration is larger for historic sites.

Attenuation of leachate concentrations, for example through dispersion or biodegradation processes, is possible for leachate-impacted groundwater. Many of the compounds detected here with elevated concentrations were found in samples collected from seeps and discharging groundwater entering surface water (e.g., all samples of DC-A, -B, -C, and HB-03 for PFAS; Figure 3-1B) from 30-60 year old landfills, showing that these sites can be chronic sources of CECs and other leachate contaminants and that attenuation processes cannot be assumed to remove contamination prior to environmental discharge. Many of the CECs exceed water quality guidelines in several samples, including PFOA and PFOS for drinking water, and BPA, pentachlorophenol, and 2,4dimethylphenol for aquatic life (including some samples of discharging groundwater), which is an indication of the seriousness of this contaminant threat posed by historic

landfills. However, the applicability of these guidelines is complicated due to the mixing of different toxic compounds (e.g., metals, ammonium, petroleum compounds, CECs), potential additive health effects (Ahrens and Bundschuh 2014; Sunderland et al. 2019), lack of guidelines for many CEC compounds, and the appropriateness of aquatic life guidelines for the groundwater matrix and endobenthic organisms (Roy et al. 2019). With the tendency for short distances between historic landfills and surface waters, combined with the extreme persistence of many CECs such as PFAS, discharge of leachate-impacted groundwater containing many of these CECs to surface waters may be common at a majority of Ontario's historic landfills.

The detailed stream investigation in Chapter 4 illustrates how groundwater with elevated concentrations of CECs discharges to a section of an urban stream adjacent to a set of 3 historic landfills. Despite landfill closure occurring around 60 years ago, the concentrations of the leachate tracers ammonium and saccharin in the shallow streambed groundwater were quite elevated (max. 200 mg-N/L and 46 μ g/L, respectively) and comparable to the maximums observed in the leachate survey (max. 225 mg-N/L and 51 μ g/L, respectively). PFAS were detected in all the shallow groundwater samples up to a maximum of 31 μ g/L for the Σ_{27} PFAS (total PFAS= 30 μ g/L for Σ_{17} PFAS from Chapter 3). The dominance of PFOS observed here in the samples near the C landfill site is similar to what is observed for older historic landfills in Chapter 3; however, the B site has strong dominance of PFECHS which was not observed in a majority of the 20 historic landfills studied in Chapter 3. This further demonstrates the variable composition

in leachate and affected groundwater plumes from historic landfills, even for those of similar age and geographic location.

The concentrations of leachate tracers and other constituents were generally two orders of magnitude higher in the shallow groundwater beneath the stream than in the stream surface water at this site. Generally, they were consistent across various seasons. This indicates a long-term chronic risk posed to endobenthic organisms, which may be greater than for epibenthic or pelagic organisms due to dilution in the surface water. Streambed exposure to leachate impacted groundwater has been shown here to have substantial variation spatially and temporally. At these sites, groundwater discharge is focused along the shores, covering a distance of about 10-20% of the stream width estimated from the temperature maps in Figures 4-6 and 4-7, with hyporheic flows dominating the middle portions and restricting contaminant discharge. As a result, leachate tracer concentrations in the shallow groundwater vary three orders of magnitude from the near-landfill shore to the middle of the stream (e.g., saccharin concentrations of 46000 ng/L and 25 ng/L, respectively, over a 1.1 m distance). Even along the shores there is substantial variation in concentrations, as illustrated by total PFAS concentrations at one location two orders of magnitude higher than either 5 m up or downstream from that location (31000 ng/L versus 710 ng/L and 260 ng/L).

The groundwater flux to the stream shows variation on diurnal, seasonal and event-based temporal scales, likely resulting in temporally variable exposure from groundwater contaminants to epibenthic and perhaps pelagic organisms. The magnitude of groundwater flux was shown to be similar in the summer and winter months, but might

increase in the spring and autumn. The summer fluxes were influenced by riparian evapotranspiration, which resulted in a diurnal pattern, with greater discharge overnight and a shift towards recharge in the afternoon. Contaminant fluxes are likely more complex around precipitation events due to bank storage and overbank flooding processes, which could cause greater mixing of surface water with riparian groundwater in the riparian zone. Baseflow conditions common in the summer months will provide less dilution of discharging groundwater as it enters the stream than when the stream has higher flow in the winter months. However, in the winter, there may be less attenuation of contaminants from plant and microbial activity. More broadly, despite these variations, long-term exposure to leachate contaminants could degrade surface water quality, posing a risk to pelagic organisms and downgradient receptors. Based on results of this study, the Dyment's Creek landfills are estimated to be contributing about 53 g/yr of PFAS to Lake Simcoe, through base flow periods (this might be higher with precipitation events added), with a rough estimate of 3200 g contributed since landfill closure. Over time, combined pollutant contributions from Dyment's Creek, other nearby urban streams, and a wastewater treatment plant to Kempenfelt Bay (Lake Simcoe) may be causing chronic detrimental effects on the lake's ecosystem and affecting the City of Barrie drinking water resource.

5.2 Implications and Recommendations

A majority of the historic landfill sites studied here, especially those closed within the last 30-60 years, have the potential to harm the environment due to elevated

contaminant concentrations in the surrounding leachate-impacted groundwater. Similar results are expected in the vast number of other known and unknown historic landfills in Ontario, and abroad, meaning the threat of historic landfills to the environment may be widespread. Environmental exposure to leachate-impacted waters appears to be chronic, lasting at least 60 years. Many CECs, such as some PFAS compounds, are extremely environmentally persistent, so continuous long-term exposure from these chemicals is expected to continue into the future. Moving forward, landfill operators should consider testing for the CECs found in this study, including PFAS and OPE compounds, BPA and cotinine. Multiple locations within a landfill site should be tested due to the variability of leachate composition. Monitoring for these compounds would provide a better assessment of the risk posed to the environment from historic landfill sites.

At a set of three landfill sites that were deemed to not have an adverse impact on an adjacent stream (Golder Associates, 2019), concerning concentrations of leachate constituents and CECs not measured in annual assessments were detected in both the shallow groundwater beneath the stream as well as the surface water. Endobenthic zone organisms were shown to have the highest leachate exposure, yet the shallow groundwater of the streambed is rarely monitored. By only sampling surface water to determine risk, common practice with landfill monitoring, the actual maximum risk posed to the ecosystem, specifically that of the endobenthic communities, is completely overlooked. To best evaluate risk, a detailed conceptual model of groundwater-surface water (GW-SW) interaction should be developed with adequate emphasis on the spatial and temporal variability of groundwater flux. In order to capture the maximum

concentrations, the location and timing of sampling should be carefully considered. It would be very beneficial to complete a preliminary investigation to identify the presence of discrete high discharge zones that may contribute substantial contaminant mass to the stream. For streams with riparian vegetation cover, GW-SW interactions will be influenced by diurnal evapotranspiration effects in the summer, suggesting that sampling during the morning prior to strong afternoon influences may be better. The relationship between seasonal changes in stream water level and groundwater discharge should be considered to determine when the contaminant mass loadings to the stream will be largest and least impacted by dilution and in-stream attenuation mechanisms (e.g., higher ammonium during winter).

The impact of leachate-impacted groundwater on the ecosystem will vary between landfills and different flow systems. At this site, exposure to leachate is greatest in the shallow sediments beneath the streambed, resulting in a potentially higher risk posed to endobenthic organisms than epibenthic or pelagic organisms. Groundwater discharge at this site is variable, resulting in regions of high concentrations typically near the shores, next to regions of relatively low concentrations near the middle of the stream. Therefore, endobenthic organism populations may differ spatially, with more pollutant-tolerant species living near discharge zones. Frequent influxes of surface water into shallow sediments (bank storage) during precipitation events may allow for brief reprieve from leachate impacts. There is a great deal of uncertainty surrounding the appropriateness of aquatic life standards for endobenthic organisms impacted by contaminated groundwater, as well as the effect of mixing of multiple contaminant types (Ahrens and Bundschuh

2014; Roy et al. 2019). Future work at Dyment's Creek will include ecological impact studies examining resident benthic invertebrate community composition and abundance, and in situ toxicity tests. This will provide valuable insight into the chronic and acute effects of discharging leachate-impacted groundwater on the benthic organisms living in the stream.

It is important to note that additional chemical data from this study is expected to become available sometime in 2021. This will help substantiate the observations on hydrologic influences on the contaminant inputs and resulting exposure, especially through the winter and snowmelt period. Further work may replicate the detailed stream study (Chapter 4) at other sites, potentially focusing on systems with different conditions, for example a larger stream or a site with different geology such as a fractured flow system. In addition, detailed sampling during precipitation events would advance the state of knowledge about temporal impacts of nearby historic landfills on streams during precipitation, which limited data here suggests might be quite substantial.

Chapter 6: References

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Appendix A: Supporting Information for Chapter 3

Appendix A1. Literature review

Table A-1. Past studies that measured some of the same contaminants of concern (CECs) as in this study in leachate or leachate-impacted groundwater from historic (> 3 decades since closure) municipal solid waste landfills (often along with modern landfills).

Study	No. historic / modern landfills	Sample type	Country	CECs included	Notes
Holm et al. 1995	1/-	Wells in plume	Denmark	Pharmaceuticals	Grindsted Landfill (1930 – 1977), which received some pharmaceutical waste
Paxeus, 2000	1/2	Leachate collection system	Sweden	Bisphenols, substituted phenols, OPE	1938 - 1978
Baun et al. 2004	4/6	Wells in landfill	Denmark	Substituted phenols	Historic sites 1930s- 1980s (incl. Grinsted Landfill)
Barnes et al. 2004	1 /-	Wells in plume	United States	Bisphenols, pharmaceuticals	Norman Landfill (1900s -1985)
Buszka et al. 2009	1/-	Wells in plume	United States	Select: OPE, bisphenols, pharmaceuticals	1960 - 1976
Busch et al. 2010	3/19	Leachate collection systems	Germany	PFAS	Closed 1979-1986; only 2 are untreated leachate; individual data not given
Eggen et al. 2010	0.5/2.5	Well in plume	Norway	Select pharmaceuticals	"old" part of landfill 1973-1989
Huset et al. 2011	1/3	Leachate collection system	United States	PFAS	1 site has 2 closed cells (1982-88; 1988- 93) and an active cell
Andrews et al. 2012	1 /1	Wells in landfill (1) and plume	United States	Pharmaceuticals, select OPE, phenols, Triclosan	Norman Landfill (1900s -1985)
Masoner et al. 2016	4/18	Wells in plume	United States	Pharmaceuticals, bisphenols, OPE, substituted phenols	1939-1989; individual data not given
Gallen et al. 2016	7/6	Leachate collection system and pond	Australia	PFAS	Most open within 1960s – early 1990s
Hepburn et al. 2019	7/-	Wells in landfill and plumes	Australia	PFAS	1930s – 1990s

Appendix A2. Materials with CECs that might end up in a landfill

Table A-2: Example of major uses of compounds within the CEC classes studied in this paper; for further detail on the use of individual compounds see recommended citations

CEC	Present/Past Uses	Recommended citations
PFAS	Surfactants, water and stain proofing,	Longpré et al. 2020
	non-stick cookware, textiles,	Health Canada 2018a
	upholstery, carpets, aqueous film	Health Canada 2018b
	forming foams, food packaging,	Buck et al. 2011
	electronic and photography	
	equipment	
OPE	Plasticizer, flame retardant, anti-wear	Wei et al. 2015
	and anti-foaming agent, lacquers,	van der Veen and de
	hydraulic fluids, floor polish,	Boer 2012
	electronics	Blum et al. 2019
		Pantelaki and Voutsa 2019
Bisphenols	Plastics, lacquers/paints,	Masoner et al. 2014
	polycarbonate and epoxy resins,	Careghini et al. 2015
	thermal paper, adhesives, brake fluid	ECCC 2018b
		Chen et al. 2016
Triclosan	Antimicrobial disinfectant, cosmetics,	Masoner et al. 2014
	drugs, natural health products	ECCC 2017
	(toothpastes, deodorant, lotions, etc.)	
Pharmaceuticals	Prescription and non-prescription	Masoner et al. 2014
	drugs, e.g., stimulant, anticonvulsant,	Sui et al. 2015
	psychiatric drugs, degradate (e.g., of	
	nicotine, caffeine)	
Substituted phenols	Disinfectant, wood preservative,	Masoner et al. 2014
	effluents of various industries such as	Villegas et al. 2016
	oil refining, petrochemicals,	
	pharmaceuticals,	
	coking operations, resins, plastics,	
	paint, pulp, paper, and wood products	
Sulfamic Acid	Industrial cleaner, herbicide, fire	Van Stempvoort et al. 2019
	proofing agent, degradate of	Freeling et al. 2020
	acesultame.	
	Various industrial uses (desalination,	
	cooling systems, food processing,	
	pulp bleaching, superplastics, oil and	
	gas extraction)	

Appendix A3. Sample handling

Field parameters temperature (T), electrical conductivity (EC), dissolved oxygen (DO), and pH were measured with hand-held probes prior to collecting each sample. For drive-point sampling along streams/ponds/lakeshores, samples were collected once the field parameters stabilized. For discharge locations, typically the plume discharge zone was mapped out during an initial visit using a screening approach (drive-point sampling every 10-20 m along the water body; Roy and Bickerton 2010) using common tracers (e.g., ammonium, chloride) and artificial sweeteners. Based on those results, several targeted locations were sampled for the full set of analyses during a second visit.

Samples were filtered (0.45-µm polyethersulfone membranes) and preserved in the field, according to Table A-3. All samples were stored on ice or in a fridge prior to and during transport to Canada Centre for Inland Waters (Burlington, ON), and further transport to ECCC lab in Vancouver, BC (substituted phenols). In-lab storage details are also provided in Table A-3. Nitrile gloves were worn to prevent contamination (e.g., salts) from human skin. Care was taken to avoid materials containing PFAS during fieldwork, including new waterproof gear, Teflon tape, etc., though a recent study suggests contamination of water samples from field materials is not likely (Rodowa et al. 2020).

Analysis [£]	Filtered	Preservation	Bottle Type and	Storage
	(0.45µm)		Volume	
Artificial sweeteners +	Y		PE 20mL	Freezer
others				
PFAS	Ν		PE 500mL -	Fridge 4°C
			MEOH rinsed	
OPE	N		amber glass	Fridge 4°C
			950mL	_
Bisphenols + others	N		amber glass	Fridge 4°C
•			950mL	C
Substituted phenols	N		amber glass	Fridge 4°C
*			950mL	C
Pharmaceuticals	N		amber glass	Fridge 4°C
			40mL	
Ammonium	Y	10% HCl until pH 5-6	PE 20mL	Fridge 4°C
Metals and major	Y	70% HNO ₃ until pH<2	PE 30mL/120mL	Fridge 4°C
cations		-		
VOCs	N	NaHSO ₄ crystals, no	glass 40mL	Fridge 4°C
		head space	-	
Dissolved carbon	Y	_	glass 120mL	Fridge 4°C
Anions	Y		PE 20mL	Fridge 4°C
SRP	Y		glass 40mL	Fridge 4°C
Alkalinity	N		PE 120mL	Fridge 4°C

Table A-3. Details on sample materials, preservation and storage.

[£] see Appendix A5 for list of analytes for each analysis

Appendix A4. Nomenclature

Table A-4. The 17 PFAS analyzed in this study, based on Nakayama et al. (2019):

Acronym	CAS #	Compound Name	n	Group
PFBA	375-22-4	Perfluorobutanoic acid	3	PFCA
PFPeA	2706-90-3	Perfluoropentanoic acid	4	PFCA
PFHxA	307-24-4	Perfluorohexanoic acid	6	PFCA
PFHpA	375-85-9	Perfluoroheptanoic acid	7	PFCA
PFOA	335-67-1	Perfluorooctanoic acid	8	PFCA
PFNA	375-95-1	Perfluorononanoic acid	9	PFCA
PFDA	335-76-2	Perfluorodecanoic acid	10	PFCA
PFUnA	4234-23-5	Perfluoroundecanoic acid	11	PFCA
PFDoDA	307-55-1	Perfluorododecanoic acid	12	PFCA
PFTriDA	72629-94-8	Perfluorotridecanoic acid	13	PFCA
PFTeDA	376-06-7	Perfluorotetradecanoic acid	14	PFCA
PFBS	375-73-5 /59933-66-3	Perfluorobutanesulfonate	3	PFSA
PFHxS	355-46-4	Perfluorohexanesulfonate	6	PFSA
PFOS	4021-47-0 / 1763-23-	Perfluorooctanesulfonate	8	PFSA
	1/2/93-39-3			
PFDS	335-77-3 /2806-15-	Perfluorodecanesulfonate	10	PFSA
	7/126105-34-8			
PFECHS	646-83-3	Perfloroethylcyclohexane	8	PFSA (cyclic)
		sulfonate		
FOSA	754-91-6	Perfluorooctanesulfonamide	8	Perfluoroalkane
				sulfonamides

n is the number of carbon atoms; PFCA – perfluoroalkyl carboxylic acids; PFSA – perfluoroalkyl sulfonic acids

Acronym	CAS #	Compound Name	Group
TEP	78-40-0	Triethylphosphate	Alkyl
ТВРО	814-29-9	Tributylphosphine oxide	Alkyl
TPrP	513-08-6	Tripropyl phosphate	Alkyl
TnBP	126-73-8	Tributylphosphate	Alkyl
TiBP	126-71-6	Tri-isobutylphosphate	Alkyl
ТРРО	791-28-6	Triphenylphosphine oxide	Aryl
TEEDP	995-32-4	Tetraethyl ethylenediphosphonate	Alkyl
TCEP	115-96-8	Tris(2-chloroethyl)phosphate	Cl
ТСРР	13674-84-5	Tris(2-chloroisopropyl) phosphate	Cl
TDCPP	13674-87-8	Tris(1,3-dichloro-2-propyl)phosphate	Cl
TPHP	115-86-6	Triphenylphosphate	Aryl
EHDPP	1241-94-7	2-ethylhexyl diphenyl phosphate	Aryl
ТОТР	1330-78-5	Tritolyl phosphate	Aryl
IDDPP	29761-21-5	Isodecyl diphenyl phosphate	Aryl
TBOEP	78-51-3	Tris(2-butoxyethyl) phosphate	Alkyl
TEHP	78-42-2	Tris(2-ethylhexyl)phosphate	Alkyl
TBPDPP	56803-37-3	Tert-butylphenyl diphenyl phosphate	Aryl
DPIPP	69515-46-4	Diphenyl-3-isopropylphenyl phosphate	Aryl
TXP (T35DMPP)	3862-12-2 /	Tris-xylenyl phosphate	Aryl
	25155-23-1	(includes Tris(3,5-dimethylphenyl)phosphate)	
	(25653-16-1)		
DTBPPP	65652-41-7	Di-tert-butylphenyl phenylphosphate	Aryl
T2IPP	64532-95-2	Tris(2-isopropylphenyl)phosphate	Aryl
TTBPP	78-33-1	Tris(p-tert-Butylphenyl) phosphate	Aryl
TDBPP	126-72-7	Tris(2,3-dibromo propyl) phosphate	Alkyl
DOPP	1754-47-8	Dioctylphenyl phosphonate	Aryl

Table A-5. The 24 OPE compounds analyzed in this study.

Appendix A5. Details on chemical analyses

Artificial Sweeteners + others: Analytes include the artificial sweeteners acesulfame, saccharin, cyclamate, and sucralose, along with perchlorate, sulfamic acid, and the pesticides glyphosate, 2,4-D, fosamine, MCPA, and picloram. The pesticides are not of interest in this study. The artificial sweeteners + others suite was determined by Ion Chromatography coupled to a tandem mass spectrometer with an electrospray ionization source in negative mode (IC/ESI/MS/MS). Direct sample injection of 100 µL was conducted onto a Dionex IONPAC® AS20 analytical column (2×250 mm) with a KOH eluent gradient. Two MRM transitions were monitored and quantification was performed using deuterated compounds to correct for matrix effects and instrument fluctuations. Positive identification required the retention time match of the native and labeled analyte to be < 2% and the calculated concentration of the two MRM transitions to be < 20% of each other for values > practical quantification limit (pql). Duplicate and a check standards were run after every 10 samples, with quantitative MRM required to be within +/-20% of the expected value for levels > pql and within +/-50% for levels >mdl (minimum detection limit) and <pql. Accuracy and precision were assessed by injecting the third lowest standard 7 times over a 96 hour period of a sample run. The average % recovery and % standard deviation were required to be 100 ± 20 % and < 10%, respectively. For each analyte, a standard curve was created with a minimum of 5 points over a range of approximately 3 orders of magnitude. Complete instrument details can be found in Van Stempvoort et al. (2020) along with the compound specific parameters for acesulfame, sucralose and perchlorate. The MRM details and compound specific parameters for sulfamic acid, cyclamate and saccharin are reported in Van Stempvoort et al. (2019). Minimum detection and practical quantification limits are provided in the data spreadsheet.

Per- and Polyfluoroalkyl Substances (PFAS): For full list of analytes see Table A-4. We have previously reported our methods for PFAS extraction from aqueous matrices using weak-anion exchange (WAX) solid phase extraction (SPE) (MacInnis et al. 2019). Briefly, a 200 ml subsample of groundwater was brought up to room temperature, spiked with isotopically labeled standards (for extraction efficiency) and adjusted to pH 3 using acetic acid. The sample is loaded onto a 150 mg WAX SPE (Waters, Mississauga, ON) that was conditioned using 5 ml 0.1% ammonia in methanol, 5 ml methanol and 5 ml of SPE-polished HPLC-grade water. Once the sample has passed through the SPE, the cartridge is dried by centrifugation. A fractional elution is used to collect neutral PFAS using 6 ml methanol and anionic PFAS using 8 ml 0.1% ammonia in methanol. Both fractions are brought to dryness using a gentle stream of nitrogen and reconstituted in 0.5 ml 1:1 methanol/water with an additional spike of a separate cocktail of isotopically labeled standards to evaluate matrix effects. Extracts are transferred to 300-µl polypropylene vials for analysis by ultra high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS, Waters Acquity UHPLC and Waters Acquity TQS MS/MS). Analytes are separated using an octadecylsilyl (C18) column with an upstream isolator column to separate any background PFAS signal. All mass

spectrometry parameters including cone voltage and collision energies for precursor to product ion transitions were optimized using authentic standards and are available in previous publications (MacInnis et al. 2019). All analytes were quantified using a 16-level calibration curve ranging from 0.01 to 15 ng/ml, R^2 >0.99. Quantitation was based on relative response to the corresponding isotopically labeled standard to correct for recovery and matrix effects. For extracts yielding concentrations outside of the calibration curve, dilution was performed for reanalysis.

QA/QC parameters included method blanks, sample spike and recovery, comparison of field and travel blanks. Method detection limits were based on the average + 3 standard deviation concentration of the blanks. For analytes not detected in the method blank, the MDL is based on a standard injection yielding a signal-to-noise ratio of 3 (Appendix 10). Extraction efficiency was based on the analyte peak area in the extract of a spiked sample compared to a sample extract that was spiked post-extraction. Extraction efficiencies for all PFCAs with 4 to 11 carbons corresponded to $102 \pm 3\%$. For PFCA with 12 or more carbon atoms, extraction efficiencies were $70 \pm 4\%$. For all PFSA, extraction efficiencies were $107\pm 8\%$.

Organophosphate Esters (OPE): For full list of analytes see Table A-5. We have previously reported methods for OPE extraction using SPE and UHPLC-MS/MS instrumental analysis (Sun et al. 2020). The OPE were extracted from 50 ml groundwater samples and spiked with 30 µl of isotopically labeled standards. Samples were passed through a 200 mg hydrophobic-lipophilic balanced SPE (Waters OASIS HLB) that was conditioned using 8 ml isopropanol and 10 ml LCMS-grade water. After fully loading the sample, the cartridge was washed with 5% methanol in water. A high vacuum was applied for 30 min for drying the SPE prior to elution. The SPE cartridge was eluted into a 15 ml glass centrifuge tube using 5 ml 90/10 methyl-tert-butyl ether in methanol. This extract was then concentrated to dryness using a gentle stream of nitrogen gas. The extract was reconstituted in 0.5 ml acetonitrile with an additional $30-\mu$ l spike of isotopically labeled standards for tracking matrix effects. The final extract was transferred to a 2-ml glass autosampler vial for UHPLC-MS/MS (Waters Acquity UHPLC and Xevo TQS mass spectrometer). QA/QC measures included method blanks, comparison of field and lab blanks suing HPLC grade water, spike and recovery using composite groundwater samples. All analytes were quantified by relative response to the analogous isotopically labeled standard using a 16-point calibration curve ranging from 0.1 to 45 ng/ml concentrations. We have previously reported all of the mass spectrometer instrument settings (Sun et al. 2020). Method detection limits were based on the average + 3 standard deviation concentration of the blanks. For analytes not detected in the method blank, the MDL is based on a standard injection yielding a signal-to-noise ratio of 3 (Appendix 10). Extraction efficiency was based on the analyte peak area in the extract of a spiked sample compared to a sample extract that was spiked post-extraction. Recovery of 14 isotopically labeled standards ranged from 18 to 69% with an average recovery corresponding to $51 \pm 29\%$.

Bisphenols + others: Analytes include bisphenol-A, bisphenol-AF, bisphenol-AP, bisphenol-B, bisphenol-F, bisphenol-P, bisphenol-S, bisphenol-Z, disperse yellow 3, and triclosan. These compounds were analyzed by direct injection and ESI-LC/MS/MS at the National Laboratory for Environmental Testing of Environment and Climate Change Canada (Burlington, ON, Canada) (NLET method B0779W). Briefly, subsamples of 0.950 mL were spiked with 50 μ L of internal standard before LC-MS/MS analysis. One Method Blank (BLK1) was run with each set of 10 samples and comprised a 0.95 mL aliquot of Lake Ontario water, collected from the Burlington pier. The BLKs act as duplicate reagent blanks. The 9 analytes were separated by HPLC and analyzed by a triple-quadrupole mass spectrometer containing an Electrospray Ionization (ESI) source. Concentrations were determined using a 6-point calibration curve with a continuing calibration every eight samples. Minimum detection limits are provided in the data spreadsheet. Complete method details are available in the attached file on Standard Operating Procedure for the Bisphenols analysis.

Substituted Phenols: Analytes include 2,4,6-trichlorophenol, 2,4-dichlorophenol, 2,4dimethylphenol, 2.4-dinitrophenol, 2-chlorophenol, 2-nitrophenol, 4.6-dinitro-2methylphenol, 4-nitrophenol, p-chloro-m-cresol, pentachlorophenol, and phenol. The substituted phenols were analyzed by High Resolution Gas Chromatography / Low Resolution Mass Spectrometry (HRGC/LRMS) in Selected Ion Monitoring Mode (SIM) at the Pacific and Yukon Laboratory for Environmental Testing of Environment and Climate Change Canada (Vancouver, BC, Canada) (NLET method V0831D). Briefly, a measured volume of sample was acidified, spiked with a surrogate and extracted with dichloromethane. For samples that have a high organic content (may apply to many of the landfill samples), which may produce chromatographic interferences, a pre-extraction under basic conditions was performed. The sample extract was evaporated to a small volume and, after the addition of deuterated internal standard, analysed as noted above, with quantitation performed using multilevel internal standard calibration curves. Minimum detection limits are provided in the data spreadsheet. Complete method details are available in the attached file on Standard Operating Procedure for the Substituted Phenols analysis.

Pharmaceuticals: Analytes include acetaminophen, aspartame, caffeine, carbamazepine, codeine, cotinine, paraxanthine, and theophylline. These pharmaceuticals were analyzed at the National Laboratory for Environmental Testing of Environment and Climate Change Canada (Burlington, ON, Canada) with direct injection followed by Electrospray Ionization-Liquid Chromotography – Mass Spectrometry (ESI-LC-MS/MS). (NLET method # B0764W). Briefly, subsamples of 0.975 mL were subject to the addition of deuterated internal standards containing Caffeine-D9, Codeine-D6, Carbamazepine-D10, Acetaminophen-D4, Cotinine-D3 and Acesulfame-D4. The 8 analytes were separated by HPLC and analyzed by a triple-quadrupole mass spectrometer containing an Electrospray Ionization (ESI) source. Concentrations are determined using a 8-point calibration curve with a continuing calibration every eight samples. Minimum detection limits are provided

in the data spreadsheet. Complete method details are available in the attached file on Standard Operating Procedure for the Pharmaceuticals analysis.

Ammonium: Ammonium was analyzed by spectrophotometry with a phenolhypochlorite reagent. Absorbance was measured at 640 nm. The minimum detection limit is provided in the data spreadsheet.

Metals and Major Cations: Thirty-five metal analytes were tested (see supplemental spreadsheet for complete list). Analytes for cations include calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+). Trace metals and major cations were analyzed at the National Laboratory for Environmental Testing of Environment and Climate Change Canada (Burlington, ON, Canada) with Inductively Coupled Plasma-Sector Field Mass Spectrometry (NLET method #2003). Minimum detection limits are provided in the data spreadsheet.

Volatile Organic Compounds (VOCs): Analytes include chlorinated alkenes, chlorinated benzenes, benzene, toluene, xylene, naphthalene, etc. (see supplemental spreadsheet for complete list). Volatile organic compounds were run on an Agilent 7890 GC and Agilent 5977 MSD with a Tekmar Stratum purge and trap concentrator and Tekmar Aquatek 100 autosampler. Analytes were concentrated on a Vocarb 3000 trap and separated with an Agilent DB624 column (0.32 mm i.d., 1.8 μ m film thickness and 30 m in length). Volatiles were purged for 11 min at 40 ml min⁻¹ at room temperature. The oven was cooled with CO₂ to 0°C, held for 1 min, then ramped at 10°C min⁻¹ to 35°C, then ramped at 4°C min⁻¹ to 92°C, held again for 1 min, and finally ramped at 2°C min⁻¹ to 102°C. Minimum detection limits are provided in the data spreadsheet.

Dissolved Inorganic Carbon (DIC) and Dissolved Organic Carbon (DOC): DIC/DOC samples were analyzed using a UV-persulfate TOC Analyzer (Shimadzu TOC-Vwp) at the National Laboratory for Environmental Testing of Environment and Climate Change Canada (Burlington, ON, Canada) with (NLET method #1021). Minimum detection limits are provided in the data spreadsheet.

Anions: Analytes include fluoride (Fl⁻), chloride (Cl⁻), nitrite (NO₂⁻), bromide (Br⁻), sulphate (SO₄⁻), nitrate (NO₃⁻) and phosphate (PO₄⁻). Anions were analyzed by Ion Chromatography using a Dionex 2500 IC system (AS50 autosampler and column compartment, GP50 pump, EG50 KOH eluent generator and ED50 conductivity detector). Anions were separated on a 4mm x 250mm Dionex AS18 column fitted with a 4mm x 50mm Dionex AG18 guard column. The potassium hydroxide eluent concentration was held at 22 mM for the first 5 min then ramped to 50 mM over 1 min and held at 50 mM until the end of the run. Minimum detection limits are in the data spreadsheet provided.

Soluble Reactive Phosphorus (SRP): SRP was analyzed by spectrophotometry using a mixed reagent containing ammonium molybdenate and antimony potassium tartrate;

absorbance was measured at 885 nm. The minimum detection limit is in the data spreadsheet provided.

Alkalinity: Alkalinity was analyzed using Hach alkalinity test kits. These kits use a drop count titration method to determine alkalinity in mg/L CaCO₃. Dilutions were performed as necessary when concentrations exceeded the range of the tests (400 mg/L). The smallest measured increments ranged from 5-400 mg/L (5-22% of sample value), depending on the degree of dilution required, although most tests were within a range of 20-200 mg/L. The minimum detection limit is in the data spreadsheet provided.

Appendix A6. Assessment of Ammonium Data

Ammonium is typically detected at elevated concentrations in municipal waste landfill leachate, with a range of 50-2200 NH₄⁺-N mg/L reported for landfills < 25 years old, in the review by Christensen et al. (2001). While leachate constituent concentrations typically decline as landfills age, ammonium is known to persist even in closed landfills for many decades to centuries (Christensen et al. 2001; Kjeldsen et al. 2002). For this reason, ammonium is a useful tracer for landfill leachate from both operating and old closed landfills. For the 20 closed landfills (1920s-1990s) of this study, NH₄⁺-N concentrations ranged from 0.01-225 mg/L (Figure A-1), with an average of 48.8 mg/L. These concentrations are on the lower end of what has been previously reported for landfill leachate (Christensen et al. 2001), though there is a lack of data for exclusively old, closed landfills.

With 15 of 20 sites having at least one sample with NH_4^+ -N >10 mg/L, these results are suggestive that many of the samples are leachate-affected. However, there is substantial variability between sites and no clear relationship with the age of the landfill (Table 3-1), as both very old (e.g., SKP, SMP, G4) and relatively young (e.g., OG, MR) sites had low concentrations (Figure A-1). Also, some sites exhibited substantial variability within a site (e.g., BBP; both are from wells at the edge of the landfill). The lower values may signify weak leachate, either from a low original organic material load or from being leached out over time. Transformation to nitrate seems unlikely given that the vast majority of samples were anoxic to suboxic. However, low NH4⁺-N could also be a result of leachate dilution (or missing the plume), as mentioned in the main text. Ammonium is also attenuated through sorption and cation exchange – as noted for the Norman landfill plume (Lorah et al. 2009). In contrast, concentrations of some samples could be elevated due to other sources, such as degrading organic matter within stream/lake/pond sediments, fertilizers, or wastewater. The possibility of other sources, dilution, and attenuating processes means it is difficult to assess the causes of composition variation in these leachate-affected samples from a single constituent.



Figure A-1. Ammonium concentrations in leachate-impacted groundwater samples from 20 historic Ontario landfills (Table 3-1).



Appendix A7. Separate graphs of those stacked in Figure 3-1 of the main manuscript

Figure 3-1A. Stacked bar plots of concentrations of the ASs for the 48 historic landfill leachate-impacted groundwater samples (ordered by approximate age, according to Table 3-1). Note the y-axis break in scale in A and B.



Figure 3-1B. Stacked bar plots of concentrations of the PFAS for the 48 historic landfill leachate-impacted groundwater samples (ordered by approximate age, according to Table 3-1). Note the y-axis break in scale in A and B.



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Figure 3-1C. Stacked bar plots of concentrations of the OPE for the 48 historic landfill leachate-impacted groundwater samples (ordered by approximate age, according to Table 3-1). Note the y-axis break in scale in A and B.



Figure 3-1D. Stacked bar plots of concentrations of the bisphenols for the 48 historic landfill leachate-impacted groundwater samples (ordered by approximate age, according to Table 3-1). Note the y-axis break in scale in A and B.



Appendix A8. Other assessments of CEC data

Figure A-2. Stacked bar plots of relative composition (%, mass basis) of the 24 OPE compounds (showing only 15 with at least one sample > 1.2%; Table 3-3) measured in the 48 samples of leachate-impacted groundwater collected from 20 historic landfills in Ontario (ordered according to Table 3-1).

Example for non-dilution leachate CEC composition variation:

Some evidence for waste composition concentration variability is apparent. For example, the BBP-02 sample had the highest total OPE concentration, almost 20 μ g/L more than the next highest sample and four times that of BBP-01 (Figure 3-1C). However, for the total PFAS concentration (Figure 3-1B), the situation is reversed, with BBP-02 at half the concentration of BBP-01. These noted concentration differences cannot be due to dilution. This example illustrates the level of difference in CEC concentrations that can be linked to leachate composition variability across and between landfills.

92	BOEP																								1.00
81	TOTP 1																							1.00	0.57
83	L 440H																						1.00	0.78	0.42
85	ЪНР																					1.00	0.53	0.78	0.58
85	DCPP 1																				1.00	0.51	0.31	0.47	0.73
62	CPP																			1.00	0.66	0.51	0.45	0.54	0.46
83	LCEP																		1.00	0.36	0.64	0.43	0.37	0.45	0.70
100	IBP																	1.00	0.67	0.56	0.75	0.56	0.39	0.53	0.91
98	Lubp .																1.00	0.89	0.69	0.43	0.68	0.54	0.46	0.63	0.93
75	L PrP															1.00	0.52	0.50	0.28	0.24	0.11	0.25	0.29	0.40	0.45
100	Ē														1.00	0.56	0.59	0.62	0.59	0.51	0.56	0.41	0.24	0.47	0.50
81	FOSA 1													1.00	0.30	-0.02	0.37	0.47	0.26	0.38	0.54	0.20	0.31	0.17	0.39
8	PFBS												1.00	0.16	0.59	0.50	0.39	0.43	0.14	0.21	0.12	0.33	0.19	0.36	0.35
86	PFHxS											1.00	0.86	0.33	0.55	0.54	0.65	0.65	0.36	0.33	0.39	0.36	0.24	0.46	0.62
100	PFECHS										1.00	0.74	0.73	0.13	0.29	0.34	0.43	0.32	0.20	0.01	0.05	0.10	0.30	0.29	0.34
100	PFOS I									1.00	0.60	0.84	0.57	0.51	0.44	0.35	0.79	0.77	0.43	0.41	0.56	0.36	0.27	0.44	0.76
100	PFUnA								1.00	0.17	0.26	0.38	0.39	-0.12	0.14	0.26	0.12	0.12	-0.07	0.07	-0.02	0.10	-0.14	-0.11	0.21
94	PFDA							1.00	0.47	0.45	0.15	0.35	0.28	0.45	0.43	0.27	0.41	0.56	0.23	0.56	0.47	0.41	0.33	0.27	0.40
100	PFNA						1.00	0.57	0.60	0.37	0.27	0.49	0.53	0.01	0.39	0.49	0.35	0.44	0.12	0.12	0.09	0.16	-0.10	0.00	0.36
100	PFOA					1.00	0.45	0.54	0.28	0.85	0.49	0.87	0.70	0.54	0.63	0.38	0.68	0.77	0.51	0.57	0.61	0.48	0.30	0.49	0.68
100	PFHpA				1.00	0.89	0.52	0.59	0.37	0.67	0.46	0.81	0.79	0.40	0.70	0.54	0.49	0.63	0.35	0.58	0.52	0.44	0.30	0.45	0.52
100	PFHxA			1.00	70.97	0.81	0.49	0.57	0.31	0.56	0.42	0.75	0.80	0.38	0.68	0.57	0.41	0.53	0.28	0.53	0.40	0.41	0.32	0.43	0.41
83	PFPeA		1.00	0.95	0.92	0.80	0.46	0.63	0.28	0.54	0.42	0.66	0.75	0.44	0.60	0.47	0.43	0.50	0.27	0.48	0.32	0.42	0.38	0.41	0.39
67	PFBA	1.00	0.94	0.91	0.89	0.75	0.50	0.59	0.27	0.50	0.29	0.60	0.62	0.39	0.74	0.80	0.45	0.57	0.44	0.56	0.65	0.34	0.45	0.40	0.45
er DF		Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear	Pear
log conce		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFOS	PFECHS	PFHxS	PFBS	FOSA	TEP	TPrP	TnBP	TIBP	TCEP	тсрр	TDCPP	ТРНР	ЕНДРР	тотр	TBOEP
correl of	DF	67	83	100	100	100	100	94	100	100	100	98	98	81	100	75	98	100	83	79	85	85	83	81	92

Figure A-3. Pearson Correlation Coefficients for PFAS and OPE in leachate-impacted groundwater samples from the 20
historic Ontario landfills (log normalized concentration, excluding <lod). (df)="" detection="" frequency="" given="" in="" row.<="" td="" top=""></lod).>
Outlined cells have correlation coefficient >0.6 , with > 0.9 in red, >0.8 in brown, >0.7 in dark yellow and >0.6 in light
yellow.

	This study	Masoner et al. 2014
Landfills ^ξ	20	19
Samples ^χ	48	19
Pharmaceuticals		
Acetaminophen	0.055	330
Aspartame	n.d. ^{\varphi}	
Caffeine	0.25	130
Carbamazepine	0.17	2.6
Codeine	0.027	0.73 E
Cotinine	6.6	51
Paraxanthine	0.036	1.3
Theophylline	n.d. ^v	0.98
Bisphenols set		
Bisphenol-A	29	6380
Bisphenol-AP	n.d. ^v	
Bisphenol-F	n.d. ^v	
Bisphenol-S	4.8	
Bisphenol-AF*	n.d. ^v	
Bisphenol-B*	0.95	
Bisphenol-P*	n.d. ^v	
Bisphenol-Z*	0.16	
Disperse Yellow 3	n.d. ^v	
Triclosan	0.053	42
Substituted Phenols		
2,4,6-Trichlorophenol	n.d. ^v	
2,4-Dichlorophenol	n.d. ^v	
2,4-Dimethylphenol	12	
2,4-Dinitrophenol	n.d. ^v	
2-Chlorophenol	1.6	
2-Nitrophenol	n.d. ^v	
4,6-Dinitro-2-	n.d. ^v	
methylphenol		
4-Nitrophenol	n.d. ^v	
p-Chloro-m-cresol	1.1	
Pentachlorophenol	1.0	53 E
Phenol	n.d. ^v	1600

Table A-6. CEC maximum concentrations (μ g/L) for the historic landfills data set of this study compared to those from Masoner et al. (2014), which are predominantly modern/active landfills.

^{ξ} number of landfills investigated; ^{χ} number of samples from all landfills investigated; ^{ψ} n.d. – non-detect; *Analyte not tested for in every sample; E flag due to concentration being off calibration curve for Masoner et al. (2014)

Appendix A9. CEC Health Concerns and Water Quality Guidelines:

As noted in the main text, all of the samples likely represent leachate diluted somewhat in background groundwater. It is quite possible that contaminant concentrations will decrease further during transport to nearby wells or surface water bodies (including their sediments), but it is not guaranteed, especially for those in very close proximity. Thus, for this assessment, no further dilution is assumed. For actual application to specific contaminated sites, the reader should check with appropriate regulations and guidance documents (e.g., Federal Interim Groundwater Quality Guidelines in Canada; Government of Canada, 2010, updated 2016).

PFAS

In addition to being environmentally persistent and bioaccumulative, PFAS compounds have been shown to cause adverse health effects in both animals and humans, including carcinogenic, immunotoxic, and metabolic effects (Sunderland et al. 2019). Most of the work has focused on PFOA and PFOS, resulting in more water quality regulations for these compounds, although some jurisdictions have released guidelines for other PFAS (see Table S7). These guidelines do not even begin to cover the 4000+ known PFAS compounds due to a lack of definitive research findings for most compounds. The overall tendency for PFAS to cause similar adverse health effects has resulted in some consideration for PFAS to be regulated as an entire class of compounds (Sunderland et al. 2019).

In 2018, Canada implemented drinking water guidelines for two of the most prevalent PFAS compounds, setting maximum acceptable concentrations (MAC) of 0.2 μ g/L and 0.6 μ g/L for PFOA and PFOS, respectively (Health Canada 2018a, 2018b). These values are based on health risks associated with lifetime human consumption, and therefore short-term exposure (ingestion) of water with concentrations slightly above the MAC are not considered to cause any known health effect. Due to both compounds commonly occurring together, and their similar health impacts, Health Canada suggests an additive approach for PFOS and PFOA when determining if water is safe. If the sum of the ratios of each compound's concentration to its respective MAC is larger than one, then the water is not safe to consume. Two years prior, the United States Environmental Protection Agency (USEPA) released lifetime drinking water health advisories of 0.07 μ g/L for both PFOA and PFOS, although some states have released guidelines with lower concentrations (USEPA 2016a, 2016b). The USEPA also suggests that the sum of PFOA and PFOS should not exceed the 0.07 μ g/L health advisory.

In this study, seven samples exceeded Health Canada's PFOA guideline and three samples exceeded Health Canada's PFOS guideline, compared to 17 and 16 samples for the respective USEPA health advisories (see Table S7). Using Health Canada's ratio sum method for PFOA and PFOS, this study found that 11 samples, collected from 7 of the different landfill sites, had ratio sums that were larger than 1 and therefore unsafe to drink. Comparatively, 27 samples from 15 of the landfill sites had combined concentrations of PFOA and PFOS greater than 0.07 μ g/L.

Health Canada (2019a) released drinking water screening values (DWSVs) intended to provide guidance for more PFAS compounds (seven of which were tested in

this study, see Table A-7) despite there being an inadequate amount of research to create formal guidelines for these compounds. Seven of our study sites had concentrations of at least one of these compounds higher than the suggested safe drinking level. Of course, the leachate-impacted groundwater measured here would undoubtedly experience further dilution upon collection for drinking water, either directly via wells or, following discharge to a surface water body, by intake pipes. Still, considering the mixture of all the PFAS and other contaminants found, drinking water sources (most likely wells) near historic landfills, whether known or not, may pose a human health risk.

With respect to protecting aquatic life in receiving surface water bodies, PFOS has a current Federal Environmental Quality Guideline (FEQGs) for Canada of 6.8 μ g/L (ECCC 2018a), which is above the maximum concentration found in this study. A FEQG for PFOA is under development. According to this guideline, the leachate of these historic landfills appears to pose much less concern for aquatic life than human health for PFOS, although aquatic organisms may experience concentrations found here with little additional dilution in some circumstances (especially endobenthic life). However, in contrast, the guideline value for PFOS in Europe has been set at 0.65 μ g/L (Directive 2013/39/EU).

OPE

The release of OPE, especially chlorinated OPE like TCEP, TCPP, and TDCPP, is a concern because they pose a toxicity risk to wildlife and are suspected to adversely affect human health as certain compounds are potentially carcinogenic and neurotoxic (van der Veen and de Boer 2012; Pantelaki and Voutsa 2019; Wei et al. 2015). Physiochemical properties of each compound can differ greatly, meaning OPE compounds can have a range of toxicity, persistence and bioaccumulative tendencies. Various OPE compounds have been found in many environmental matrices at elevated levels (Pantelaki and Voutsa 2019; Wei et al. 2015). Multiple countries have identified the risk of OPE compounds and put in place measures to restrict their use, particularly for TCEP and other chlorinated OPE in children's toys and furniture; however there is consideration on regulating the entire group of OPE compounds (Blum et al. 2019). There are currently no water quality guidelines available for aquatic life or human health for these OPE compounds. However, assessments of risk to human health and the environment have been made for some of these compounds under the Canadian Environmental Protection Act (Government of Canada, 2020).

Bisphenols

The FEQG for Canada, which is applicable to the protection of aquatic life, for BPA is $3.5 \ \mu g/L$ (ECCC 2018b), while there is no current standard for the U.S. There are no similar guidelines for drinking water in either country. Ten of the leachate-affected groundwater samples (from eight landfills) surpassed the FEQG concentration, indicating some ecological concern for poorly-diluted receiving waters (Table A-7). Three of those samples were directly impacting a stream (2 discharge, 1 culvert); therefore, for these samples especially there is an immediate threat to aquatic organisms.

Triclosan

A FEQG exists for triclosan of 0.47 μ g/L (ECCC 2017); however, triclosan was only detected in 4% of the leachate-impacted groundwater samples from this study with a maximum concentration of only 0.05 μ g/L (Table A-7). This suggests that triclosan is of little concern at old closed landfills near surface water bodies.

Substituted Phenols

For the compound pentachlorophenol, which was detected in 12.5% of samples, the minimum detection limit is the same as the aquatic life freshwater quality guideline of 0.5 μ g/L, resulting in all detections exceeding the standard (CCREM 1987). However, the sample concentrations were all below Canada's drinking water maximum acceptable concentration for pentachlorophenol of 60 μ g/L (Health Canada 2019b). Generally, the remaining substituted phenols tested here were below their respective aquatic life freshwater quality guidelines, with the exception of one sample with 2,4-dimethylphenol at 12 μ g/L compared to the guideline of 4 μ g/L (CCME 1999). For some of the other compounds, their detection limits were similar to their aquatic life freshwater guideline. Thus, while it seems that the 10 substituted phenols tested here are not of major concern for historic landfill leachate, it is difficult to be certain given these relatively high detection limits.

Pharmaceuticals

The only pharmaceutical with a guideline is carbamazepine, which was detected at values much lower than the long-term aquatic life freshwater guideline of $10 \,\mu g/L$ (CCME 2018, Table A-7), suggesting it is not a substantial risk to nearby surface waters.

Common Leachate Contaminants

Many common leachate contaminants that have drinking or aquatic life water quality guidelines were measured in this study along with the CECs. These compounds were not included in Table A-7 or in the text above, as they are not the focus of this study, but can be referenced in the supplemental data spreadsheet.

Table A-7: Concentrations of individual CECS in leachate-impacted groundwater
samples from the 20 Ontario historic landfills compared to their respective water quality
guidelines (predominantly from Canada).

Analyte	This study	Water Qualit	y Guidelines	Samples exceeding guideline				
	max (u g/L)	Valua	Tuno	(total 48 samples from 20				
	(µg/L)	(ug/L)	туре	landfills)				
PFAS		(μg/L)						
PFOA	0.85	0.21	Drinking	7 from 5 landfills				
			water					
		0.07^{2}	Drinking	17 from 10 landfills				
			water					
PFOS	2.8	0.63	Drinking	3 from 2 landfill				
			water					
		6.84	Aquatic life	0				
		0.07^{5}	Drinking	16 from 9 landfills				
			water					
PFBA	0.29	306	Drinking	0				
			water					
PFPeA	0.21	0.26	Drinking	2 from 2 landfills				
	0.17	2.26	water					
PFHxA	0.67	0.2°	Drinking	5 from 4 landfills				
	0.07	0.06	water	1.0 1.1 1011				
РЕНрА	0.27	0.26	Drinking	1 from 1 landfill				
DENIA	1.0	0.026	Water Driving	1 from 1 lon d£11				
PFNA	1.0	0.02°	Drinking	1 from 1 landfill				
DEDC	0.71	156	Drinking	0				
ггдэ	0.71	15	water	0				
PFHyS	13	0.66	Drinking	3 from 2 landfills				
11 HAS	1.5	0.0	water	5 Hom 2 Jundinis				
Pharmaceuticals								
Carbamazepine	0.17	107	Aquatic life	0				
Bisphenols			•					
BPA	29	3.5 ⁸	Aquatic life	10 from 8 landfills				
Triclosan	0.053	0.479	Aquatic life	0				
Substituted Phenols								
2,4-	12	410	Aquatic life	1 from 1 landfill				
Dimethylphenol								
2-Chlorophenol	1.6	711	Aquatic life	0				
p-Chloro-m-cresol	1.1	7 ¹¹	Aquatic life	0				
Pentachlorophenol	1.0	60 ¹²	Drinking	0				
			water					
Ļ		0.511	Aquatic life	4 from 4 landfills				

^ξ number of landfills investigated; ^{*μ*} number of samples from all landfills investigated; ^{*ψ*} n.d. – non-detect; ¹Health Canada 2018a; ²USEPA 2016a; ³Health Canada 2018b; ⁴ECCC 2018a⁵USEPA 2016b; ⁶Health Canada 2019a; ⁷CCME 2018; ⁸ECCC 2018b; ⁹ECCC 2017; ¹⁰CCME 1999; ¹¹CCREM 1987; ¹²Health Canada 2019b

Appendix A10. Data set

An accompanying Excel spreadsheet (Propp_SI_landfill_data.xlsx) contains the entire data set associated with this landfill survey, including QAQC information for the PFAS and OPE analyses (separate tab).

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Appendix B1: Supplemental Tables and Figures for Chapter 4



Figure B-1: Temperature-depth plots for temperature rod CSE showing (A) the fall temperature profile reversal and (B) the spring temperature profile reversal.



Figure B-2: Groundwater flux results from VLFUX2 with stream stage for (A) the B site in late summer, (B) the B site in spring, (C) the C site in late summer, and (D) the C site in spring. Legends shared between (A) and (B), and (C) and (D), respectively.



Figure B-3: Comparison of the temperatures measured by the barometric pressure transducers to temperature measured in the stream

43	hlorobenz(1.00	0.83	0.72	0.72	0.87	0.81	0.76	-0.08	0.34
38	Vaphthalene C.									1.00	0.78	0.86	0.83	0.79	0.88	0.83	0.83	-0.21	0.30
73	Benzene 1								1.00	0.78	0.86	0.89	0.75	0.77	0.89	0.85	0.78	-0.25	0.32
18	Chloroethane							1.00	-0.03	0.11	-0.14	0.16	-0.14	-0.06	-0.03	-0.12	-0.21	-0.61	-0.40
40	Sulfamic Acid						1.00	-0.32	0.60	0.50	0.58	0.54	0.63	0.56	0.60	0.57	0.64	0.10	0.42
100	NH4+N					1.00	0.55	0.07	0.84	0.75	0.81	0.87	0.65	0.75	0.84	0.77	0.69	-0.18	0.41
32	Sucralose				1.00	-0.13	-0.40	0.68	-0.18	0.06	-0.17	0.07	-0.17	-0.09	-0.12	-0.19	-0.24	-0.50	-0.50
13	Cyclamate			1.00	-0.17	0.62	0.42	-0.06	0.49	0.51	0.49	0.54	0.45	0.46	0.51	0.49	0.58	-0.15	0.27
90	accharin (1.00	0.62	-0.47	0.83	0.64	-0.16	0.75	0.61	0.69	0.70	0.69	0.69	0.77	0.77	0.77	-0.04	0.50
98	cesulfame S	1.00	-0.62	-0.43	0.81	-0.38	-0.47	0.62	-0.30	-0.10	-0.28	-0.12	-0.25	-0.26	-0.24	-0.33	-0.37	-0.44	-0.64
	A	esulfame	accharin	yclamate	ucralose	NH4+N	famic Acid	lloroethane	Benzene	aphthalene	lorobenzene	Cr	Ni	Cs	Co	Nb	в	CI	Br
		Act	ŝ	<u>ن</u>	ŝ		Sul	5		z	5 CP								

November sampling campaigns (n=60). Detection frequency (DF) given in top row. Coloured cells have correlation Figure B-4: Pearson Correlation Coefficients for log normalized groundwater concentrations from the August and coefficient >0.6, with > 0.9 in red, >0.8 in orange, >0.7 in dark yellow and >0.6 in beige.

Table B-1: Common organic contaminants exceeding water quality guideline in groundwater samples (n=99) (CCME webpage: http://st-ts.ccme.ca/en/ Accessed October 31st, 2020)

Anglyta	This study	Water Qua	N. samples		
Anaryte	(µg/L)	Value (µg/L)	Туре	guideline	
Benzene	220	5 (AL 370)	Drinking water	16	
Trichloroethene	27	5	Drinking water	5	
		21	Aquatic life	1	
Toluene	2.4	2	Aquatic life	1	
Chlorobenzene	36	1.3	Aquatic life	18	
1,4-	9.4	5 (AL 26)	Drinking water	7	
dichlorobenzene					
1,2-	2.6	0.7 (DW 200)	Aquatic life	5	
dichlorobenzene					



Figure B-5: Biplots of (A) benzene vs ammonium, (B) benzene vs acesulfame, (C) chloroethane vs acesulfame, and (D) chloroethane vs saccharin

Acronym	CAS #	Compound Name	n	Group
PFBA	375-22-4	Perfluorobutanoic acid	3	PFCA
PFPeA	2706-90-3	Perfluoropentanoic acid	4	PFCA
PFHxA	307-24-4	Perfluorohexanoic acid	6	PFCA
PFHpA	375-85-9	Perfluoroheptanoic acid	7	PFCA
PFOA	335-67-1	Perfluorooctanoic acid	8	PFCA
PFNA	375-95-1	Perfluorononanoic acid	9	PFCA
PFDA	335-76-2	Perfluorodecanoic acid	10	PFCA
PFUnA	4234-23-5	Perfluoroundecanoic acid	11	PFCA
PFDoDA	307-55-1	Perfluorododecanoic acid	12	PFCA
PFTriDA	72629-94-8	Perfluorotridecanoic acid	13	PFCA
PFTeDA	376-06-7	Perfluorotetradecanoic acid	14	PFCA
PFHxDA	67905-19-5	Perfluorohexadecanoic acid	16	PFCA
PFBS	375-73-5 /59933-66-3	Perfluorobutanesulfonate	3	PFSA
PFPeS	22767-49-3	Perfluoropentanesulfonate	5	PFSA
PFHxS	355-46-4	Perfluorohexanesulfonate	6	PFSA
PFHpS	22767-50-6/375-92-8	Perfluoroheptanesulfonate	7	PFSA
PFOS	4021-47-0 / 1763-23-1/ 2793-39-3	Perfluorooctanesulfonate	8	PFSA
PFDS	335-77-3 /2806-15-7/ 126105-34-8	Perfluorodecanesulfonate	10	PFSA
PFDoDS	70259-86-8/ 1260224- 54-1 79780-39-5	Perfluorododecanesulfonate	12	PFSA
PFECHS	646-83-3	Perfloroethylcyclohexane sulfonate	8	PFSA (cyclic)
FBSA	30334-69-1	Perfluorobutylsulphonamide	4	Perfluoroalkane sulfonamide
FOSA	754-91-6	Perfluorooctanesulfonamide	8	Perfluoroalkane sulfonamide
HFPO-DA	13252-13-6/ 2062-98-8	Hexafluoropropylene oxide dimer acid	6	PFECA
ADONA	958445-44-8/51460-26- 5/77063-04-6	3H-perfloro-3-(3- methoxypropoxy)propanoic acid	7	PFECA
9-Cl-PF3ONS	73606-19-6	6:2 chlorinated polyfluoroalkyl ether sulfonate	8	PFESA
11-Cl-PFOUdS	83329-89-9	8:2 chlorinated polyfluoroalkyl ether sulfonate	10	PFESA
8Cl-PFOS	754925-54-7	Sodium 8-chloroperfluoro-1- octanesulfonate	8	Cl-substituted PFSA

Table B-2: The 24 PFAS analyzed in this study, based on Nakayama et al. (2019)

PFCA – Perfluoroalkyl carboxylic acid

PFSA – Perfluoroalkyl sulfonic acid

PFECA – Perfluoroalkyl ether carboxylic acids

PFESA – Polyfluoroalkyl ether sulphonic acids
Transect	North to South Shore Position	Distance	Depth	Temperature	EC	pН	Cl
SW				20.4	1156	7.66	375
0	0	30	7	20.6	1160	7.51	395
0		155	13	20.7	1159	7.35	382
0	310	300	2	20.6	1159	7.33	375
5	0	0	9	20.7	1152	7.41	378
5		120	19	20.8	1165	7.35	376
5		200	20	20.8	1166	7.39	360
5	310	310	9	20.8	1165	7.36	416
10	10	15	7	20.8	1171	7.42	385
10		120	20.5	20.7	1173	7.38	365
10		200	21	20.9	1161	7.38	371
10	300	300	8	20.8	1166	7.35	460
15	20	20	5	20.8	1168	7.38	376
15		130	21	20.9	1167	7.29	424
15		210	26	20.9	1172	7.31	365
15	310	310	17	21	1103	7.25	448
20	30	30	11	21	1175	7.37	365
20		160	24	21	1138	7.3	378
20		300	37	20.9	1156	7.27	380
20	410	410	38	21	1172	7.08	615

Table B-3: Epibentic zone assessmnet using YSI multiparameter probes measureing north to south along transects at B site. Bolded values represent potential leachate influence

Transect	North to South Shore Position	Distance	Depth	Temperature	EC	pН	Cl
SW				21.7	1134	7.63	302
0	50	80	4	21.9	1135	7.53	318
0		210	11	21.7	1133	7.49	289
0	370	360	2	21.7	1123	7.42	297
10	40 (sticks to 80)	100	6	21.7	1145	7.44	329
10		200	9	21.7	1145	7.45	341
10	380	370	6	21.7	1136	7.48	352
20	80	90	9	21.8	1143	7.53	335
20		190	21	21.7	1146	7.5	350
20	350	300	12	21.6	1143	7.44	345
30	35	40	9	21.8	1140	7.21	412
30		200	7	21.8	1140	7.27	382
30		350	8	21.7	1130	7.33	380
30	470	450	5	21.6	1019	7.35	375
35	60	80	6	21.7	1094	7.38	426
35		210	8	21.7	1137	7.38	411
35	390	380	7.5	21.6	1091	7.42	411
40	40	40	5	21.5	1292	6.94	443
40		140	2	21.6	1127	7.02	429
40		270	8	21.7	1078	7.21	397
40	420	420	23	21.6	1142	7.29	380
45	60	70	7	21.7	1135	7.18	419
45		210	4	21.7	1137	7.26	419
45	340 (log)	330	5	21.7	1132	7.34	422

Table B-4: Epibentic zone assessmnet using YSI multiparameter probes measureing north to south along transects at C site. Bolded values represent potential leachate influence



Figure B-6: Difference in mass discharge for (A) saccharin and (B) ammonium between the upstream and downstream sampling locations (see Figure 4-1 for locations) plotted against the number of hours in between the collection of the downstream and upstream water samples. Labels indicate the sampling day and month, and open symbols represent days when precipitation occurred during or preceding sampling.



Figure B-7: Mass discharges at the upstream and downstream sampling locations (as indicated on Figure 4-1) for (A) ammonium (NH_4^+ -N) and nitrate (NO_3^-), and (B) saccharin and acesulfame. Dashed lines are only to guide the eye, as variation between sampling times is expected. Lines were excluded for nitrate due to the low frequency of analysis for this compound. Vertical gridlines at one-month intervals.



Figure B-8: Biplot of BPA and BPS versus PFOS concentrations in the ten shallow groundwater samples analyzed for CECs from August 20th, 2019. The trendlines were used to predict bisphenol concentrations in the surface water based on PFOS stream concentrations.

Appendix B2: Images of Study Site



Figure B-9: Picture of downstream discharge gauging location during summer (location shown on Figure 4-1). Note upstream road culvert and debris throughout stream.



Figure B-10: Picture of upstream discharge gauging location during winter (location shown on Figure 4-1). Note the snow piles on shores due to the plowing of snow from an uphill parking lot towards the right of the image (not shown).



Figure B-11: Stretch B during a (A) summer baseflow and (B) a high flow precipitation event on October 16th, 2019.



Figure B-12: Stretch C during a (A) summer baseflow and (B) a high flow precipitation event on October 16th, 2019.